UNIVERSIDAD COMPLUTENSE DE MADRID
FACULTAD DE CIENCIAS QUÍMICAS
DEPARTAMENTO DE INGENIERÍA QUÍMICA

TESIS DOCTORAL

Extracción de hidrocarburos aromáticos de naftas y gasolinas de reformado y pirólisis empleando una mezcla binaria de líquidos iónicos como disolvente

MEMORIA PARA OPTAR AL GRADO DE DOCTOR
PRESENTADA POR

Marcos Larriba Martínez

Directores

Francisco Rodríguez Somolinos
Julián García González

Madrid, 2015

Universidad Complutense de Madrid

Facultad de Ciencias Químicas

Departamento de Ingeniería Química

Tesis Doctoral

Extracción de hidrocarburos aromáticos de naftas y gasolinas de reformado y pirólisis empleando una mezcla binaria de líquidos iónicos como disolvente

MEMORIA

que para optar al Título de Doctor por la Universidad Complutense de Madrid en el Programa de Doctorado de Ingeniería Química presenta

Marcos Larriba Martínez

Directores:

Dr. D. Francisco Rodríguez Somolinos

Dr. D. Julián García González

D. Francisco Rodríguez Somolinos y D. Julián García González, Catedrático y Profesor Titular en el Departamento de Ingeniería Química de la Universidad Complutense de Madrid,

Certifican que este trabajo de investigación titulado: “Extracción de hidrocarburos aromáticos de naftas y gasolinas de reformado y pirólisis empleando una mezcla binaria de líquidos iónicos como disolvente” constituye la memoria que presenta Marcos Larriba Martínez para optar al grado de Doctor y que ha sido realizada en los laboratorios del Departamento de Ingeniería Química de la Universidad Complutense de Madrid bajo su dirección.

Y para que conste a los efectos oportunos, firman el presente certificado en Madrid a 8 de abril de 2015.

Dr. D. Francisco Rodríguez Somolinos   Dr. D. Julián García González

Agradecimientos

En primer lugar, debo expresar mi profundo agradecimiento a mis dos directores por ofrecerme la gran oportunidad de realizar esta tesis doctoral. A Francisco Rodríguez Somolinos le agradezco su continuo apoyo y asesoramiento durante todo el periodo que ha transcurrido desde que comencé esta investigación, mientras que a Julián García González le quiero agradecer su confianza y todos los impagables aprendizajes que he recibido de él como docente e investigador.

A continuación quiero expresar mi gratitud a todas las personas con las que he compartido grupo de investigación durante estos años. En primer lugar, gracias a los profesores Mercedes Oliet Palá, Virginia Alonso Rubio y Juan Carlos Domínguez Toribio por su ayuda y asesoramiento. Mi sincero agradecimiento a Silvia, por su ayuda durante el inicio de esta tesis sin la cual no podría haber continuado adelante. Por supuesto a Pablo, compañero pero sobre todo amigo, que ha soportado a mi lado todas las fases (buenas y malas) de la tesis; ha sido un placer compartir dos tesis unidas por una corriente de extracto, creo que hemos formado un gran equipo. Gracias a Ana, María y Tamara por su amistad tanto dentro como fuera del laboratorio y que durará para siempre aunque estemos lejos. También quiero agradecer la compañía y los aprendizajes que he obtenido de todos los compañeros que he tenido durantes estos años en el grupo: Ester, Belén, Susana, Emilio, Vicky y Mª del Mar. Y no puedo olvidar la ayuda prestada por Laura en la experimentación y la gran suerte de haber contado con la ayuda y la amistad de Jean-Baptiste.

La palabra agradecimiento para hablar de mi familia se queda pequeña. A mis padres Alfredo y María del Carmen, a mi hermana Ágata y a mis abuelos Santiago y María del Carmen sólo puedo decirles una frase: gracias por aguantarme.

En estos agradecimientos también deben aparecer aquellas personas que forman una parte fundamental en mi vida, aunque no sean de mi familia. A Jose por cambiarme la vida y atreverse a seguir cambiándomela. Gracias a Borja por ser un referente en mi vida en todo menos en nadar espalda. A Raquel por su amistad desde el primer día de carrera y su maravillosa compañía. A Enrique por su amistad en la distancia y por estar siempre disponible para darme los mejores consejos en los peores momentos. A Stephane por estar siempre aunque esté lejos. A Victor por su amistad y por ser la única persona que no me ha molestado que me preguntara como llevaba la tesis. Y a mis amigos de SMB por hacerme reir siempre y por permanecer juntos año tras año.

Por supuesto si he logrado llegar hasta aquí ha sido gracias a lo que me han enseñado mis profesores. En especial gracias a Violeta Marco por enseñarme que mi camino andaba tras la Química. También debo mostrar mi agradecimiento a todos mis alumnos por aguantarme, escucharme y mostrarme una vocación inesperada.

Por último, a Joaquín por enseñarme que un gran descubrimiento siempre encuentra al principio una gran oposición. A Miguel por su lección de vida. Y a Adrián, en cumplimiento de una promesa que no pude hacerte pero que cumplo como si lo hubiese hecho.

Arroja sus estudios y la sabiduría,

y se quita la máscara, la piel de la cultura,

los ojos de la ciencia, la corteza tardía

de los conocimientos que descubre y procura.

Entonces solo sabe del mal, del exterminio.

Miguel Hernández

El hombre acecha (1937-39)

ÍNDICE

ÍNDICE

ABSTRACT/RESUMEN

Title: Extraction of aromatic hydrocarbons from naphtha and reformer and pyrolysis gasolines using a binary mixture of ionic liquids as solvent.

1. Introduction

Benzene, toluene, ethylbenzene and xylenes (BTEX) are usually obtained by liquid-liquid extraction from pyrolysis and reformer gasolines using organic solvents such as sulfolane. In the USA, reformer gasoline is the major raw material for BTEX, whereas pyrolysis gasoline is the most important source of aromatics in Japan and Europe.[1]

In this work, we have studied the separation of the BTEX from pyrolysis and reformer gasolines and also the dearomatization of the naphtha feed to ethylene crackers using binary ionic liquid mixtures as solvents. Aromatic content in the ethylene crackers feed is between 10 – 25 wt. %. BTEX presented in the naphtha feed to ethylene crackers are not converted to olefins and their presence increases operating costs and the size of the furnaces. Therefore, the extraction of BTEX from this naphtha could reduce costs and could produce income by selling the aromatics extracted.[2] However, there are no technologies available to separate BTEX from streams with an aromatic content lower than 20 wt. %. Because of this, we have proposed the use of ionic liquids to perform the dearomatization of the naphtha feed to ethylene crackers.

Recovery of aromatics is currently performed by liquid-liquid extraction, being the UOP Sulfolane process the most widely used method at industrial scale. However, the Sulfolane process has several drawbacks such as the high energy consumption and the need to recover the sulfolane dissolved in the raffinate stream. In this process, the separation of the aromatics is made in an extractor followed by an extractive stripper and an extract recovery distillation column. Due to the high boiling point of the sulfolane (560 K), the solvent regeneration and the recovery of the extracted solutes have a high energy consumption.[2,3]

Ionic liquids are liquid salts at temperatures lower than 373.2 K, being their nonvolatile character their most remarkable property. The disadvantages of the Sulfolane Process could be solved using ionic liquids as solvents due to their nonvolatile nature and the negligible solubility of ionic liquids in hydrocarbons. These solvents have been extensively studied in the dearomatization, denitrogenation, and desulfuration of liquid fuels, showing good extractive properties and a nonvolatile nature that could reduce investment and operating costs of the extraction units. A wide number of pure ionic liquids have been specifically applied in the liquid-liquid extraction of benzene, toluene, ethylbenzene or xylenes from their binary mixtures with an aliphatic hydrocarbon. However, only a very limited number of pure ionic liquids has exhibited extractive and physical properties comparable to sulfolane values.[4] For that reason, in this work we have studied the use of binary ionic liquid mixtures in order to obtain an ionic liquid-based solvent with intermediate extractive and physical properties between those of the ionic liquids forming the mixture and comparable or higher properties than the sulfolane values.

2. Content of the PhD Thesis

The aim of this work was to find a binary ionic liquid mixture with adequate physical and extractive properties to be used as solvent in the liquid-liquid extraction of BTEX from reformer gasoline, pyrolysis gasolines, and the naphtha feed to ethylene crackers. From the experimental results, extraction columns using sulfolane and the ionic liquid mixture have been simulated using the Kremser method to compare the performance of both solvents.

First, the ionic liquids used in this work were chosen considering the conclusions of the papers published until the date on the liquid-liquid extraction of aromatics using ionic liquids. Once the pure ionic liquids were selected, their extractive properties in the separation of toluene from its mixtures with *n*-heptane were experimentally determined. Densities, viscosities, and surface tensions of the pure ionic liquids were also measured. Taking into account the extractive and physical properties of the pure ionic liquids, two binary mixtures of ionic liquids were proposed as those with the greatest potential to be employed in an industrial process of extraction of BTEX.

Then, densities, dynamic viscosities, and extractive properties in the separation of several aromatics from alkanes of the binary mixtures of ionic liquids {[emim][TCM] + [emim][DCA]} and {[4empy][Tf_2N] + [emim][DCA]} were measured as a function of composition in the ionic liquid mixture. According to the results obtained in this experimental stage, the binary mixture {[4empy][Tf_2N] + [emim][DCA]} with a [4empy][Tf_2N] mole fraction of 0.3 was revealed as the most promising extraction solvent.

Finally, the liquid-liquid extraction of BTEX from reformer gasoline, pyrolysis gasolines from mild and severe cracking, and the naphtha feed to ethylene crackers was studied using the {[4empy][Tf_2N] + [emim][DCA]} ionic liquid mixture and sulfolane as solvents. Liquid-liquid extraction experiments were made at temperatures between 303.2 K and 323.2 K and solvent to feed ratios from 1.0 to 5.0 to select the most adequate conditions to perform the separation of BTEX from the four refinery streams. To conclude, the Kremser method was used to simulate the countercurrent extraction columns in the separation of BTEX using sulfolane and the binary ionic liquid mixture as solvents, studying the effect of the number of equilibrium stages in the extraction yield of BTEX and in the purity of the aromatics obtained.

3. Conclusions

The binary ionic liquid mixture {[4empy][Tf_2N] + [emim][DCA]} with a [4empy][Tf_2N] mole fraction of 0.3 was revealed as a potential substitute of sulfolane in the liquid-liquid extraction of BTEX from refinery streams. Thermophysical properties of this ionic liquid mixture were similar to sulfolane values and, therefore, the {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} could be applied in an industrial process of liquid-liquid extraction of aromatics.

According to the results of the simulations of the extraction column by the Kremser method, the purity of the extracted BTEX from the naphtha feed to ethylene crackers using the {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} mixture was higher than that using sulfolane, whereas the extraction yields of BTEX using the ionic liquid-based solvent were lower than the sulfolane values. In the liquid-liquid extraction of BTEX from reformer gasoline and pyrolysis gasolines were achieved the same values of extraction yields using the ionic liquid mixture than in the Sulfolane process. However, the employment of the {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} could require a higher number of equilibrium stages than that using sulfonane, whereas a higher purity of the extracted BTEX could be achieved using the ionic liquid mixture.

References

(1) **Franck, H. G.; Staldelhofer, J. W.** Industrial Aromatic Chemistry; Springer-Verlag: Berlin, **1988**.

(2) **Gary, J.; Handwerk, G.; Kaiser, M.** Petroleum Refining Technology and Economics, 5th ed.; CRC Press: Boca Raton, **2007**.

(3) **Meyers, R. A.** Handbook of Petroleum Refining Processes, 3rd ed.; McGraw-Hill: New York, **2004**.

(4) **Meindersma, G. W.; Hansmeier, A. R.; de Haan, A. B.** Ionic Liquids for Aromatics Extraction. Present Status and Future Outlook. Ind. Eng. Chem. Res. **2010**, 49, 7530–7540.

Título: Extracción de hidrocarburos aromáticos de naftas y gasolinas de reformado y pirólisis empleando una mezcla binaria de líquidos iónicos como disolvente

1. Introducción

El benceno, el tolueno, el etilbenceno y los xilenos (BTEX) se obtienen habitualmente mediante extracción líquido-líquido de gasolinas de pirólisis y reformado empleando disolventes orgánicos como el sulfolano. En los Estados Unidos, la principal fuente de obtención de BTEX es la gasolina de reformado, mientras que en Japón y Europa la gran mayoría de la producción de BTEX se realiza a partir de gasolina de pirólisis.[1]

En esta tesis doctoral se ha estudiado la separación de los BTEX presentes en las gasolinas de reformado y pirólisis y en la nafta alimentada al cracker de etileno empleando mezclas binarias de líquidos iónicos como disolventes. Se ha incluido como posible fuente de BTEX la nafta alimentada al cracker de etileno debido a que los aromáticos presentes en esta corriente no son convertidos a olefinas en el cracker y, por tanto, su presencia aumenta los costes de operación y el tamaño de los hornos. Por tanto, si se separasen los aromáticos antes de ser introducidos en el horno de craqueo se reducirían los costes de operación y se podría obtener un beneficio adicional por la venta de los BTEX extraídos. El contenido de aromáticos en esta corriente oscila entre el 10 y 25 % en masa; sin embargo, no existe ninguna tecnología actual de separación de BTEX que permita extraer aromáticos de forma rentable de corrientes con un contenido de aromáticos inferior al 20 %. Por este motivo, se ha estudiado la viabilidad del empleo de mezclas binarias de líquidos iónicos como disolvente de extracción de BTEX de la nafta alimentada al cracker de etileno.

La separación de aromáticos mayoritariamente se realiza a escala industrial mediante extracción líquido-líquido, siendo el proceso Sulfolano desarrollado por UOP el más empleado. En el proceso Sulfolano la separación de los BTEX se realiza en una columna de extracción líquido-líquido seguida por un *stripper* extractivo y una columna de destilación. Sin embargo, este proceso presenta algunos inconvenientes como el elevado consumo energético y la necesidad de recuperar el sulfolano disuelto en la corriente de refinado. Como consecuencia del alto punto de ebullición del sulfolano (560 K), la regeneración del disolvente y la recuperación de los hidrocarburos extraídos conllevan unos elevados costes energéticos.[2,3]

Alguno de los inconvenientes que presenta el proceso Sulfolano podrían solventarse empleando líquidos iónicos como disolventes de extracción de aromáticos debido a su naturaleza no volátil y a la despreciable solubilidad de los líquidos iónicos en los hidrocarburos que forman la corriente de refinado. Estos disolventes de nueva generación han sido ampliamente estudiados como disolventes en la desaromatización y la desulfuración de combustibles líquidos mostrando buenas propiedades extractivas. Además, como consecuencia de su carácter no volátil su empleo podría reducir los costes de operación y de inmovilizado.

Hasta la fecha se han probado un elevado número de líquidos iónicos puros como disolventes en la extracción de benceno, tolueno, etilbenceno o xilenos de sus mezclas binarias con un hidrocarburo alifático. Sin embargo, únicamente un reducido número de líquidos iónicos puros han mostrado propiedades físicas y extractivas similares a las del sulfolano.[4] Por este motivo, en este trabajo se ha propuesto y estudiado el empleo de mezclas binarias de líquidos iónicos para, al mezclarlos, obtener un disolvente basado en líquidos iónicos con propiedades físicas y extractivas similares a las del sulfolano.

2. Contenido de la tesis doctoral

El objetivo principal de esta tesis doctoral ha sido el estudio de la extracción líquido-líquido de BTEX de gasolinas de reformado y pirólisis y de la nafta alimentada al cracker de etileno empleando una mezcla binaria de líquidos iónicos con propiedades adecuadas para ser empleada a escala industrial. A partir de los resultados experimentales y empleando el método de Kremser, se ha realizado la simulación de las columnas de extracción líquido-líquido, comparando los resultados obtenidos con la mezcla de líquidos iónicos seleccionada y el sulfolano como disolventes.

En primer lugar, los líquidos iónicos a emplear en esta tesis doctoral se han seleccionado considerando las conclusiones de los trabajos publicados hasta la fecha sobre la extracción de aromáticos empleando líquidos iónicos. A continuación, las propiedades extractivas de los líquidos iónicos puros en la separación de tolueno de sus mezclas con *n*-heptano se han determinado experimentalmente. Asimismo, los líquidos iónicos puros seleccionados se han caracterizado mediante la determinación de sus densidades, viscosidades y tensiones superficiales. Considerando las propiedades físicas y extractivas de los líquidos iónicos puros se han seleccionado las mezclas binarias de líquidos iónicos {[emim][TCM] + [emim][DCA]} y {[4empy][Tf_2N] + [emim][DCA]} como las que presentan mayor potencial para ser empleadas en un proceso industrial de extracción líquido-líquido de BTEX.

A continuación, las densidades, viscosidades y las propiedades extractivas de las dos mezclas binarias de líquidos iónicos en la separación de diferentes hidrocarburos aromáticos de sus mezclas binarias con alcanos se han determinado en función de la composición en la mezcla binaria de líquidos iónicos. A partir de estos resultados se ha seleccionado la composición en la mezcla más adecuada para realizar la extracción de aromáticos.

La mezcla binaria {[4empy][Tf_2N] + [emim][DCA]} con una fracción molar de [4empy][Tf_2N] igual a 0,3 fue seleccionada como el disolvente de extracción de hidrocarburos aromáticos con mayor potencial considerando tanto sus propiedades extractivas como sus propiedades físicas.

Finalmente, se ha realizado la extracción líquido-líquido de los BTEX presentes en la gasolina de reformado, las gasolinas de pirólisis suave y severa y la nafta alimentada al cracker de etileno empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} y el sulfolano como disolventes. Para seleccionar las condiciones de operación más adecuadas para realizar la separación de los aromáticos presentes en las cuatro corrientes de refinería, los ensayos de extracción líquido-líquido se han llevado a cabo a temperaturas entre 303,2 K y 323,2 K empleando valores de relación másica disolvente/alimento entre 1,0 y 5,0. Para concluir, se han simulado las columnas de extracción líquido-líquido en la separación de los BTEX de las cuatro corrientes de refinería mediante el método de Kremser, estudiando la influencia del número de pisos en el extractor sobre el rendimiento de extracción de los BTEX y sobre la pureza de los aromáticos extraídos y comparando los resultados obtenidos con ambos disolventes de extracción.

3. Conclusiones

La mezcla binaria de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} con una fracción molar de [4empy][Tf_2N] igual a 0,3 se ha mostrado como un posible sustituto del sulfolano en la extracción líquido-líquido de BTEX de corrientes de refinería. Las propiedades termofísicas de esta mezcla binaria de líquidos iónicos han sido similares a las exhibidas por el sulfolano, por lo que la mezcla binaria de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} podría emplearse como disolvente de extracción de aromáticos en un proceso industrial.

De acuerdo con los resultados obtenidos en la simulación de las columnas de extracción mediante el método de Kremser, empleando como disolvente de extracción de aromáticos de la nafta alimentada al cracker de etileno la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} la pureza de los hidrocarburos aromáticos extraídos sería superior a la alcanzada con el sulfolano, pero los rendimientos de extracción de los aromáticos serían algo inferiores. Por otro lado, en la extracción de BTEX de las gasolinas de reformado y pirólisis utilizando la mezcla binaria de líquidos iónicos se obtuvieron los mismos rendimientos de extracción de BTEX que en el proceso Sulfolano. Sin embargo, el empleo de la mezcla binaria {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} requeriría un mayor número de pisos en el extractor que en el proceso Sulfolano pero la pureza de los BTEX extraídos por la mezcla de líquidos iónicos sería sustancialmente superior.

Bibliografía

(1) **Franck, H. G.; Staldelhofer, J. W.** Industrial Aromatic Chemistry; Springer-Verlag: Berlin, **1988**.

(2) **Gary, J.; Handwerk, G.; Kaiser, M.** Petroleum Refining Technology and Economics, 5^a ed.; CRC Press: Boca Raton, **2007**.

(3) **Meyers, R. A.** Handbook of Petroleum Refining Processes, 3^a ed.; McGraw-Hill: New York, **2004**.

(4) **Meindersma, G. W.; Hansmeier, A. R.; de Haan, A. B.** Ionic Liquids for Aromatics Extraction. Present Status and Future Outlook. Ind. Eng. Chem. Res. **2010**, 49, 7530–7540.

1. INTRODUCCIÓN

1.1. Aplicaciones de los hidrocarburos aromáticos

Los hidrocarburos aromáticos y más concretamente la fracción BTEX (benceno, tolueno, etilbenceno y xilenos) son empleados en petroquímica como disolventes y para la síntesis química de multitud de compuestos como plásticos, colorantes, resinas y productos de química fina. La producción mundial anual de BTEX es aproximadamente de 110 millones de toneladas. En la Figura 1.1 se muestra la evolución de la demanda mundial de benceno, tolueno y xilenos entre los años 2004 y 2012. Como se puede observar, el benceno es el hidrocarburo aromático que presenta una mayor demanda, con una producción anual mundial cercana a 50 millones de toneladas en 2012. La demanda de benceno y xilenos se ha visto incrementada considerablemente durante la última década. Por el contrario, la demanda de tolueno ha permanecido prácticamente constante en ese periodo (HPP Science, 2013 y ThyssenKrupp, 2014)

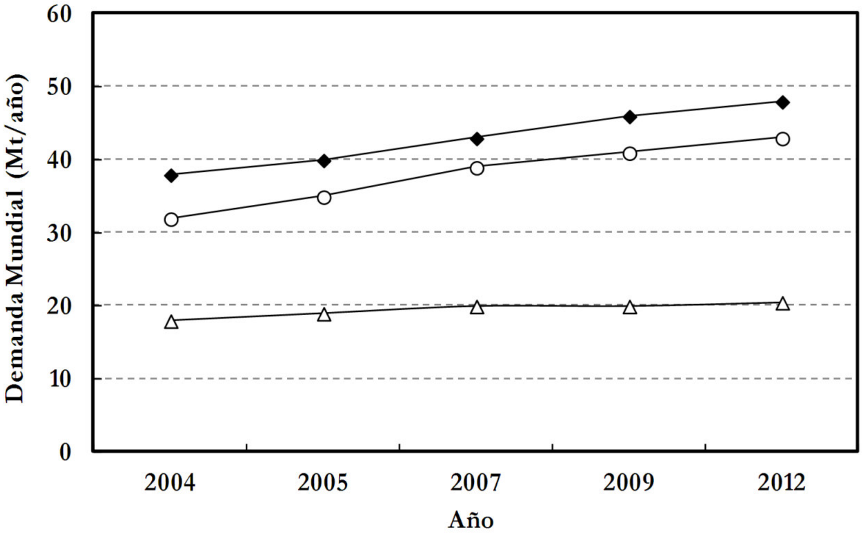


Figura 1.1. Demanda mundial de benceno (♦), tolueno (Δ) y xilenos (○) entre 2004 y 2012 (Adaptado de HPP Science, 2013 y ThyssenKrupp, 2014).

El benceno es el hidrocarburo aromático con una mayor demanda debido a que presenta un gran abanico de aplicaciones. En la Figura 1.2 se muestran los diferentes productos que son sintetizados a partir del benceno. Uno de los principales derivados del benceno es el etilbenceno, que se produce mediante una reacción de alquilación de Friedel-Crafts empleando etileno (Franck y Stadelhofer, 1988). El etilbenceno se obtiene también de forma directa de diferentes corrientes de refinería que presentan un elevado contenido en aromáticos. Sin embargo, debido a la proximidad de los puntos de ebullición del etilbenceno y los xilenos, que dificultan la purificación de este hidrocarburo mediante destilación, la gran mayoría del etilbenceno demandado se obtiene a partir del benceno mediante síntesis química.

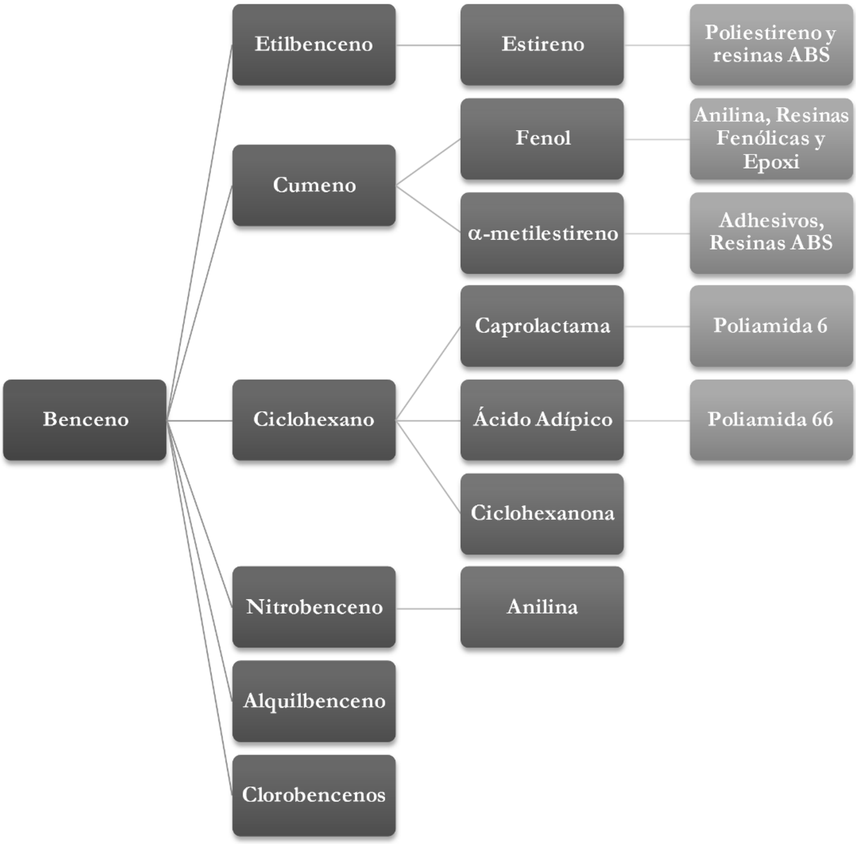


Figura 1.2. Principales productos obtenidos a partir del benceno.

Mediante una alquilación catalítica con propileno se produce cumeno a partir del benceno. El estireno y algunos derivados del cumeno son utilizados, a su vez, para la fabricación de diferentes tipos de resinas: fenólicas, epoxi y ABS. Mediante oxidación del cumeno se obtiene el fenol, que presenta multitud de aplicaciones en la síntesis de compuestos como la anilina y productos de química fina (Franck y Stadelhofer, 1988).

A partir del benceno y mediante un proceso de hidrogenación catalítica en fase líquida se obtiene el ciclohexano (Chauvel y Lefebvre, 1989). Por su parte, el ciclohexano es empleado en la síntesis de poliamidas o nylon 6 y 66 a partir de caprolactama y ácido adípico, respectivamente. Otros derivados reseñables del benceno son los alquilbencenos, utilizados en la fabricación de detergentes, el nitrobenceno, con el que se fabrica anilina, colorantes y explosivos y los clorobencenos para obtener insecticidas y colorantes (Kirk y Othmer, 1998).

En la Figura 1.3 se muestran los principales productos sintetizados a partir de los xilenos. Como se puede observar, cada uno de los isómeros presenta rutas de aplicación diferenciadas. El *o*-xileno se somete a un proceso de oxidación catalítica junto con naftaleno para producir anhídrido ftálico. Este compuesto es empleado en la fabricación de resinas alquídicas, consumidas en la obtención de esmaltes, pinturas y barnices.

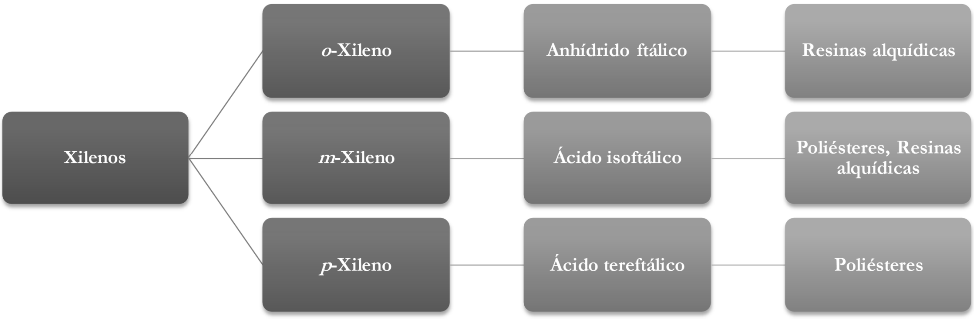


Figura 1.3. Principales productos obtenidos a partir de xileno.

El ácido isoftálico es el principal derivado del *m*-xileno obtenido mediante la oxidación del hidrocarburo aromático en presencia de oxígeno. De forma análoga al anhídrido ftálico, el ácido isoftálico se emplea en la fabricación de resinas alquídicas, aunque también encuentra su aplicación en la fabricación de polímeros como el Nomex, que presenta una alta resistencia al fuego (Kirk y Othmer, 1998). Por último, a partir del *p*-xileno se sintetiza el ácido tereftálico mediante una reacción de oxidación. El ácido tereftálico se utiliza como intermedio en la producción de poliésteres, destacando su uso en la síntesis del tereftalato de polietileno (PET).

Por último, en la Figura 1.4 se recogen los principales productos sintetizados a partir de tolueno. Una gran parte de la producción de tolueno se destina a la fabricación de espumas flexibles de poliuretano, sintetizadas a partir del diisocianato de tolueno, que procede a su vez del nitrotolueno. Asimismo, el nitrotolueno puede emplearse en la producción de explosivos como el TNT (1,3,5-trinitrotolueno). Finalmente, una fracción de la producción mundial de tolueno se destina a su uso como disolvente de diferentes sustancias como aceites, pinturas, adhesivos y lacas y como aditivo antidetonante en combustibles al presentar un número de octano superior a 100 (Kirk y Othmer, 1998; Fahim y col., 2010).

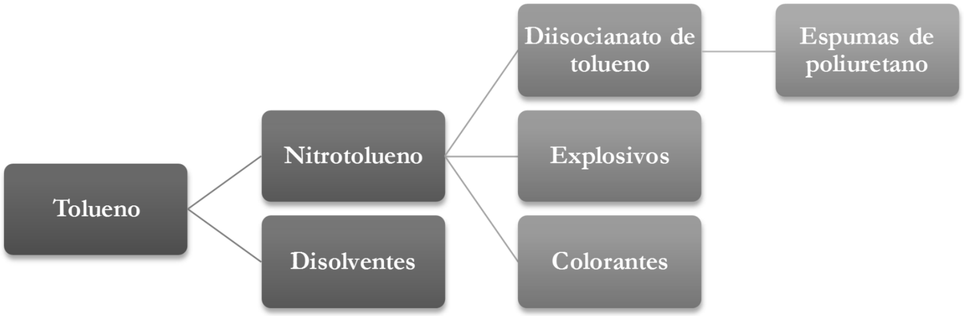


Figura 1.4. Principales productos obtenidos a partir de tolueno.

1.2. Principales fuentes de obtención de hidrocarburos aromáticos

Los hidrocarburos aromáticos más ligeros (benceno, tolueno, etilbenceno y xilenos) se obtienen de dos corrientes de refinería: la gasolina de reformado y la gasolina de pirólisis. Una pequeña cantidad de BTEX también se obtiene del aceite ligero de los hornos de coque. En la Figura 1.5, se muestra el peso porcentual de cada una de estas fuentes en la obtención de BTEX a nivel mundial. Como se puede observar, casi la totalidad de la producción de aromáticos proviene de las gasolinas de reformado y de pirólisis.

La mayor parte de la demanda mundial de tolueno se cubre mediante la separación de este hidrocarburo de la gasolina de reformado. Por este motivo, parte del tolueno obtenido suele transformarse en benceno, que presenta una mayor demanda, como se ha expuesto en el apartado anterior, mediante procesos de hidrodealquilación (HDA) o desproporcionamiento (TDP). En la Figura 1.6, se muestra el reparto porcentual de las fuentes principales de obtención de benceno, siendo la principal la gasolina de pirólisis seguida de la gasolina de reformado.

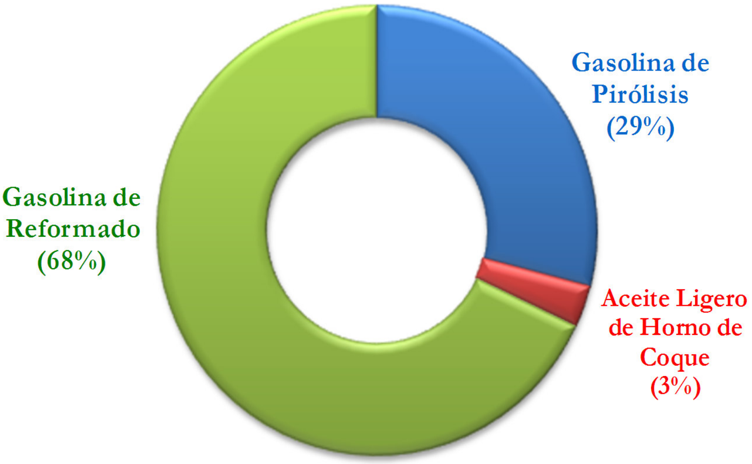


Figura 1.5. Principales fuentes de obtención de BTEX a nivel mundial (Adaptado de HPP Science, 2013 y ThyssenKrupp, 2014).

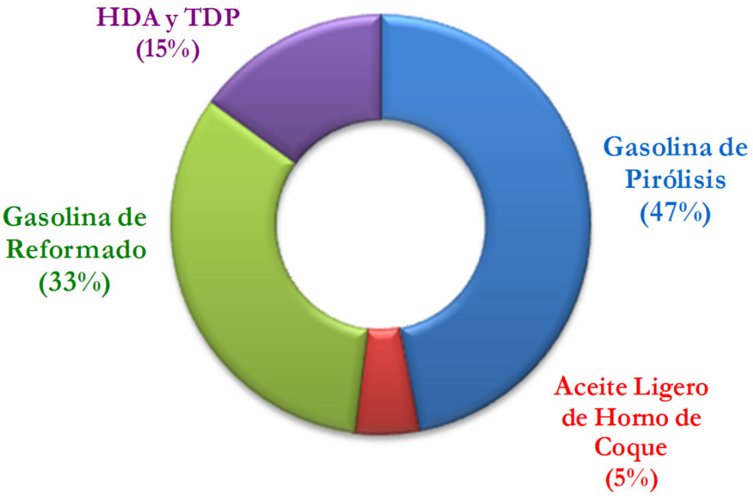


Figura 1.6. Principales fuentes de obtención de benceno a nivel mundial (Adaptado de HPP Science, 2013 y ThyssenKrupp, 2014).

A continuación, se van a describir los diagramas de flujo que permiten la obtención de hidrocarburos aromáticos a partir de sus dos principales fuentes: las gasolinas de reformado y pirólisis. Asimismo, se realizará el análisis y descripción de la composición más habitual de ambas corrientes, que se tomarán como referencia en la preparación de muestras sintéticas de hidrocarburos en los ensayos de extracción de aromáticos de esta tesis.

Adicionalmente, se ha incluido la nafta alimentada al cracker de etileno como una tercera posible fuente de obtención de hidrocarburos aromáticos, tal y como propusieron Meindersma y col. (2008). En la actualidad, esta corriente no se utiliza en las refinerías para la obtención de hidrocarburos aromáticos empleando las tecnologías y los disolventes convencionales, debido a que no es viable económicamente por el reducido contenido en aromáticos que presenta. Sin embargo, en esta tesis doctoral se ha considerado como una posible fuente de BTEX teniendo en consideración los buenos resultados obtenidos en la extracción de aromáticos con líquidos iónicos en mezclas de hidrocarburos con bajo contenido en aromáticos (Meindersma y col., 2008).

1.2.1. Gasolina de reformado

El empleo del reformado catalítico de naftas se ha visto estimulado gracias a la creciente demanda de gasolinas de alto octanaje para ser utilizadas en los automóviles. Aproximadamente el 50 % de la gasolina consumida en los Estados Unidos se obtiene mediante reformado, aunque se estima que este porcentaje podría variar en el futuro como consecuencia de las restricciones ambientales del contenido en aromáticos en las gasolinas (Gary y col., 2007).

Las corrientes alimentadas a las unidades de reformado suelen ser naftas con intervalos de puntos de ebullición entre 80 ºC y 190 ºC y con un elevado contenido en parafinas y nafténicos. Mediante reacciones de deshidrogenación, ciclación e isomerización los compuestos alimentados se transforman en hidrocarburos con un mayor octanaje, como los compuestos aromáticos y las isoparafinas. Las condiciones de operación del reformado deben favorecer la generación de los productos buscados mediante las siguientes reacciones, que suceden simultáneamente en el reactor de reformado:

1. Las parafinas son isomerizadas y algunas se transforman en nafténicos.
2. Las olefinas son saturadas para obtener parafinas que reaccionen según el punto anterior.
3. Los nafténicos se convierten en hidrocarburos aromáticos.

Además de las reacciones anteriores, se debe evitar que se produzcan en el interior del reactor procesos de craqueo de parafinas y nafténicos para formar butano y otras parafinas ligeras, la formación de coque y la desalquilación de las cadenas laterales de los aromáticos y nafténicos. Para lograr estos objetivos, el reformado se realiza en presencia de catalizadores heterogéneos de platino soportados sobre alúmina (Meyers, 2004; Gary y col., 2007).

El proceso de reformado catalítico más empleado a nivel mundial es el Platforming que fue desarrollado por la Universal Oil Products (UOP). La temperatura del reactor catalítico en dicho proceso se mantiene entre 525 ºC y 540 ºC, mientras que la presión de trabajo oscila entre 350 kPa y 4.800 kPa. La presión de operación se selecciona en función de la composición de la alimentación, del rendimiento de reformado buscado y de la estabilidad y desactivación del catalizador (Meyers, 2004).

El rendimiento de obtención de hidrocarburos aromáticos en el reformado catalítico suele oscilar entre el 50 y 60 %, mientras que el rendimiento de no aromáticos con un número de carbonos superior a cinco se sitúa habitualmente en torno al 25 % (Meyers, 2004). La composición de la gasolina de reformado obtenida depende de las condiciones de operación del reformado y de la composición de la corriente alimentada a la unidad. En la Tabla 1.1 se muestra la composición más habitual de la gasolina de reformado.

Debido al elevado contenido en tolueno y xilenos, en la unidad de obtención de aromáticos esta gasolina suele someterse inicialmente a un *splitter* que separa las líneas de obtención de xilenos de la de producción de benceno y tolueno, como se muestra en el diagrama de flujo de la Figura 1.7.

Tabla 1.1. Composición típica de la gasolina de reformado (Franck y Stadelhofer, 1988).

Hidrocarburo	% en masa
Benceno	5,0
Tolueno	24,0
Etilbenceno	4,0
o-Xileno	5,0
m-Xileno	9,0
p-Xileno	4,0
Aromáticos C_9-C_{10}	4,0
No aromáticos	45,0

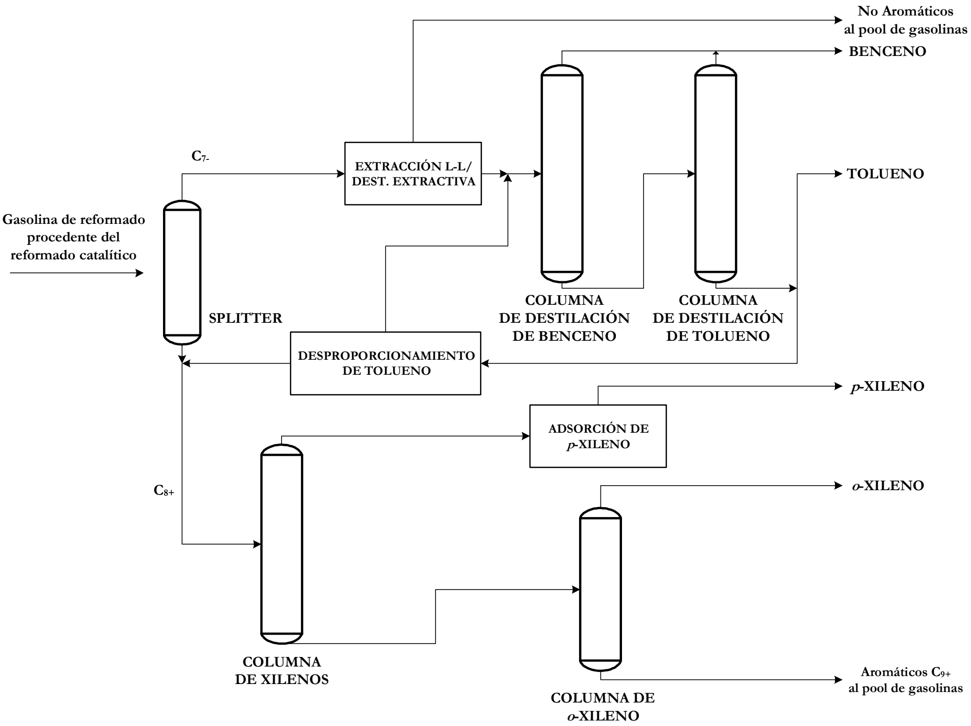


Figura 1.7. Diagrama de flujo del proceso de obtención de aromáticos a partir de gasolina de reformado (Adaptado de ThyssenKrupp, 2014).

La fracción obtenida por cabeza del *splitter*, formada por hidrocarburos de menos de siete átomos de carbono, es llevada a la unidad de separación de hidrocarburos aromáticos, que suele consistir en un proceso de extracción líquido-líquido o una destilación extractiva en función del contenido total en aromáticos. Los hidrocarburos no aromáticos presentes en la corriente de refinado son enviados al *pool* de gasolinas, mientras que el benceno y el tolueno extraídos se separan mediante dos columnas de destilación.

Una fracción del tolueno obtenido se desproporciona para incrementar la producción de xilenos y benceno. Por su parte, los xilenos obtenidos de la gasolina de reformado se separan mediante una columna de destilación para obtener *o*-xileno y *p*-xileno.

1.2.2. Gasolina de pirólisis

La gasolina de pirólisis es el principal subproducto obtenido en la producción de etileno y propileno mediante craqueo con vapor de naftas u otros cortes ligeros. En Europa y Japón, gran parte de los hidrocarburos aromáticos son obtenidos de la gasolina de pirólisis, mientras que la principal fuente de BTEX en Estados Unidos es la gasolina de reformado (Franck y Stadelhofer, 1988; Ramos Carpio, 1997).

La producción mundial actual de etileno se estima en 130 millones de toneladas anuales, mientras que la producción anual mundial de propileno es de 48 millones de toneladas. En el proceso de craqueo con vapor de naftas para la obtención de olefinas, entre un 20 % y un 30 % de la corriente de naftas alimentada produce gasolina de pirólisis. Al ser un subproducto con un gran volumen de producción anual y debido al alto contenido en BTEX de la gasolina de pirólisis, esta corriente suele emplearse tanto para la obtención de hidrocarburos aromáticos como para incrementar el octanaje del pool de gasolinas (Ali, 2012).

La composición de la gasolina de pirólisis varía en función tanto de las condiciones en las que se realiza el craqueo con vapor de naftas como de la composición de la nafta alimentada. Así, conforme aumenta la severidad de las condiciones de craqueo se ve incrementada la proporción de benceno en la gasolina de pirólisis (Franck y Stadelhofer, 1988). En la Tabla 1.2 se muestran las composiciones más habituales de las denominadas gasolinas de pirólisis suave y pirólisis severa. Como se puede observar, el contenido en no aromáticos es menor en la gasolina de pirólisis severa al verse incrementado tanto el porcentaje de benceno como de tolueno. El contenido en xilenos de ambas corrientes es similar e inferior al 10 % en masa.

Tabla 1.2. Composición típica de las gasolinas de pirólisis suave y severa (Franck y Stadelhofer, 1988).

Hidrocarburo	Gasolina de pirólisis suave % en masa	Gasolina de pirólisis severa % en masa
Benceno	22,0	33,8
Tolueno	17,5	19,4
o-Xileno	2,3	1,1
m-, *p*-Xileno y Etilbenceno	6,0	6,6
Estireno	3,2	5,3
No aromáticos	41,0	27,4

En la Figura 1.8 se representa el diagrama de flujo del proceso de obtención de hidrocarburos aromáticos a partir de gasolina de pirólisis. Esta corriente no se emplea de forma directa para la obtención de aromáticos sino que debe someterse a un proceso de hidrogenación de olefinas y diolefinas en dos etapas antes de separar los aromáticos mediante un proceso de extracción líquido-líquido o de destilación extractiva (Franck y Stadelhofer, 1988).

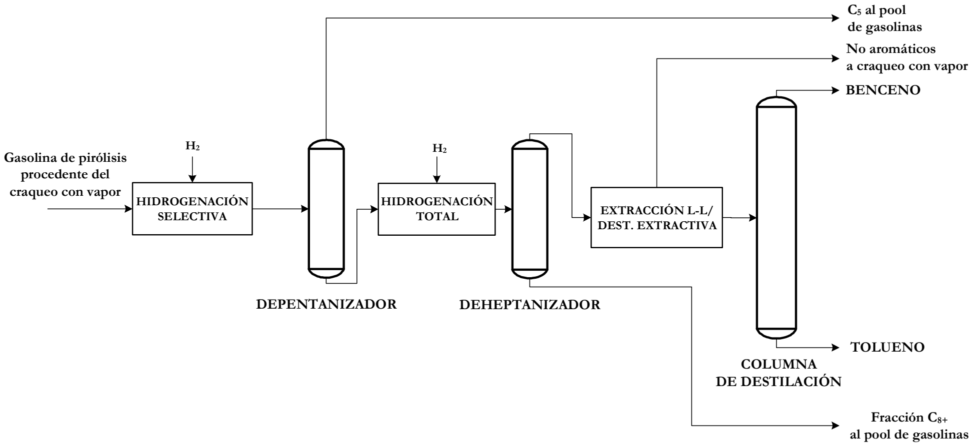


Figura 1.8. Diagrama de flujo del proceso de obtención de aromáticos a partir de gasolina de pirólisis (Adaptado de ThyssenKrupp, 2014).

La primera etapa de hidrogenación se realiza a bajas temperaturas para saturar las diolefinas sin producir fenómenos de polimerización. A continuación, la fracción de menos de cinco átomos de carbono se separa en el depentanizador y es enviada al *pool* de gasolinas. Las olefinas son totalmente saturadas en la segunda etapa de hidrogenación. Antes de realizar la separación de los hidrocarburos aromáticos mediante extracción líquido-líquido o destilación extractiva, se realiza la separación de compuestos con más de ocho átomos de carbono, como los xilenos y el etilbenceno, que son igualmente enviados al *pool* de gasolinas. Finalmente, se procede a la separación de los BTEX de los compuestos no aromáticos, destinando la corriente de refinado formada por alifáticos al craqueo con vapor, mientras que los hidrocarburos aromáticos extraídos se separan entre sí mediante columnas de destilación.

1.2.3. Nafta alimentada al cracker de etileno

En función de la procedencia de la nafta alimentada al cracker de producción de etileno, el contenido en aromáticos en dicha corriente oscila entre el 10 % y 25 % en masa. Los hidrocarburos aromáticos que se introducen en dicho proceso no se convierten en olefinas, por lo que su presencia en los hornos de craqueo provoca un sobredimensionamiento innecesario y un incremento de los costes de operación (Meindersma y de Haan, 2008). Si la mayor parte de los hidrocarburos aromáticos presentes en las naftas alimentadas al cracker de etileno pudieran ser extraídos antes de ser introducidas en los hornos, se incrementaría la eficiencia térmica y la capacidad de producción de etileno. Según cálculos realizados por Meindersma y de Haan (2008), los beneficios por la venta de los hidrocarburos extraídos serían cercanos a los 48 millones de euros en un cracker con una capacidad de 300 t/h, además de verse reducidos de forma considerable los costes de operación de la unidad.

En la Tabla 1.3 se muestra la composición más habitual de la nafta alimentada al cracker de etileno. Como se puede observar, el contenido total en aromáticos ronda el 10 % en masa, aunque en algunos casos la nafta alimentada del cracker puede tener hasta un 25 % en masa de aromáticos. En la actualidad no existe ninguna tecnología disponible que permita la separación de BTEX de corrientes con un contenido en este tipo de compuestos inferior al 25 % en masa. Por este motivo, no se aborda en las refinerías la extracción de los aromáticos presentes en las naftas empleando disolventes convencionales como el sulfolano o la *N*-metilpirrolidona (Meindersma y col., 2005).

Sin embargo, debido a las buenas propiedades extractivas que han mostrado los líquidos iónicos en la separación de aromáticos de mezclas con alifáticos con un bajo contenido en BTEX y la naturaleza no volátil de estos disolventes iónicos, en esta tesis doctoral se ha realizado la evaluación de la nafta alimentada al cracker de etileno como una posible fuente de obtención de hidrocarburos aromáticos. Por tanto, se ha estudiado la aplicación de los líquidos iónicos en la separación de BTEX de cuatro corrientes de refinería: la gasolina de reformado, las gasolinas de pirólisis suave y de pirólisis severa y la nafta alimentada al cracker de etileno.

Tabla 1.3. Composición típica de la nafta alimentada al cracker de etileno (Meindersma y de Haan, 2008).

Hidrocarburo	% en masa
Benceno	1,8
Tolueno	3,0
Etilbenceno	2,0
o-Xileno	1,0
p-Xileno	1,9
No aromáticos	90,3

1.3. Tecnologías convencionales de separación de hidrocarburos aromáticos a escala industrial

Las corrientes de gasolinas de reformado y pirólisis y las naftas presentan una gran variedad de hidrocarburos aromáticos y alifáticos mezclados en diferentes proporciones. La dificultad de la separación de los hidrocarburos aromáticos de corrientes de refinería se debe a la proximidad entre los puntos de ebullición de los diferentes hidrocarburos y a la formación de múltiples mezclas azeotrópicas. Estos hechos impiden la separación de los aromáticos mediante procesos de destilación convencional. En la Tabla 1.4, se muestran las temperaturas de ebullición y las densidades a 20 ºC de los hidrocarburos aromáticos y alifáticos más habituales en dichas corrientes así como la temperatura a la cual forman mezclas azeotrópicas con benceno.

Tabla 1.4. Temperaturas de ebullición y densidades de los hidrocarburos más habituales en las gasolinas de reformado y pirólisis y en las naftas alimentadas al cracker de etileno (Franck y Stadelhofer, 1988).

Hidrocarburo	T_{eb}/ºC	ρ a 20 ºC/g·cm^{-3}	Azeótropo con benceno/ºC
n-Hexano	69,0	0,654	68,5
n-Heptano	98,4	0,684	80,1
Ciclohexano	80,6	0,779	77,7
2,3-Dimetilpentano	89,8	0,695	79,2
Benceno	80,1	0,879	-
Tolueno	110,6	0,867	-
Etilbenceno	136,2	0,867	-
o-Xileno	144,4	0,880	-
m-Xileno	139,1	0,864	-
p-Xileno	138,4	0,861	-

Las tecnologías de separación de hidrocarburos aromáticos más empleadas son la extracción líquido-líquido y la destilación extractiva, variando la viabilidad económica del proceso en función del contenido en aromáticos de la corriente alimentada. La extracción líquido-líquido se utiliza para la separación de BTEX de corrientes con un contenido en aromáticos en masa entre el 20 % y el 65 %, mientras que la destilación extractiva encuentra su aplicación en corrientes con un porcentaje en aromáticos que oscile entre el 65 % y el 90 % en masa (Weissermel y Arpe, 2003; Meindersma y de Haan, 2008).

1.3.1. Extracción líquido-líquido

Existen en la actualidad diferentes procesos comerciales de extracción líquido-líquido para la separación de hidrocarburos aromáticos de corrientes de refinería. Las principales diferencias entre estas tecnologías radican en el disolvente empleado. Algunos de los disolventes más utilizados en extracción de aromáticos son el dietilenglicol, el trietilenglicol, el sulfolano, el dimetilsulfóxido (DMSO) y la *N*-metilpirrolidona (NMP) (Franck y Stadelhofer, 1988; Houmbourger y col., 2000; Firnhaber y col., 2000; Weissermel y Arpe, 2003). A continuación se muestran los requerimientos que debe presentar un disolvente de extracción de aromáticos para poder ser aplicado a escala industrial (Gary y col., 2007):

1. Altos valores de selectividad aromáticos/alifáticos.
2. Altos valores de coeficientes de reparto de los aromáticos.
3. Capacidad para formar dos fases a temperaturas moderadas.
4. Capacidad para facilitar una separación rápida de las fases.
5. Buena estabilidad térmica.
6. Ser no corrosivo y no reactivo.

Proceso Udex (UOP-Dow)

En 1951, se construyó la primera planta de separación de hidrocarburos aromáticos empleando el denominado proceso Udex desarrollado por Dow y UOP. Los disolventes de extracción empleados en este proceso fueron el dietilenglicol y el trietilenglicol con pequeñas adiciones de agua.

El principal inconveniente del proceso Udex fue la elevada relación másica disolvente/alimento necesaria, que podía alcanzar valores cercanos a 20/1, como consecuencia de la baja capacidad de extracción de aromáticos del dietilenglicol. Adicionalmente, los costes de operación del proceso eran muy elevados debido a las condiciones de temperatura (150 ºC) y presión (9 bar) en las que se producía la extracción líquido-líquido. Por este motivo, a partir de 1963 la mayoría de las unidades del proceso Udex fueron reemplazadas por el proceso Sulfolano (Franck y Stadelhofer, 1988; Gary y col., 2007).

Proceso Sulfolano (Shell-UOP)

El proceso Sulfolano desarrollado por Shell y UOP es utilizado actualmente para la recuperación de BTEX con alta pureza de gasolinas de reformado y de pirólisis. El nombre del proceso deriva del disolvente utilizado: el 1,1-dióxido de tetrahidrotiofeno, también conocido como sulfolano, cuya estructura se muestra en la Figura 1.9.

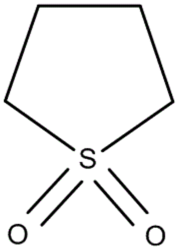


Figura 1.9. Estructura del 1,1-dióxido de tetrahidrotiofeno o sulfolano.

La capacidad de extracción del sulfolano es muy superior a la del dietilenglicol; a un valor concreto de selectividad, el coeficiente de reparto de los aromáticos empleando sulfolano es casi el doble que con los disolventes empleados en el proceso Udex. Esta mayor capacidad de extracción de los BTEX del sulfolano causa que los costes de operación y la relación disolvente/alimento del proceso Sulfolano sean muy inferiores a los alcanzados por el proceso que utilizaba dietilenglicol y el trietilenglicol como disolventes (Meyers, 2004; Gary y col., 2007).

Adicionalmente, el sulfolano presenta unas propiedades físicas que permiten minimizar los costes operativos (Meyers, 2004):

- Alta densidad (1,26 $g \cdot cm^{-3}$ a 20 ºC). Las importantes diferencias de densidad existentes entre el sulfolano y los hidrocarburos alimentados a la unidad de separación de aromáticos permiten minimizar las dimensiones del extractor.
- Bajo calor específico (1,52 $J \cdot g^{-1}$ a 20 ºC). Este valor reduce los costes energéticos en la sección de purificación y los intercambiadores de calor.
- Alto punto de ebullición (287 ºC). El punto de ebullición del sulfolano es considerablemente más alto que el que presenta el *o*-xileno (144,4 ºC), que es el hidrocarburo aromático más pesado que suele ser recuperado mediante este proceso. Este hecho facilita la regeneración del disolvente presente en la corriente de extracto.

El proceso Sulfolano consta principalmente de tres operaciones: una extracción líquido-líquido, un *stripping* extractivo para lograr la separación de los aromáticos del resto de hidrocarburos presentes en la corriente de refinería alimentada a la unidad y una destilación para separar solutos y disolvente. En la Figura 1.10 aparece representado el diagrama de flujo del proceso Sulfolano.

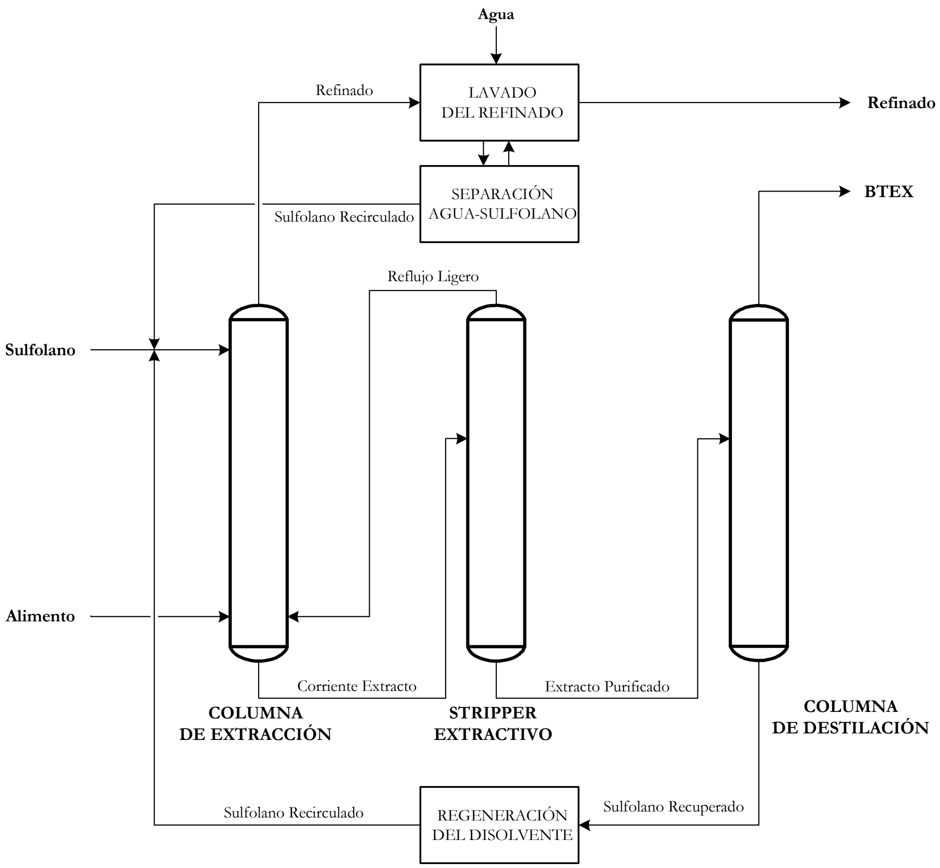


Figura 1.10. Diagrama de flujo del proceso Sulfolano desarrollado por Shell y Universal Oil Products (UOP) (Adaptado de Gary y col., 2007).

La corriente de entrada se calienta a 100-115 ºC se introduce a la columna de extracción, que generalmente suele tratarse de una columna de discos rotatorios en contracorriente (RDC). En ella se produce el proceso de extracción líquido-líquido con una relación másica disolvente/alimento de entre 3/1 y 6/1. En esta columna se obtiene por cabeza la corriente de refinado y por fondo la corriente de extracto, la cual es enviada al *stripper* extractivo. La corriente de refinado, formada mayoritariamente por hidrocarburos alifáticos, se envía directamente a la columna de lavado con agua para recuperar la fracción de sulfolano disuelta en esta corriente.

La recuperación selectiva del sulfolano del refinado se produce debido a la alta afinidad del disolvente polar por el agua y las bajas solubilidades en ella de los hidrocarburos no aromáticos. Antes de recircular el disolvente a la columna de extracción líquido-líquido se procede a la eliminación del agua disuelta en el sulfolano por rectificación (Franck y Stadelhofer, 1988; Meindersma y de Haan, 2008).

Por su parte, la corriente extracto es alimentada al *stripper* extractivo que opera a 180 ºC y 300-400 mmHg. En este equipo, se produce un proceso de destilación extractiva que permite obtener por la parte superior del stripper una corriente rica en hidrocarburos alifáticos, que es recirculada al extractor para provocar el desplazamiento de los hidrocarburos no aromáticos más pesados de la fase rica en disolvente. Por fondo del stripper se obtiene un extracto purificado que se calienta hasta 190 ºC antes de ser introducido en una columna de destilación, donde se producirá la separación de los hidrocarburos aromáticos del sulfolano. Por la parte inferior de esta columna de destilación se extrae una corriente rica en sulfolano que se recircula a la parte superior de la columna de extracción líquido-líquido. Los porcentajes de recuperación de los hidrocarburos aromáticos del proceso Sulfolano suelen ser iguales o superiores al 99,9 % para el benceno, 99,0 % para el tolueno, mientras que se recuperan al menos el 97,0 % de los xilenos presentes en la corriente de alimentación (Gary y col., 2007; Wauquier, 2000)

Proceso DMSO (IFP)

El Institut Français du Pétrole (IFP) ha desarrollado un proceso alternativo de extracción de hidrocarburos aromáticos denominado proceso DMSO. El nombre del proceso está relacionado con el disolvente de extracción utilizado: el dimetilsulfóxido (DMSO), al que suele adicionarse agua en un contenido cercano al 10 % en masa (Franck y Stadelhofer, 1988).

En la Figura 1.11 se muestra el diagrama de flujo del proceso DMSO de extracción de aromáticos. La operación de extracción líquido-líquido se realiza en dos columnas que trabajan en condiciones de temperatura (20-30 ºC) y presión (1 bar), sustancialmente más suaves que las utilizadas en los procesos Udex y Sulfolano. La relación másica disolvente/alimento en las columnas de extracción es similar a la empleada en el proceso Sulfolano con valores que oscilan entre 3/1 y 5/1. La recuperación del dimetilsulfóxido se suele realizar en una tercera columna mediante el empleo de un disolvente auxiliar parafínico con un bajo punto de ebullición como el butano. Los rendimientos de extracción de aromáticos del proceso DMSO son superiores al 99 % para el benceno, mayores del 99,5 % para el tolueno y cercanos al 97 % para los xilenos (Franck y Stadelhofer, 1988; Zaiz y col., 2013).

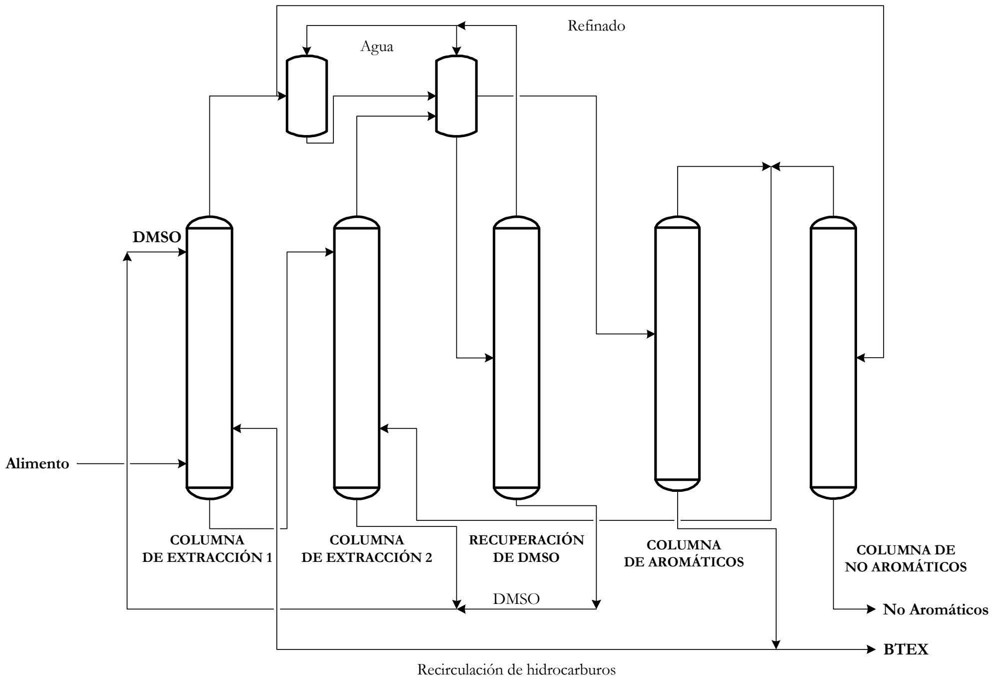


Figura 1.11. Diagrama de flujo del proceso DMSO desarrollado por el Institut Français du Pétrole (IFP) que emplea dimetilsulfóxido como disolvente (Adaptado de Franck y Stadelhofer, 1988).

Proceso Arosolvan (Lurgi)

El último de los procesos de extracción líquido-líquido que se va a describir es el proceso Arosolvan, desarrollado por la empresa alemana Lurgi. Esta tecnología de separación de hidrocarburos aromáticos emplea como disolvente de extracción la *N*-metilpirrolidona con una pequeña adición de agua que oscila entre el 12 % y el 14 % en masa. El proceso Arosolvan combina la extracción líquido-líquido con un *stripper* extractivo de forma análoga al proceso Sulfolano y con una relación másica disolvente/alimento entre 4/1 y 5/1. Sin embargo, las condiciones en las que se realiza la etapa de extracción son suaves y similares a las utilizadas por el proceso DMSO operando a temperatura entre 20 ºC y 40 ºC y a presión atmosférica. En la Figura 1.12 se muestra el diagrama de flujo del proceso Arosolvan que permite la separación de BTEX de hidrocarburos no aromáticos.

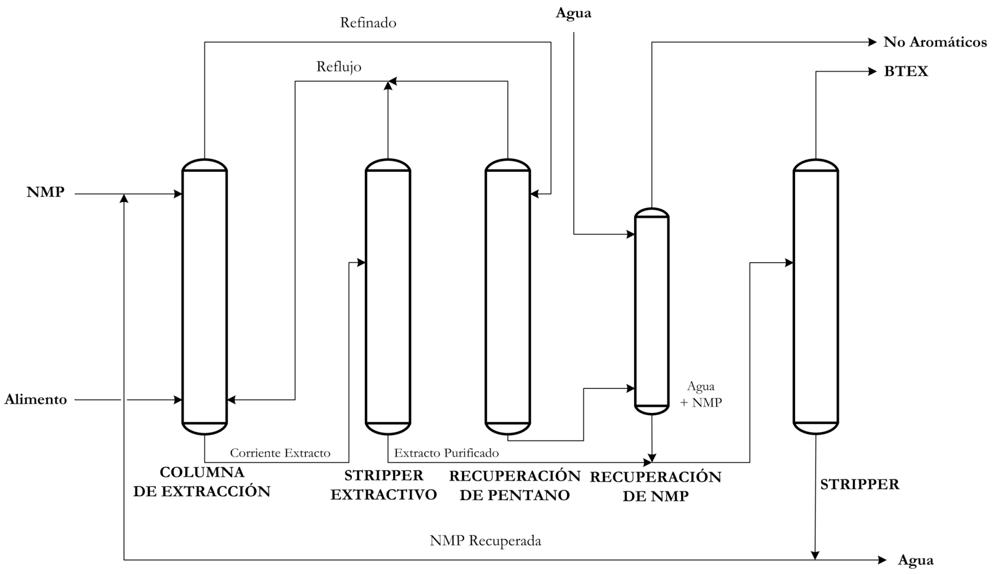


Figura 1.12. Diagrama de flujo del proceso Arosolvan desarrollado por Lurgi que emplea *N*-metilpirrolidona como disolvente.

1.3.2. Destilación extractiva

Cuando el contenido en aromáticos de la corriente de refinería oscila entre el 65 % y el 90 % en masa, la extracción líquido-líquido deja de ser viable económicamente frente a los procesos de destilación extractiva. La destilación extractiva tiene lugar en presencia de un agente másico con un alto poder disolvente de los aromáticos y una baja volatilidad relativa en relación con los compuestos que se deben separar. El objetivo del agente másico es cambiar las diferencias entre las presiones de vapor de los hidrocarburos presentes para facilitar su separación por destilación.

Proceso Morphylane (ThyssenKrupp Uhde)

El proceso más utilizado para la separación de aromáticos mediante destilación extractiva es el proceso Morphylane desarrollado por ThyssenKrupp Uhde. Esta tecnología emplea como agente másico la *N*-formilmorfolina que reduce las presiones de vapor de los aromáticos favoreciendo el proceso de destilación extractiva. En la Figura 1.13 se muestra el diagrama de flujo del proceso Morphylane.

La *N*-formilmorfolina se introduce en la columna de destilación extractiva por la parte superior para que su actuación como agente másico se produzca a lo largo de todos los pisos de la columna. Los vapores de los hidrocarburos no aromáticos dejan la columna por la parte superior y se recirculan parcialmente tras ser condensados. La corriente obtenida por fondo de la columna de destilación extractiva está formada por el disolvente y los aromáticos extraídos. La regeneración del disolvente y la obtención de los BTEX se realizan en un *stripper*. El rendimiento de recuperación del benceno en el proceso Morphylane alcanza valores comparables a los obtenidos con el proceso Sulfolano, alcanzando rendimientos superiores al 99 % (ThyssenKrupp, 2014).

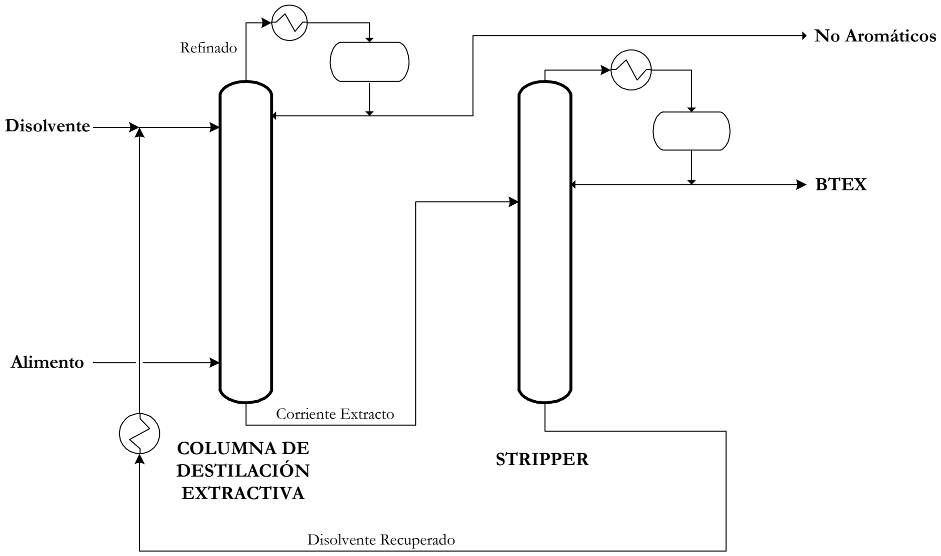


Figura 1.13. Diagrama de flujo del proceso Morphylane de destilación extractiva para la separación de BTEX (Adaptado de ThyssenKrupp, 2014).

1.4. Extracción líquido-líquido de hidrocarburos aromáticos con líquidos iónicos

En este apartado se van a presentar las propiedades más relevantes de los líquidos iónicos. Se enumerarán las principales conclusiones obtenidas en los trabajos que han estudiado la extracción de aromáticos con líquidos iónicos y se realizará un diseño conceptual del proceso de extracción de aromáticos de corrientes de refinería a escala industrial empleando estos disolventes.

1.4.1. Propiedades de los líquidos iónicos

Los líquidos iónicos son compuestos formados por iones que poseen puntos de fusión inferiores a 100 ºC. En 1914, el químico Walden sintetizó el primer líquido iónico, cuya temperatura de fusión era de 12 ºC. Sin embargo, no fue hasta la década de los 90 cuando se vio incrementado el interés por este tipo de compuestos (Sowmiah y col., 2009). Estos disolventes iónicos están formados por un catión orgánico de elevado volumen como los imidazolios, piridinios y pirrolidinos y un anión orgánico o inorgánico, entre los que destacan: [Cl], [Br], [BF_4], [PF_6], [$EtSO_4$], [Tf_2N], [SCN], [DCA] y [TCM] (Rogers y Seddon, 2003).

En compuestos iónicos convencionales, como el cloruro sódico, las energías de enlace son muy intensas como consecuencia de la proximidad de los iones en el cristal, lo que provoca temperaturas de fusión superiores a los 800 ºC. Para obtener un líquido iónico se debe evitar que los iones formen un cristal con un alto grado de compacidad minimizándose así estas fuerzas. El empaquetamiento iónico se impide con la síntesis de iones de elevado tamaño y con importantes diferencias estructurales entre los iones que conforman el líquido iónico. Además, la gran capacidad de los cationes orgánicos utilizados para deslocalizar la carga positiva hace que los puntos de fusión y las fuerzas de atracción se reduzcan considerablemente (Rogers y Seddon, 2003; Plechkova y Seddon, 2008).

La estructura de los iones afecta a las propiedades del líquido iónico, siendo el catión el principal responsable del comportamiento químico, mientras que el anión determina la mayor parte de las propiedades físicas del compuesto (Rogers y Seddon, 2003). La propiedad más destacable de los líquidos iónicos es su reducida presión de vapor, lo que ocasiona que sean considerados como compuestos no volátiles. Esta excepcional propiedad ha provocado que se hayan desarrollado un gran número de estudios experimentales en los que se ha analizado la posible sustitución de los compuestos orgánicos volátiles por líquidos iónicos como disolventes en diferentes procesos industriales (DeSimone y col, 2002).

Las propiedades físicas de los líquidos iónicos están fuertemente influenciadas por la presencia de impurezas, siendo el agua y los cloruros las que producen un mayor efecto (Torrecilla y col., 2008). Por este motivo, los datos de propiedades físicas de líquidos iónicos deben ir siempre acompañados por la especificación del compuesto, donde se indique la pureza del líquido iónico, así como el contenido en agua e impurezas (Rogers y Seddon, 2003).

La densidad de los líquidos iónicos varía en función de la estructura de los iones que los forman. Como tendencia general, un mayor peso molecular de los iones provoca un aumento en la densidad del líquido iónico (Fredlake y col., 2004). En la selección del líquido iónico más adecuado para ser empleado como disolvente en un proceso, su densidad debe diferir suficientemente de la del resto de compuestos para permitir una fácil separación. Los valores de esta propiedad en los líquidos iónicos abarcan un amplio intervalo, que oscila entre 0,8 y 3,3 g/cm^3, aunque la gran mayoría de los líquidos iónicos poseen una densidad superior a la del agua (Rogers y Seddon, 2003; Sowmiah y col., 2009).

La viscosidad de los líquidos iónicos es una característica fundamental para su aplicación en procesos industriales, ya que marcará el diseño de las operaciones de agitación y bombeo. La viscosidad de este tipo de compuestos es más elevada que la de los disolventes orgánicos convencionales, oscilando entre los 10 y 1000 mPa·s a temperatura ambiente (Plechkova y Seddon, 2008).

El límite superior de temperatura de operación en los disolventes convencionales viene marcado por la temperatura de ebullición. Sin embargo, la mayoría los líquidos iónicos se descomponen antes de vaporizarse. Por este motivo, se debe determinar la estabilidad térmica del líquido iónico o de la mezcla de líquidos iónicos mediante análisis termogravimétrico (TGA) tanto dinámico como isotermo (Navarro y col., 2014a). La temperatura máxima de operación de los líquidos iónicos oscila entre 100 ºC y 400 ºC (Anjan, 2005).

Para asegurar el correcto diseño de los futuros procesos industriales basados en líquidos iónicos, las propiedades termofísicas de estos disolventes se deben determinar experimentalmente (França y col., 2009) y, si es posible, se deben implementar modelos predictivos de estas propiedades para reducir, en la medida de lo posible, el número de determinaciones experimentales (Jacquemin y col., 2007; Palomar y col., 2007).

1.4.2. Propiedades que debería presentar un líquido iónico para ser empleado como disolvente de extracción de aromáticos

Los requerimientos que debe presentar un líquido iónico, de igual forma que el resto de disolventes, para ser empleado en el proceso de separación de hidrocarburos aromáticos de sus mezclas con hidrocarburos alifáticos mediante extracción líquido-líquido son (Meindersma y col., 2005):

- Alta solubilidad de los compuestos aromáticos en el líquido iónico.
- Baja o nula solubilidad de los hidrocarburos alifáticos en el líquido iónico.
- Separación sencilla del líquido iónico de los compuestos orgánicos que se encuentran disueltos en la fase de extracto.
- Propiedades termofísicas adecuadas para ser empleado en un proceso a escala industrial.

La idoneidad de un líquido iónico como disolvente de extracción de aromáticos de sus mezclas con hidrocarburos alifáticos se evalúa principalmente mediante el análisis de los valores del coeficiente de reparto de los aromáticos y de la selectividad aromáticos/alifáticos. Un valor elevado del coeficiente de reparto indica que la capacidad de extracción de hidrocarburos aromáticos del líquido iónico es adecuada, y por tanto, se requerirá un caudal bajo de disolvente para alcanzar una buena separación.

La selectividad está relacionada con la pureza de los hidrocarburos aromáticos extraídos. Este parámetro interesa que sea lo mayor posible para simplificar las operaciones de purificación de los aromáticos y mejorar su salida comercial. En la selección de un disolvente de extracción, además de los valores de selectividad y coeficiente de reparto del soluto, también deben considerarse sus propiedades físicas al tener una importante influencia sobre el diseño de los procesos industriales.

La densidad del líquido iónico seleccionado debe ser cercana al valor mostrado por el sulfolano (1,252 $g \cdot cm^{-3}$ a 40 ºC), ya que este valor permite tener una diferencia de densidades entre el disolvente de extracción y los hidrocarburos adecuada en el extractor. Para que en el interior del extractor se alcance un comportamiento hidrodinámico correcto, tanto la viscosidad como la tensión superficial del líquido iónico utilizado deberían ser cercanos a los valores del sulfolano (8,05 $mPa \cdot s$ y 47,2 $mN \cdot m^{-1}$ a 40 ºC). Por último, la estabilidad térmica del líquido iónico seleccionado debe ser suficiente para soportar ciclos consecutivos de extracción y regeneración sin que se degrade.

1.4.3. Diseño conceptual del proceso de extracción de hidrocarburos aromáticos empleando líquidos iónicos

Los principales inconvenientes del proceso Sulfolano son los elevados costes energéticos de la unidad de separación de los hidrocarburos del disolvente como consecuencia de su alto punto de ebullición (287 ºC) y la necesidad de recuperar el sulfolano disuelto en la frase de refinado. La prácticamente nula presión de vapor de los líquidos iónicos permitiría simplificar el tren de separación de los aromáticos extraídos del disolvente, realizando este proceso mediante *stripping* o varias destilaciones *flash* en serie (Anjan, 2005; Navarro y col., 2015).

Por otro lado, la muy baja solubilidad de los líquidos iónicos en la fase de refinado simplificaría el proceso de extracción (Arce y col., 2007). En la Figura 1.14 se muestra una propuesta de diagrama de flujo para un proceso industrial de extracción de aromáticos utilizando líquidos iónicos.

En el diagrama de flujo del proceso propuesto, la extracción de los aromáticos se realizaría en una columna de extracción en la que el disolvente formado por un líquido iónico o una mezcla binaria de líquidos iónicos se alimentaría por la parte superior de la columna debido a su mayor densidad respecto a la mezcla de hidrocarburos alimentada, obteniendo la corriente de extracto por la parte inferior y la corriente de refinado por cabeza de columna. Las condiciones de operación de la columna de extracción de aromáticos utilizando líquidos iónicos serían considerablemente más suaves (20-40 ºC y 1 atm) que las empleadas en el proceso Sulfolano (100-115 ºC y 2 atm) (Meindersma y col., 2008; Franck y Stadelhofer, 1988). De esta forma, se reducirían los costes de operación de la unidad de extracción de BTEX.

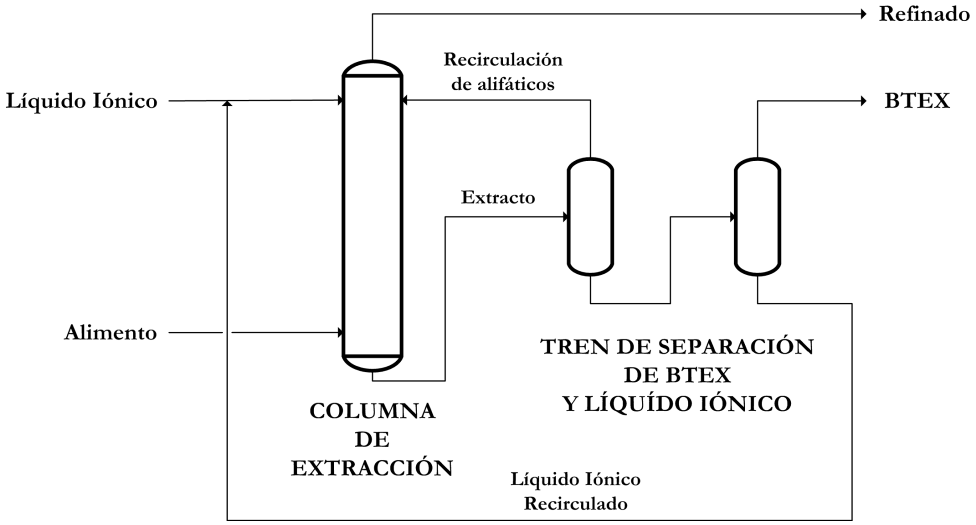


Figura 1.14. Diagrama de flujo de un proceso de extracción de hidrocarburos aromáticos empleando líquidos iónicos.

La sección de recuperación de los aromáticos extraídos también se vería simplificada de forma sustancial con respecto al proceso Sulfolano, como consecuencia de la volatilidad prácticamente nula de los líquidos iónicos. Como se indicó en el apartado 1.3.1 de la presente memoria, el tren de purificación empleando sulfolano está formado por un stripper extractivo que trabaja a 180 ºC y en condiciones de vacío y una columna de destilación que permite obtener una corriente rica en sulfolano que se recircula al extractor.

Esta sección de recuperación de los hidrocarburos se vería sustituida en un proceso que utilice líquidos iónicos por un *stripper* o varias destilaciones *flash* en serie. De acuerdo con los resultados experimentales de Navarro y col. (2015), la presencia de un líquido iónico incrementa considerablemente la volatilidad relativa de los alifáticos respecto de los aromáticos, por lo que en un primer flash o en el *stripper* se podría obtener una corriente rica en alifáticos que se recircularía al extractor. En un segundo flash, por la prácticamente nula volatilidad de los líquidos iónicos se obtendrían los BTEX por cabeza y una corriente rica en líquido iónico (Navarro y col., 2015).

1.4.4. Conclusiones de los trabajos publicados sobre extracción de hidrocarburos aromáticos con líquidos iónicos

Hasta la fecha, más de 130 líquidos iónicos han sido investigados como posibles alternativas al sulfolano en la extracción de hidrocarburos aromáticos de sus mezclas con hidrocarburos alifáticos. Aproximadamente el 75 % de los estudios experimentales realizados en este campo han empleado líquidos iónicos basados en el catión imidazolio, mientras que casi el 20 % de las investigaciones han utilizado líquidos iónicos basados en el catión piridinio. La selección de estos cationes se ha debido al carácter aromático de los mismos, buscando incrementar la afinidad de los hidrocarburos aromáticos por el disolvente (Meindersma y col., 2010; Meindersma y de Haan, 2012).

La evaluación del potencial de un líquido iónico como disolvente sustituto del sulfolano en la extracción de aromáticos se realiza mediante un análisis comparativo entre las propiedades extractivas alcanzadas por ambos disolventes. Para simplificar los ensayos de determinación del equilibrio líquido-líquido y los métodos de análisis, en los trabajos publicados hasta la fecha se han estudiado sistemas ternarios formados por un hidrocarburo aromático, generalmente el tolueno, un hidrocarburo alifático, el *n*-heptano, y el disolvente de extracción.

De los líquidos iónicos estudiados, únicamente un número muy reducido de ellos han presentado conjuntamente selectividades y coeficientes de reparto de los aromáticos superiores a los valores del sulfolano. De forma general, existe una relación inversa entre la selectividad y el coeficiente de reparto que presentan los líquidos iónicos puros en la extracción de aromáticos, es decir, los líquidos iónicos que muestran una elevada selectividad presentan un bajo coeficiente de reparto del tolueno y viceversa. Esta relación inversa entre ambas propiedades extractivas limita enormemente el potencial de los líquidos iónicos puros para ser empleados en la extracción de hidrocarburos aromáticos a escala industrial (Meindersma y col., 2010).

Fletcher y col. (2003) estudiaron las interacciones entre iones en mezclas binarias de líquidos iónicos. Estos autores concluyeron que una mezcla de líquidos iónicos en proporciones adecuadas presentaba propiedades intermedias entre las mostradas por los líquidos iónicos puros. Este hecho, ha sido aplicado en la extracción de hidrocarburos aromáticos con líquidos iónicos. Una mezcla binaria formada por un líquido iónico con alta selectividad y otro líquido iónico con un coeficiente de reparto del tolueno elevado actúa como disolvente de extracción con propiedades extractivas intermedias entre las alcanzadas por los dos líquidos iónicos puros (García y col., 2012a).

Además de las propiedades extractivas, las mezclas binarias de líquidos iónicos presentan propiedades físicas como la densidad, la viscosidad, la tensión superficial y la estabilidad térmica intermedias entre los valores de los líquidos iónicos puros (Larriba y col., 2012; Navarro y col. 2014a). Por este motivo, en la selección de dos líquidos iónicos para formar una mezcla con potencial para ser utilizada a escala industrial en la extracción de aromáticos se deben tener en consideración tanto sus propiedades extractivas como las físicas. Sin embargo, teniendo en cuenta el gran número de líquidos iónicos disponibles, el número de posibles mezclas binarias de líquidos iónicos podría superar el millón (Rogers y col., 2003). Este elevado número, pone de manifiesto la necesidad de implementar modelos predictivos de las propiedades físicas y extractivas de mezclas binarias de líquidos iónicos para reducir el número de determinaciones experimentales necesarias.

En la Tabla 1.5, se muestran las propiedades extractivas de los líquidos iónicos puros y las mezclas binarias de líquidos iónicos más relevantes en la extracción de tolueno de *n*-heptano en mezclas de hidrocarburos con un 10 % de tolueno junto con los valores mostrados por el sulfolano. Además de los valores de los coeficientes de reparto del tolueno en base molar y las selectividades tolueno/*n*-heptano, se ha incluido la densidad y la viscosidad de los diferentes disolventes de extracción, ya que estas propiedades físicas son las que determinan el comportamiento fluidodinámico en la columna de extracción líquido-líquido (Buchbender y col., 2012).

Como se puede observar, únicamente cuatro líquidos iónicos puros entre los mostrados han superado conjuntamente los valores de coeficiente de reparto del tolueno y selectividad tolueno/*n*-heptano alcanzados por el sulfolano: el [bmim][DCA], el [bmim][SCN], el [bmim][TCM] y el [bpy][BF_4] (Hansmeier y col., 2010; Meindersma y col., 2010; García y col., 2010).

Tabla 1.5. Coeficiente de reparto del tolueno en base molar, selectividades tolueno/*n*-heptano, densidades y viscosidades a 313,2 K de diferentes disolventes de extracción en la separación de tolueno de *n*-heptano.

Disolvente	D_2	$\alpha_{2,1}$	$\rho/\mathrm{g\cdot cm^{-3}}$	$\eta/\mathrm{mPa\cdot s}$	**Referencias**
[emim][MeSO$_4$]	0,174	**87,9**	1,276	42,9	(García y col., 2012b; Costa y col., 2011)
[emim][EtSO$_4$]	0,250	**30,7**	1,228	67,4	(González y col., 2011; Larriba y col., 2011)
[bmim][DCA]	**0,492**	**46,0**	1,051	16,7	(Hansmeier y col., 2010)
[bmim][SCN]	**0,416**	**44,3**	1,062	32,2	(Hansmeier y col., 2010)
[bmim][TCM]	**0,850**	**49,3**	1,034	18,4	(Meindersma y col., 2010; Carvalho y col., 2010)
[bmim][Tf$_2$N]	**1,102**	19,4	1,442	28,5	(García y col., 2011a; Esperança y col., 2006)
[hmim][Tf$_2$N]	**1,326**	12,5	1,349	36,2	(Corderí y col., 2012; Kandil y col., 2007)
[3empy][EtSO$_4$]	0,250	**29,2**	1,219	77,1	(González y col., 2010; González y col., 2008)
[bpy][BF$_4$]	**0,356**	**54,6**	1,203	74,8	(García y col., 2010; Larriba y col., 2012)
[bpy][Tf$_2$N]	**1,358**	23,8	1,434	33,7	(García y col., 2011b; Larriba y col., 2012)
[4bmpy][Tf$_2$N]	**1,724**	25,2	1,398	30,6	(García y col., 2011b; Larriba y col., 2013)
{[bpy][BF$_4$] + [bpy][Tf$_2$N]}	**0,518**	**32,5**	1,310	57,5	(García y col., 2012a; Larriba y col., 2012)
{[bpy][BF$_4$] + [4bmpy][Tf$_2$N]}	**0,611**	**32,9**	1,296	59,6	(García y col., 2012c; Larriba y col., 2013)
{[4bmpy][Tf$_2$N] +[emim][EtSO$_4$]}	**0,704**	21,7	1,339	55,9	(García y col., 2012d; Larriba y col., 2015)
{[4bmpy][Tf$_2$N] +[emim][TFES]}	**0,481**	**32,8**	1,409	43,8	(García y col., 2013; Larriba y col., 2015)
Sulfolano	**0,275**	**29,4**	**1,253**	**8,05**	

La aplicación industrial del [bpy][BF_4] sería complicada por su viscosidad, casi 10 veces superior a la del sulfolano. Por un motivo similar también se pueden descartar las tres mezclas binarias de líquidos iónicos que han mostrado propiedades extractivas superiores a los valores del sulfolano: {[bpy][BF_4] + [bpy][Tf_2N]}, {[4bmpy][Tf_2N] + [emim][$EtSO_4$]} y {[4bmpy][Tf_2N] + [emim][TFES]. Sus viscosidades fueron entre 5 y 7 veces mayores que la viscosidad del sulfolano, lo que ocasionaría que su empleo a escala industrial incrementase considerablemente los costes de bombeo y agitación y dificultaría los procesos de transferencia de materia en el extractor líquido-líquido.

Los líquidos iónicos [bmim][DCA], [bmim][SCN] y [bmim][TCM] además de presentar mejores propiedades extractivas que las del sulfolano, se encuentran entre los que exhiben valores de viscosidad más reducidos. Sin embargo, los líquidos iónicos basados en los aniones dicianamida ([DCA]), tiocianato ([SCN]) y tricianometano ([TCM]) presentan dos ligeros inconvenientes: una densidad algo inferior a la del sulfolano y una estabilidad térmica inferior a la mostrada por otros líquidos iónicos como los basados en el anión bis(trifluorometilsulfonil)imida ([Tf_2N]) (Fredlake y col., 2004; Crosthwaite y col., 2005).

Ambos inconvenientes podrían ser reducidos o solventados al ser mezclados con un líquido iónico que presente mayor estabilidad térmica y una densidad mayor que el sulfolano. Como se puede observar en la Tabla 1.5, los líquidos iónicos que presentan una mayor densidad son los basados en el anión [Tf_2N], siendo además esta familia de líquidos iónicos la que ha mostrado una mayor estabilidad térmica (Crosthwaite y col., 2005) y coeficientes de reparto del tolueno más elevados (García y col., 2011a).

1.5. Objetivos y etapas de la investigación

El objetivo principal del presente trabajo es estudiar la extracción de hidrocarburos aromáticos de la nafta alimentada al cracker de etileno, la gasolina de reformado y las gasolinas de pirólisis suave y severa empleando una mezcla de líquidos iónicos. En primer lugar se han seleccionado los líquidos iónicos a emplear en esta tesis doctoral considerando las conclusiones alcanzadas por los trabajos publicados hasta la fecha sobre extracción de aromáticos con estos disolventes.

A continuación, se han estudiado las propiedades extractivas de los diferentes líquidos iónicos puros seleccionados en la extracción de tolueno de sus mezclas con *n*-heptano. Considerando las propiedades extractivas y las propiedades físicas de los líquidos iónicos puros se han seleccionado las dos mezclas binarias de líquidos iónicos que presentan mayor potencial para ser empleadas a escala industrial en la extracción de aromáticos. Tras determinar las propiedades físicas y extractivas de las dos mezclas de líquidos iónicos propuestas, se ha seleccionado la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} como la más adecuada para realizar la extracción de aromáticos de corrientes de refinería.

Finalmente, empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} y el sulfolano se han realizado ensayos experimentales de extracción de BTEX de las cuatro corrientes de refinería en función de la temperatura y la relación másica disolvente/alimento, para así determinar las condiciones óptimas de operación. A partir de los resultados experimentales se ha realizado la simulación de las columnas de extracción líquido-líquido mediante el método de Kremser, comparando los resultados obtenidos empleando ambos disolventes.

Selección de los líquidos iónicos

Por todo lo expuesto en el apartado en el que se han analizado las conclusiones de los trabajos publicados hasta la fecha sobre extracción de aromáticos con líquidos iónicos, se ha seleccionado trabajar en esta tesis doctoral con líquidos iónicos basados en los aniones [DCA], [SCN], [TCM] y [Tf_2N].

A continuación, se va a realizar la exposición de los motivos que han justificado la elección de los cationes que conforman los líquidos iónicos empleados. Esta selección se ha decantado, entre los diferentes cationes disponibles, por los cationes imidazolio y piridinio, ya que, como se ha explicado en el apartado 1.4.4., éstos han mostrado buenas propiedades extractivas de hidrocarburos aromáticos.

Para potenciar las propiedades más relevantes de los líquidos iónicos basados en los aniones [DCA], [SCN] y [TCM], se ha seleccionado trabajar con cationes imidazolio, ya que los líquidos iónicos basados en este catión muestran una menor viscosidad y una mayor selectividad aromático/alifático que los basados en el catión piridinio (Meindersma y de Haan, 2012).

Para la selección de la longitud de cadena alquílica en el catión imidazolio, se ha tenido en consideración que un incremento en la longitud de esta cadena reduce el valor de la selectividad aromático/alifático, aumenta la viscosidad y reduce la densidad (Arce y col., 2007; García y col. 2010a; Jacquemin y col., 2007). Por tanto, para ser aplicados en extracción de hidrocarburos aromáticos de corrientes de refinería se deberán seleccionar líquidos iónicos con cationes imidazolio con cadenas alquílicas de poca longitud.

Por todo ello, los cinco líquidos iónicos seleccionados han sido los siguientes:

- 1-etil-3-metilimidazolio dicianamida ([emim][DCA]).
- 1-butil-3-metilimidazolio dicianamida ([bmim][DCA]).
- 1-etil-3-metilimidazolio tiocianato ([emim][SCN]).
- 1-butil-3-metilimidazolio tiocianato ([bmim][SCN]).
- 1-etil-3-metilimidazolio tricianometano ([emim][TCM]).

Por último, se ha seleccionado el catión que formará el líquido iónico basado en el anión [Tf_2N]. El objetivo de emplear un líquido iónico de esta familia es incrementar los valores de coeficiente de reparto de tolueno, la densidad y la estabilidad térmica al ser mezclado con otro líquido iónico basado en los aniones [DCA], [SCN] o [TCM]. Trabajando con la misma longitud de cadena alquílica de los sustituyentes y un mismo anión, un líquido iónico basado en el catión piridinio muestra un mayor coeficiente de reparto del aromático (Hansmeier y col., 2010; Meindersma y de Haan, 2012); por este motivo, parece más adecuado emplear un catión piridinio que un imidazolio para ser combinado con el anión [Tf_2N].

Las densidades y estabilidades térmicas mostradas por las familias de imidazolios y piridinios con igualdad de longitud de cadena alquílica son muy similares al ser más dependientes de la estructura del anión, por lo que estas propiedades no han sido tenidas en consideración para la selección del catión del líquido iónico (Esperança y col., 2006; Tokuda y col., 2006; Fredlake y col., 2004; Crosthwaite y col., 2005).

Una vez seleccionado el catión piridinio, se ha elegido trabajar con dos cadenas alquílicas unidas al anillo de piridinio, ya que de esta forma se reduce ligeramente la viscosidad (Larriba y col., 2012 y 2013) y se ve incrementado el coeficiente de reparto de los aromáticos (García y col., 2011b).

De forma análoga a los líquidos iónicos basados en el catión imidazolio, se ha seleccionado trabajar con un líquido iónico con cadenas alquílicas cortas para incrementar la densidad y reducir la viscosidad (Jacquemin y col., 2005). Por último, la presencia de un grupo metilo en posición 3 o 4 del anillo de piridinio mejora sustancialmente la solubilidad de los aromáticos en el líquido iónico (Kim y col., 2013). Por todo lo expuesto, el líquido iónico seleccionado ha sido el 1-etil-4-metilpiridinio bis(trifluorometilsulfonil)imida ([4empy][Tf_2N]).

Extracción de tolueno de n-heptano utilizando líquidos iónicos puros

Una vez seleccionados los seis líquidos iónicos puros a emplear en la tesis doctoral, en una primera fase experimental se realizó el estudio de la extracción líquido-líquido de hidrocarburos aromáticos en sistemas ternarios formados por un hidrocarburo alifático (*n*-heptano), un aromático (tolueno) y un líquido iónico a una temperatura de 313,2 K. Asimismo, los líquidos iónicos puros fueron caracterizados mediante la determinación de su densidad, viscosidad y tensión superficial en función de la temperatura. Los resultados obtenidos en esta etapa se recogen en las Publicaciones 1 y 2 del apartado de anexos:

- **Publicación 1:** M. Larriba, P. Navarro, J. García, F. Rodríguez. Liquid−Liquid Extraction of Toluene from Heptane Using [emim][DCA], [bmim][DCA], and [emim][TCM] Ionic Liquids. Industrial & Engineering Chemistry Research, 2013, 52, 2714-2720.
- **Publicación 2:** M. Larriba, P. Navarro, J. García, F. Rodríguez. Selective Extraction of Toluene from *n*-Heptane using [emim][SCN] and [bmim][SCN] Ionic Liquids as Solvents, Journal of Chemical Thermodynamics, 2014, 79, 266-271.

Extracción de aromáticos de alifáticos utilizando mezclas de líquidos iónicos

A partir de las propiedades tanto extractivas como físicas de los líquidos iónicos puros se realizó la selección de las dos mezclas binarias de líquidos iónicos con mayor potencial como disolventes: {[emim][TCM] + [emim][DCA]} y {[4empy][Tf_2N] + [emim][DCA]}. Para realizar la selección de estas mezclas se consideraron las predicciones de las propiedades extractivas de las mezclas realizadas mediante la ecuación de Yalkowsky y Roseman.

A continuación, se realizaron ensayos de equilibrio pseudoternario en sistemas formados por un alifático, un aromático y cada una de las mezclas de líquidos iónicos a una temperatura de 313,2 K. En esta misma fase experimental se determinaron las densidades y las viscosidades de las mezclas binarias de líquidos iónicos en función de la temperatura y la composición. Considerando las propiedades extractivas y físicas de las mezclas de líquidos iónicos se determinó la composición óptima de cada una de las mezclas binarias para realizar la extracción de aromáticos. Los resultados obtenidos en esta etapa se recogen en las Publicaciones 3, 4, 5 y 6 del apartado de anexos:

- **Publicación 3:** M. Larriba, P. Navarro, J. García, F. Rodríguez. Separation of Toluene from *n*-Heptane, 2,3-Dimethylpentane, and Cyclohexane using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids as Extraction Solvents. Separation and Purification Technology, 2013, 120, 392-401.
- **Publicación 4:** M. Larriba, P. Navarro, J. García, F. Rodríguez. Liquid–liquid Extraction of Toluene from *n*-Heptane by {[emim][TCM] + [emim][DCA]} Binary Ionic Liquid Mixtures. Fluid Phase Equilibria, 2014, 364, 48-54.

- **Publicación 5:** M. Larriba, P. Navarro, J. García, F. Rodríguez. Liquid−Liquid Extraction of Toluene from *n*-Alkanes using {[4empy][Tf_2N] + [emim][DCA]} Ionic Liquid Mixtures. Journal of Chemical & Engineering Data, 2014, 59, 1692-1699.
- **Publicación 6:** M. Larriba, P. Navarro, J. García, F. Rodriguez. Extraction of Benzene, Ethylbenzene, and Xylenes from *n*-Heptane using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids. Fluid Phase Equilibria, 2014, 380, 1-10.

Extracción de aromáticos de corrientes de refinería empleando la mezcla de líquidos iónicos seleccionada

En la última etapa experimental de esta tesis doctoral, una vez que se seleccionó la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} como la más adecuada para realizar la extracción de hidrocarburos aromáticos de sus mezclas con alifáticos y la composición óptima en dicha mezcla, se abordó la separación de aromáticos de mezclas sintéticas de hidrocarburos representativas de cuatro corrientes de refinería: la nafta alimentada al cracker de etileno, la gasolina de reformado y las gasolinas de pirólisis suave y severa.

Para la selección de las composiciones de estas mezclas se tomaron como referencia las composiciones habituales de estas corrientes mostradas en el apartado 1.2 de la memoria. Para simplificar el procedimiento de análisis, el contenido en *o*-xileno, *m*-xileno y *p*-xileno de las composiciones habituales de las corrientes de refinería estuvo representado en las mezclas sintéticas por *p*-xileno. Por el mismo motivo, el contenido en no aromáticos estuvo formado por porcentajes iguales de *n*-hexano, *n*-heptano y *n*-octano. En la Tabla 1.6 se muestran las composiciones de las mezclas sintéticas representativas de las cuatro corrientes de refinería.

Tabla 1.6. Composiciones de las mezclas sintéticas representativas de corrientes de refinería empleadas en esta tesis doctoral.

	Nafta	Gasolina de reformado	Gasolina de pirólisis suave	Gasolina de pirólisis severa
Hidrocarburo	% en masa			
Benceno	1,8	5,0	22,0	33,8
Tolueno	3,0	24,0	17,6	19,3
Etilbenceno	2,0	4,0	-	-
p-Xileno	3,2	22,0	11,5	13,0
n-Hexano	30,0	15,0	16,3	11,3
n-Heptano	30,0	15,0	16,3	11,3
n-Octano	30,0	15,0	16,3	11,3

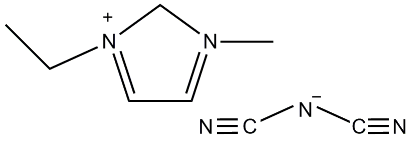
Finalmente, a partir de los resultados experimentales de la extracción de aromático de las cuatro corrientes, se realizó la simulación de las columnas de extracción mediante el método de Kremser. Los resultados obtenidos en esta última etapa se recogen en las Publicaciones 7, 8 y 9 del apartado de anexos:

- **Publicación 7:** M. Larriba, P. Navarro, E.J. González, J. García, F. Rodríguez. Separation of BTEX from a naphtha feed to ethylene crackers using a binary mixture of [4empy][Tf_2N] and [emim][DCA] ionic liquids. Separation and Purification Technology, 2015, 144, 54-62.
- **Publicación 8:** M. Larriba, P. Navarro, J. García, F. Rodríguez. Liquid−Liquid Extraction of BTEX from Reformer Gasoline Using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids. Energy and Fuels, 2014, 28, 6666-6676.
- **Publicación 9:** M. Larriba, P. Navarro, E.J. González, J. García, F. Rodríguez. Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid-liquid extraction using a binary mixture of [4empy][Tf_2N] and [emim][DCA] ionic liquids. Fuel Processing Technology, 2015, DOI: 10.1016/j.fuproc.2015.03.009.

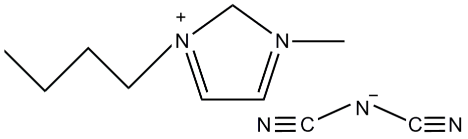
2. PROCEDIMIENTO EXPERIMENTAL Y MÉTODOS DE ANÁLISIS

2.1. Materiales

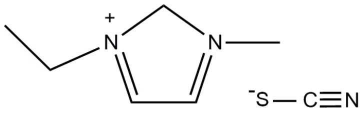
Los seis líquidos iónicos utilizados en los ensayos de extracción líquido-líquido realizados en esta tesis doctoral fueron suministrados por Iolitec GmbH (Alemania). En la Figura 2.1 se muestran las estructuras de los líquidos iónicos, mientras que en la Tabla 2.1 se resumen las purezas y los contenidos en agua y haluros de los disolventes de extracción empleados incluyendo el sulfolano que se ha empleado como disolvente de referencia.



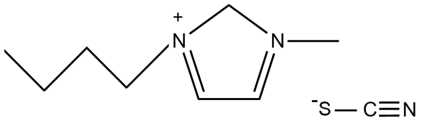
[emim][DCA]



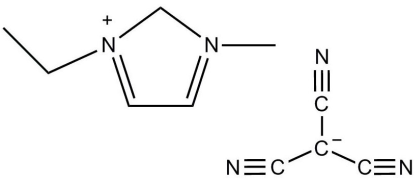
[bmim][DCA]



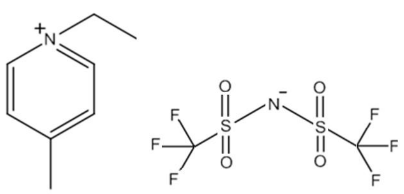
[emim][SCN]



[bmim][SCN]



[emim][TCM]



[4empy][Tf$_2$N]

Figura 2.1. Estructura y abreviatura de los líquidos iónicos empleados en esta tesis doctoral.

Tabla 2.1. Suministrador y pureza de los disolventes de extracción de aromáticos utilizados en la tesis doctoral.

Líquido iónico	Suministrador	Pureza en masa	Contenido en agua en masa	Contenido en haluros en masa
[emim][DCA][a]	Iolitec	> 0,98	937 ppm	< 2 %
[bmim][DCA][b]	Iolitec	> 0,98	1810 ppm	< 2 %
[emim][SCN][c]	Iolitec	> 0,98	960 ppm	< 2 %
[bmim][SCN][d]	Iolitec	> 0,98	1725 ppm	< 2 %
[emim][TCM][e]	Iolitec	> 0,98	383 ppm	< 0,5 %
[4empy][Tf$_2$N][f]	Iolitec	> 0,99	89 ppm	< 100 ppm
Sulfolano	Sigma-Aldrich	> 0,99	-	-

[a] 1-etil-3-metilimidazolio dicianamida
[b] 1-butil-3-metilimidazolio dicianamida
[c] 1-etil-3-metilimidazolio tiocianato
[d] 1-butil-3-metilimidazolio tiocianato
[e] 1-etil-3-metilimidazolio tricianometano
[f] 1-etil-4-metilpiridinio bis(trifluorometilsulfonil)imida

La pureza de los líquidos iónicos fue determinada por el suministrador mediante Resonancia Magnética Nuclear (RMN), el contenido en agua utilizando el método de Karl Fischer y el contenido en haluros empleando cromatografía iónica. En los ensayos de extracción de aromáticos y en la determinación de las propiedades físicas, los líquidos iónicos fueron utilizados tal y como fueron proporcionados por el suministrador, sin someterlos a ningún proceso de purificación adicional.

Los líquidos iónicos fueron almacenados en un desecador para evitar su hidratación con la humedad presente en el ambiente. Además, por el mismo motivo, la manipulación de los líquidos iónicos se realizó en el interior de una cámara de guantes como la mostrada en la Figura 2.2. Antes de realizar la preparación de los ensayos de extracción, la cámara de guantes fue llenada con nitrógeno seco industrial S1 proporcionado por Praxair para poder manipular los líquidos iónicos en su interior bajo una atmósfera libre de humedad y mantener constante el contenido de agua en los mismos.

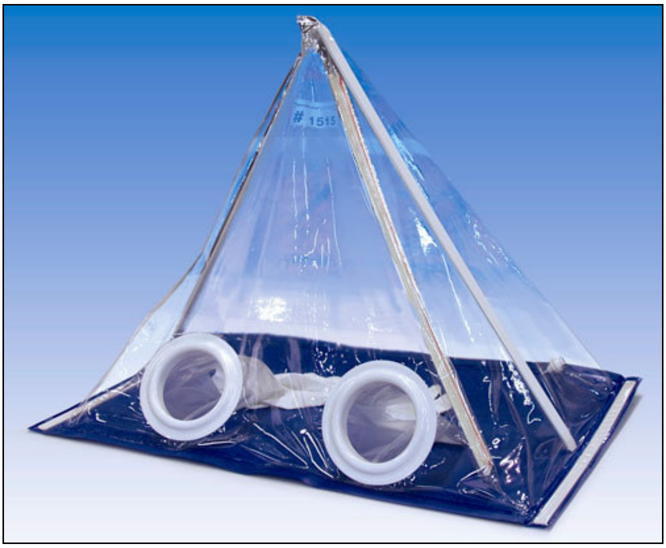


Figura 2.2. Cámara de guantes *Pyramid* de Erlab donde se realizó la manipulación de los líquidos iónicos.

En los ensayos experimentales de extracción de hidrocarburos aromáticos se emplearon doce hidrocarburos suministrados por Sigma-Aldrich para confeccionar las diferentes mezclas sintéticas de hidrocarburos. En la Tabla 2.2 se muestran las purezas de los hidrocarburos utilizados. La pureza indicada en la tabla fue determinada por el suministrador mediante cromatografía de gases, teniendo todos los hidrocarburos una pureza en masa superior al 99 %.

Se han utilizado cuatro hidrocarburos alifáticos de cadena lineal (el *n*-hexano, el *n*-heptano, el *n*-octano y el *n*-nonano), un hidrocarburo alifático cíclico (el ciclohexano) y un alifático ramificado (el 2,3-dimetilpentano). También se emplearon seis hidrocarburos aromáticos: el benceno, el tolueno, el etilbenceno y los tres isómeros del xileno (*o*-xileno, *m*-xileno y *p*-xileno).

Tanto en la preparación de muestras en el interior de la cámara de guantes como en los métodos de análisis que se describirán en el apartado siguiente se han empleado gases suministrados por Praxair, recogiendo en la Tabla 2.3 los gases utilizados y sus purezas.

Tabla 2.2. Suministrador y pureza de los hidrocarburos utilizados.

Hidrocarburo	Suministrador	Pureza en fracción másica
n-Hexano	Sigma-Aldrich	> 0,995
n-Heptano	Sigma-Aldrich	> 0,997
n-Octano	Sigma-Aldrich	> 0,99
n-Nonano	Sigma-Aldrich	> 0,99
2,3-Dimetilpentano	Sigma-Aldrich	> 0,99
Ciclohexano	Sigma-Aldrich	> 0,995
Benceno	Sigma-Aldrich	> 0,995
Tolueno	Sigma-Aldrich	> 0,995
Etilbenceno	Sigma-Aldrich	> 0,998
o-Xileno	Sigma-Aldrich	> 0,99
m-Xileno	Sigma-Aldrich	> 0,99
p-Xileno	Sigma-Aldrich	> 0,99

Tabla 2.3. Suministrador y pureza de los gases utilizados.

Gas	Suministrador	Pureza
Nitrógeno Industrial Seco	Praxair	-
Helio	Praxair	3X
Aire	Praxair	3X
Hidrógeno	Praxair	3X

2.2. Ensayos de extracción líquido-líquido

En primer lugar, se van a describir las diferentes etapas del procedimiento experimental seguidas en la preparación de los ensayos de extracción líquido-líquido de hidrocarburos aromáticos. Posteriormente, se realizará la descripción detallada de los procedimientos de análisis empleados para la determinación de las composiciones de las fases de extracto y de refinado obtenidas en los ensayos de extracción.

2.2.1. Procedimiento experimental

2.2.1.1. Ensayos de extracción líquido-líquido de hidrocarburos aromáticos en sistemas ternarios y pseudoternarios

Los ensayos de extracción líquido-líquido de hidrocarburos aromáticos fueron realizados en viales de vidrio de 8 mL con un tapón roscado que proporciona un cierre hermético. Se empleó una técnica gravimétrica para determinar la composición de la mezcla alimentada a los viales en los ensayos de extracción. Para ello, se determinó inicialmente la masa del vial vacío mediante una balanza analítica Mettler Toledo XS 205 con una precisión de $\pm 1 \cdot 10^{-5}$ g como la mostrada en la Figura 2.3. A continuación, se añadió gravimétricamente la mezcla de hidrocarburos formada por un alifático y un aromático. Finalmente, se agregó al vial la masa correspondiente del líquido iónico o de la mezcla de líquidos iónicos.

Para realizar la extracción de los hidrocarburos aromáticos, los viales con los hidrocarburos y el disolvente de extracción se introdujeron en un agitador orbital Vortemp 1550 a (313,2 ± 0,1) K durante 5 h a una velocidad de agitación de 800 rpm. El tiempo y la velocidad de agitación empleados fueron seleccionados para garantizar que en el vial se alcanzaba el equilibrio termodinámico entre las fases de extracto y de refinado. En la Figura 2.4 se muestra una fotografía de este equipo.

Una vez transcurrido el tiempo de agitación para alcanzar el equilibrio, los viales de 8 mL se introdujeron durante 12 h en un bloque termostático Labnet Digital Dry Bath D1100, como el mostrado en la Figura 2.5, a la misma temperatura a la que se realizó el ensayo de extracción líquido-líquido. El tiempo fue seleccionado para garantizar una correcta separación de las fases de extracto y de refinado.

Figura 2.3. Balanza analítica Mettler Toledo XS 205.

Figura 2.4. Agitador orbital Vortemp 1550 con control de temperatura.

Figura 2.5. Bloque termostático Labnet Digital Dry Bath D1100.

2.2.1.2. Ensayos de extracción de hidrocarburos aromáticos presentes en mezclas sintéticas representativas de corrientes de refinería

La preparación de los ensayos de extracción de aromáticos de corrientes de refinería representativas de la nafta alimentada al cracker de etileno, la gasolina de reformado, las gasolinas de pirólisis suave y severa presentaron algunas diferencias respecto al procedimiento descrito para los sistemas ternarios y pseudoternarios.

En primer lugar se realizó la preparación gravimétrica de las mezclas sintéticas de hidrocarburos representativas de cada una de las corrientes de refinería con las composiciones indicadas en las Tabla 1.6. A continuación, se adicionó gravimétricamente la mezcla de hidrocarburos a los viales de 8 mL de vidrio con tapón roscado para, posteriormente, añadir al vial el disolvente de extracción.

Para analizar la influencia de la relación disolvente/alimento (S/F) en los resultados obtenidos, se prepararon ensayos de extracción con valores de S/F en masa de 1,0, 2,0, 3,0, 4,0 y 5,0. Para adicionar correctamente las cantidades de la mezcla de hidrocarburos y del disolvente cumpliendo la relación disolvente/alimento objetivo, se determinó la densidad de la mezcla de hidrocarburos antes de preparar los ensayos de extracción. Estos ensayos se realizaron empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} con una fracción molar de [4empy][Tf_2N] igual a 0,3 y sulfolano como disolventes para comparar sus propiedades extractivas.

El efecto de la temperatura sobre la extracción de aromáticos también fue determinado realizando ensayos de extracción líquido-líquido a 303,2, 313,2 y 323,2 K utilizando el agitador orbital Vortemp 1550 y el bloque termostático Labnet Digital Dry Bath D1100 a la temperatura correspondiente.

2.2.2. Métodos de análisis

El análisis de las fases de refinado y de extracto se ha realizado mediante diferentes técnicas debido a que la presencia de líquido iónico en la fase de extracto condiciona el método analítico empleado. La composición de la fase de refinado ha sido determinada mediante cromatografía de gases con inyector automático de líquidos (GC), mientras que la composición de la fase de extracto fue analizada utilizando cromatografía de gases con inyector de espacio de cabeza o *headspace* (HS-GC).

2.2.2.1. Análisis de la fase de refinado

Para determinar la composición de la fase de refinado se tomaron por triplicado aproximadamente 50 μL de muestra de dicha fase empleando una pipeta Pasteur de vidrio y se disolvieron en 1 mL de acetona en viales de vidrio de 2 mL. A continuación, se llevó a cabo el análisis de dichas muestras utilizando un Cromatógrafo de gases Agilent 7890A equipado con un muestreador automático de líquidos Agilent 7693. En la Figura 2.6 se muestra una fotografía de estos equipos. Asimismo, se recogen en la Tabla 2.4 las condiciones del método analítico utilizado para determinar la composición de la fase de refinado.

Figura 2.6. Cromatógrafo de gases Agilent 7890A y muestreador automático de líquidos Agilent 7693.

Tabla 2.4. Condiciones del método analítico utilizado para determinar la composición de la fase de refinado en el cromatógrafo de gases Agilent 7890A.

Variable del método	Valor
Temperatura del portal de inyección	523,2 K
Temperatura del horno	348,2 K
Temperatura del Detector FID	573,2 K
Caudal de Helio	2 mL·min^{-1}
Columna	Agilent HP-5
Dimensiones de la columna	30 m × 0,32 m × 0,25 μm
Split	1:100

Para determinar la composición de la muestra inyectada en el GC a partir de las áreas obtenidas para cada compuesto en el cromatograma se utilizó el método del factor de respuesta. Para ello, se prepararon mediante gravimetría patrones formados por mezclas binarias de hidrocarburos de composición conocida y se inyectaron en el GC utilizando el mismo método de análisis que el empleado con las muestras. El hidrocarburo aromático de la mezcla se tomó como compuesto de referencia asignándole un factor de respuesta igual a la unidad. El factor de respuesta del resto de hidrocarburos se calculó empleando la siguiente expresión:

$$f_j = \frac{A_i}{A_j}\frac{w_j}{w_i} \qquad \textbf{(2.1)}$$

donde f_j es el factor de respuesta del hidrocarburo, A_j el área del pico en el cromatograma correspondiente a dicho hidrocarburo y w_j su fracción másica en el patrón. A_i y w_i son el área y la fracción másica en el patrón del hidrocarburo aromático tomado como compuesto de referencia.

Con los factores de respuesta determinados para cada uno de los hidrocarburos, se corrigieron las áreas obtenidas en los cromatogramas del análisis de las muestras de la fase de refinado y se calculó la fracción másica de cada hidrocarburo en dicha muestra. De cada ensayo de extracción líquido-líquido se analizaron tres muestras procedentes de la fase de refinado, siendo inyectadas tres veces cada una de estas muestras. Los resultados recogidos en las diferentes publicaciones son la media aritmética de las composiciones medidas en cada uno de los análisis.

2.2.2.2. Detección de líquidos iónicos en la fase de refinado

Diferentes autores han tratado de cuantificar la solubilidad de los líquidos iónicos en los hidrocarburos aromáticos y alifáticos que forman la fase de refinado. A escala industrial, si la solubilidad del líquido iónico en el refinado es elevada podría ocasionar la necesidad de recuperar el disolvente arrastrado por la corriente de refinado como ocurre en el proceso Sulfolano, que requiere una columna de lavado del refinado con agua.

La solubilidad de los líquidos iónicos en el refinado se ha asumido igual a cero ya que en diferentes trabajos publicados no se ha detectado su presencia en dicha fase mediante análisis con Resonancia Mágnetica Nuclear de protón (^{1}H-RMN) o a través de un balance de materia utilizando cromatografía de gases (Arce y col., 2007; García y col., 2010a; González y col., 2013; Domínguez y col., 2014).

Para comprobar que la presencia de líquido iónico en la fases de refinado se puede considerar como despreciable, se obtuvieron muestras de dicha fase y se analizaron utilizando un espectrómetro Bruker Advance 500 MHz de Resonancia magnética nuclear de protón (^{1}H-RMN) como el mostrado en la Figura 2.7.

Figura 2.7. Espectrómetro Bruker Advance 500 MHz de Resonancia magnética nuclear de protón (^{1}H-RMN).

Se tomaron aproximadamente 50 μL de muestra de cada fase de refinado empleando una pipeta Pasteur de vidrio y se disolvieron en 700 μL de acetona deuterada en tubos de RMN de vidrio de 5 mm de diámetro. En ninguno de los análisis realizados por ^{1}H-RMN a muestras de fases de refinado se detectaron señales correspondientes a líquidos iónicos. Por este motivo se consideró que la solubilidad de estos compuestos en la fase de refinado era despreciable. Este hecho es una importante ventaja de los líquidos iónicos frente a los disolventes orgánicos convencionales, ya que procesos como el Sulfolano deben incluir una etapa de lavado con agua para recuperar la fracción de disolvente disuelta en la corriente de refinado (ver Figura 1.10).

2.2.2.3. Análisis de la fase de extracto

Debido a la naturaleza no volátil de los líquidos iónicos y a su presencia mayoritaria en la fase de extracto, estas muestras no pudieron ser analizadas mediante un método de GC como el empleado para la fase de refinado. La técnica seleccionada para analizar las fases de extracto fue el método de Extracción Múltiple de Espacio de Cabeza (MHE).

Esta técnica cuantitativa se basa en la realización de extracciones consecutivas del vapor presente en el espacio de cabeza de un mismo vial para determinar la cantidad de analito volátil como la suma de las áreas de pico obtenidas hasta la evaporación total del analito.

La técnica de MHE presenta la gran ventaja de que el líquido iónico no se introduce en la columna cromatográfica por su carácter no volátil, determinándose la cantidad del mismo en la muestra como la diferencia entre la masa de muestra inicial y la masa de compuestos volátiles.

Otro aspecto positivo de la técnica de MHE frente a otras técnicas analíticas es la posibilidad de analizar la composición de las fases obtenidas en la extracción de aromáticos de mezclas formadas por más de dos hidrocarburos. En los análisis por ^{1}H-RMN, se producen solapamientos entre las señales de los diferentes hidrocarburos y las señales de los líquidos iónicos al realizar ensayos de extracción multicomponente. Por otro lado, utilizando cromatografía de gases junto con un balance de materia, los balances en sistemas multicomponente son complejos y la reproducibilidad de los resultados es baja, debido a que el líquido iónico es inyectado en el cromatógrafo quedando retenido en una precolumna. En esta tesis doctoral, gracias al empleo de la técnica MHE se han realizado ensayos de extracción de aromáticos de mezclas sintéticas formadas hasta por siete hidrocarburos, constituyendo estos resultados el primer estudio experimental de la extracción simultánea de BTEX de mezclas con alcanos utilizando líquidos iónicos como disolvente.

Para realizar un análisis mediante la técnica MHE se debe emplear un GC acoplado con un inyector de espacio de cabeza (HS-GC). En la Figura 2.8, se muestra el cromatógrafo de gases Agilent 7890A acoplado con el inyector de espacio de cabeza Agilent 7697A.

Figura 2.8. Cromatógrafo de gases Agilent 7890A (izquierda) acoplado con el inyector de espacio de cabeza Agilent 7697A (derecha).

A continuación se presentan los fundamentos teóricos de la técnica cuantitativa MHE (Kolb y Ettre, 1997). Si se realizaran infinitas extracciones del vapor presente en el espacio de cabeza de un vial cerrado y se llevaran a cabo análisis cromatográficos consecutivos, la suma total de las áreas de pico obtenidos para cada compuesto se podría calcular de acuerdo a la expresión (2.2). La suma de estas áreas de pico es proporcional a la cantidad total de analito presente en la muestra introducida en el vial de HS-GC (W_o) de acuerdo con la ecuación (2.3):

$$\sum_{i=1}^{i=\infty} A_i = A_1 + A_2 + \ldots + A_i \qquad \textbf{(2.2)}$$

$$W_o \propto \sum_{i=1}^{i=\infty} A_i \qquad \textbf{(2.3)}$$

Kolb y Ettre describieron el proceso de evaporación de volátiles y extracción de los mismos como un proceso de primer orden en el que la concentración de volátil en el vapor presente en el espacio de cabeza en función del tiempo varía de acuerdo a la expresión:

$$\frac{dC}{dt} = qC \qquad \textbf{(2.4)}$$

donde la constante *q* está relacionada con la velocidad en que este proceso sucede. Integrando la ecuación anterior, la concentración *C* del compuesto a cada tiempo depende de la constante *q* y la concentración inicial de analito C_o:

$$C = C_o \mathrm{e}^{-qt} \tag{2.5}$$

Si el proceso descrito se realiza de forma escalonada, como sucede con la técnica MHE, el área de pico será función de la concentración de analito en el espacio de cabeza en el momento en que se realiza la extracción. Por tanto, el tiempo se puede sustituir por el número de extracción (*i*) y la concentración del analito será proporcional al área de pico obtenida mediante el análisis del vapor extraído:

$$A_i = A_1 \mathrm{e}^{-q(i-1)} \tag{2.6}$$

Sustituyendo la ecuación (2.6) que representa el área obtenido para cada compuesto en una determinada extracción en la ecuación (2.2), se obtiene la expresión que permite calcular la suma total de áreas del compuesto volátil hasta su extracción total:

$$\sum_{i=1}^{i=\infty} A_i = A_1 + A_1 \mathrm{e}^{-q} + A_1 \mathrm{e}^{-2q} + \ldots + A_1 \mathrm{e}^{-q(i-1)} \tag{2.7}$$

La ecuación (2.7) se corresponde con una progresión geométrica en la que la suma total de los miembros individuales de la progresión se puede determinar de la siguiente forma:

$$\sum_{i=1}^{i=\infty} A_i = \frac{A_1}{1 - \mathrm{e}^{-q}} \tag{2.8}$$

Por tanto, la suma total de las áreas de pico correspondiente a las infinitas extracciones se puede calcular a partir del valor de la primera área de pico (A_1) y de la constante *q*.

Para determinar el valor de la constante q se realiza una regresión lineal del logaritmo neperiano de las áreas obtenidas en cada extracción frente al número de extracciones según la siguiente ecuación:

$$\ln A_i = -q(i-1) + \ln A_1 \qquad \textbf{(2.9)}$$

En la Figura 2.9 se muestra un ejemplo de las regresiones realizadas para cada uno de los análisis de las fases de extracto. En el ejemplo mostrado en la figura, en la muestra analizada se detectó la presencia de dos compuestos volátiles: tolueno y *n*-heptano, ya que el ensayo de extracción líquido-líquido realizado se correspondía con un sistema ternario. En el caso de los ensayos de extracción de aromáticos de mezclas representativas de corrientes de refinería, se realizó una regresión lineal para cada uno de los hidrocarburos presentes en la muestra. De esta forma se determinó el valor de la constante q para cada componente en cada análisis y se pudo calcular la suma de las áreas de cada hidrocarburo hasta evaporación total utilizando la ecuación (2.8).

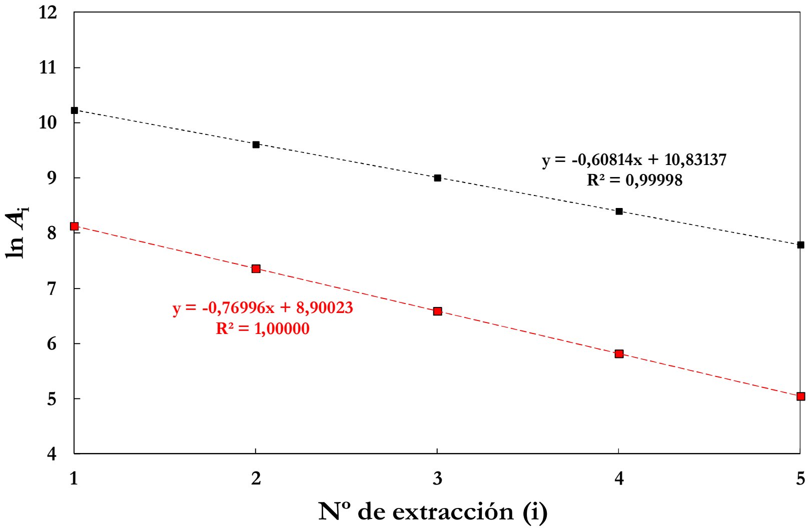


Figura 2.9. Regresión lineal de las áreas determinadas en el análisis por MHE de una muestra de fase de extracto obtenida en la separación de tolueno de *n*-heptano utilizando [emim][SCN]. En color negro se muestra el ajuste para las áreas del tolueno y en rojo las de *n*-heptano.

Para determinar la relación entre la suma de áreas del hidrocarburo y la masa del analito añadido en la muestra, se empleó un método de estándar externo. Este método consistió en la preparación de viales de espacio de cabeza con aproximadamente 10 μL de un hidrocarburo, determinando gravimétricamente la masa de hidrocarburo adicionado. Analizando cada estándar mediante MHE se obtendrá la relación entre la suma total de áreas del estándar ($\Sigma A_{\text{estándar}}$) y la masa de hidrocarburo adicionada al vial ($W_{\text{estándar}}$). Conociendo estos parámetros y la suma de áreas de la muestra analizada (ΣA_i) se puede calcular la masa de cada hidrocarburo en la muestra de fase de extracto (W_i) mediante la siguiente ecuación:

$$W_i = \sum_{i=1}^{i=\infty} A_i \frac{W_{\text{estándar}}}{\sum_{i=1}^{i=\infty} A_{\text{estándar}}} \qquad \textbf{(2.10)}$$

De cada ensayo de extracción, se tomaron tres muestras de 100 μL de la fase de extracto, que fueron introducidas en viales de 20 mL de HS-GC. La masa añadida de muestra fue determinada gravimétricamente. Los viales de HS-GC se introdujeron en el horno del inyector a 393,2 K durante 1 h y a una velocidad de agitación de 100 rpm para favorecer la evaporación de los hidrocarburos del líquido iónico. Las condiciones utilizadas en el GC se corresponden con las ya descritas en la Tabla 2.7. Se realizaron cinco extracciones de cada vial mediante la técnica MHE, obteniendo coeficientes de correlación en la determinación del factor q superiores a 0,999, siendo siempre estos valores mayores que el recomendado por Kolb y Ettre (0,998) para garantizar los resultados de la técnica MHE. La masa de cada hidrocarburo se calculó de acuerdo con la expresión (2.10), mientras que la masa de líquido iónico en la muestra se determinó como la diferencia entre la masa de muestra añadida al vial y la suma de las masas de los hidrocarburos.

2.3. Determinación de las propiedades físicas de los disolventes de extracción

2.3.1. Densidad

Las densidades de los líquidos iónicos, de las mezclas binarias de líquidos iónicos y del sulfolano fueron medidas en un densímetro Anton Paar DMA-5000 de tubo oscilante en U, cuya fotografía se muestra en la Figura 2.10. En esta metodología de medición, el tubo en U, lleno con el líquido a determinar su densidad, se hace oscilar, siendo el periodo de oscilación función de la densidad del fluido (Anton Paar, 2005). Las mediciones se realizaron en el intervalo de temperaturas (293,15 – 353,15 ± 0,01) K a presión atmosférica, inyectando aproximadamente 1 mL del líquido cuya densidad se quiere determinar. El control de la temperatura se realizó con dos sensores Pt100 integrados. Este equipo realiza automáticamente una corrección del valor obtenido para la densidad en función de la viscosidad de la muestra inyectada. La correcta calibración del equipo fue comprobada antes de cada determinación de densidad mediante la medición de la densidad de agua ultrapura a 293,15 K. La precisión del equipo, proporcionada por el fabricante, es igual a $\pm 1 \cdot 10^{-6}\ \mathrm{g{\cdot}cm^{-3}}$, mientras que la incertidumbre de cada medición fue estimada a partir de determinaciones por triplicado de la densidad de los líquidos iónicos puros o de las mezclas binarias de líquidos iónicos.

Figura 2.10. Densímetro Anton Paar DMA-5000 de tubo oscilante en U.

2.3.2. Viscosidad dinámica

Las viscosidades dinámicas de los líquidos iónicos, de las mezclas binarias de líquidos iónicos y del sulfolano fueron determinadas en un Microviscosímetro Automático Anton Paar (AMVn) a presión atmosférica y en el intervalo de temperaturas 293,15 K – 353,15 K. La temperatura en las mediciones fue controlada mediante un sensor Pt100 con una incertidumbre de 0.01 K. Una imagen del viscosímetro utilizado se muestra en la Figura 2.11. El principio de medición del AMVn es el de caída de bola, el cual consiste en la determinación del tiempo que tarda en caer una bola de densidad conocida en el interior de un capilar lleno con el líquido cuya viscosidad se quiere determinar. El capilar empleado tiene un diámetro interno de 1,8 mm y un volumen total de 400 μL, mientras que el diámetro de la bola es de 1,5 mm. Este capilar permite la medición de la viscosidad de fluidos con valores entre 2,5 y 70 mPa·s. La calibración del capilar fue realizada por el suministrador mediante mediciones con fluidos estándar de viscosidad conocida. De acuerdo con la información suministrada por el fabricante la precisión del equipo es del ± 0.1 %, mientras que la incertidumbre estimada en las medidas fue determinada mediante mediciones por triplicado de las diferentes muestras.

Figura 2.11. Viscosímetro automático Anton Paar AMVn de caída de bola.

2.3.3. Tensión superficial

Las tensiones superficiales de los líquidos iónicos puros y las mezclas binarias de líquidos iónicos fueron medidas utilizando un tensiómetro Dataphysics OCA 15 plus de gota colgante entre 298,15 K y 323,15 K. La temperatura a la que se realizó la medición fue controlada mediante un baño Julabo F12-EC con una precisión de ± 0,1 K. En la Figura 2.12 se muestra una fotografía del tensiómetro empleado.

La metodología de medición de la tensión superficial de gota colgante se basa en la ecuación de Young-Laplace. Esta ecuación relaciona la forma y los parámetros característicos de una gota colgante de un líquido con su tensión superficial. Estos parámetros característicos son el diámetro máximo de la gota, el diámetro de cuello y el radio de curvatura en el ápice de la gota (Dataphysics, 2002). El líquido fue dosificado mediante una jeringa para formar una gota en el interior de una cámara termostatizada. La forma de la gota fue recogida mediante una cámara equipada con un sensor CCD, siendo la tensión superficial calculada mediante el software SCA 20 OCA. La incertidumbre de las mediciones fue estimada a partir de medidas realizadas por triplicado, siendo siempre inferior a ± 0,1 $mN \cdot m^{-1}$.

Figura 2.12. Tensiómetro Dataphysics OCA 15 plus de gota colgante.

3. RESULTADOS

3.1. Extracción de tolueno de *n*-heptano utilizando líquidos iónicos puros

En la primera etapa de la tesis doctoral se estudió el equilibrio líquido-líquido de sistemas ternarios formados por {*n*-heptano + tolueno + líquido iónico} utilizando cinco de los líquidos iónicos puros: [emim][DCA], [bmim][DCA], [emim][SCN], [bmim][SCN] y [emim][TCM]. Se estudió el equilibrio ternario de los cinco sistemas a 313,2 K en todo el intervalo de composiciones. Asimismo, se estudió la separación de tolueno de *n*-heptano de una mezcla de ambos hidrocarburos con un 10 % en masa de tolueno empleando el [4empy][Tf_2N], ya que el equilibrio ternario completo de este sistema ya había sido determinado previamente por el grupo de investigación (García y col., 2011b). Los resultados de estos ensayos de extracción líquido-líquido se recogen en las Publicaciones 1, 2 y 3 de los anexos.

3.1.1. Propiedades extractivas de los líquidos iónicos puros

Para evaluar y comparar la actuación de los seis líquidos iónicos en la separación de tolueno de *n*-heptano, se calcularon los coeficientes de reparto del tolueno (D_2) y las selectividades tolueno/*n*-heptano ($\alpha_{2,1}$) de acuerdo a las siguientes ecuaciones:

$$D_2 = \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}} \qquad \textbf{(3.1)}$$

$$\alpha_{2,1} = \frac{x_2^{\mathrm{II}} x_1^{\mathrm{I}}}{x_2^{\mathrm{I}} x_1^{\mathrm{II}}} = \frac{D_2}{D_1} \qquad \textbf{(3.2)}$$

donde x es la fracción molar del compuesto y los subíndices 1 y 2 hacen referencia al *n*-heptano y el tolueno, respectivamente. El superíndice I indica la fase de refinado, mientras que el superíndice II hace referencia al extracto.

En la Tabla 3.1 se recogen los valores de los coeficientes de reparto del tolueno y de las selectividades tolueno/*n*-heptano de los seis líquidos iónicos empleados. Se ha optado por comparar los valores de las propiedades extractivas en la separación de tolueno de *n*-heptano de una mezcla de ambos hidrocarburos con un 10 % en masa de tolueno, debido a que este porcentaje de aromático es el más utilizado para comparar propiedades extractivas de líquidos iónicos y coincide con el contenido en aromáticos de la nafta alimentada al cracker de etileno (Meindersma y col., 2010; Meindersma y de Haan, 2012).

Como se puede observar, todos los líquidos iónicos mostraron unos valores de selectividad tolueno/*n*-heptano superiores al del sulfolano, además el [bmim][DCA], el [bmim][SCN], el [emim][TCM] y el [4empy][Tf_2N] exhibieron también un coeficiente de reparto del tolueno mayor que el valor del sulfolano. Un aumento en la longitud de cadena alquílica en el catión imidazolio provocó un incremento del valor del coeficiente de reparto del tolueno pero a costa de un descenso en la selectividad.

Tabla 3.1. Propiedades extractivas de los líquidos iónicos en la separación de tolueno de *n*-heptano de una mezcla de ambos hidrocarburos con un 10 % en masa de tolueno a 313.2 K.

Líquido iónico	D_2	$\alpha_{2,1}$
[emim][DCA]^a	0,273	71,5
[bmim][DCA]^a	0,432	42,5
[emim][SCN]^b	0,194	98,1
[bmim][SCN]^b	0,336	50,7
[emim][TCM]^a	0,441	43,4
[4empy][Tf_2N]^c	1,000	29,5
Sulfolano^c	0,275	29,4

[a] Publicación 1 del apartado de anexos.
[b] Publicación 2 del apartado de anexos.
[c] Publicación 3 del apartado de anexos.

El orden de los valores de selectividad tolueno/*n*-heptano de los líquidos iónicos formados por el catión [emim] al modificar el anión fue el siguiente: [SCN] > [DCA] > [TCM]. Debido a la relación inversa entre la selectividad y el coeficiente del reparto del tolueno, el orden de los valores de D_2 al modificar los aniones fue el contrario que el indicado para la selectividad. El [4empy][Tf_2N] mostró un coeficiente de reparto del tolueno muy superior al alcanzado por los restantes líquidos iónicos y al exhibido por el sulfolano. Además, la selectividad tolueno/*n*-heptano del [4empy][Tf_2N] fue prácticamente coincidente con el valor del sulfolano.

3.1.2. Análisis de la consistencia de los datos obtenidos

La correlación de Othmer-Tobias es la más utilizada para comprobar la consistencia de los datos de equilibrio líquido-líquido en sistemas formados por un hidrocarburo alifático, un hidrocarburo aromático y un líquido iónico (Othmer y Tobías, 1942; González y col., 2010; Domínguez y col., 2011; Al-Jimaz y col., 2013; Mokhtarani y col., 2013; Gómez y col., 2014). A continuación se muestra la ecuación de la correlación de Othmer-Tobias:

$$\ln\left(\frac{1-w_3^{\text{II}}}{w_3^{\text{II}}}\right)=a+b\ln\left(\frac{1-w_1^{\text{I}}}{w_1^{\text{I}}}\right) \tag{3.3}$$

donde w_3^{II} es la fracción másica de líquido iónico en la fase de extracto y w_1^{I} es la fracción másica de *n*-heptano en la fase de refinado, mientras que *a* y *b* son los parámetros de ajuste de la correlación de Othmer-Tobias.

En la Tabla 3.2 se muestran los parámetros de ajuste de la correlación de Othmer-Tobias para los cinco sistemas ternarios {*n*-heptano (1) + tolueno (2) + líquido iónico (3)} estudiados. La fiabilidad de los datos experimentales se determina mediante el grado de ajuste a la correlación.

Tabla 3.2. Parámetros de ajuste de la correlación de Othmer-Tobias (*a*,*b*), coeficientes de regresión (R^2) y desviaciones estándar (σ).

a	*b*	R^2	σ
n-Heptano (1) + Tolueno (2) + [emim][DCA] (3)			
–2,5286	0,6577	0,9758	0,2082
n-Heptano (1) + Tolueno (2) + [bmim][DCA] (3)			
–2,0581	0,6848	0,9900	0,0961
n-Heptano (1) + Tolueno (2) + [emim][SCN] (3)			
–2,8708	0,6588	0,9747	0,2179
n-Heptano (1) + Tolueno (2) + [bmim][SCN] (3)			
–2,2949	0,6866	0,9877	0,1155
n-Heptano (1) + Tolueno (2) + [emim][TCM] (3)			
–1,8098	0,7536	0,9925	0,0878

Analizando los valores del coeficiente de correlación (R^2) próximos a la unidad y los pequeños valores de desviación estándar (σ) se puede comprobar el alto grado de consistencia de los resultados experimentales. La correlación de Othmer-Tobias se empleó para comprobar la consistencia de los datos experimentales de equilibrio líquido-líquido tanto de los cinco sistemas anteriores, como de los datos experimentales de sistemas pseudoternarios formados por {alifático (1) + aromático (2) + mezcla binaria de líquidos iónicos (3)} recogidos en las Publicaciones 3, 4, 5 y 6 del apartado de anexos.

3.1.3. Modelado de los datos de equilibrio líquido-líquido

Los datos de equilibrio líquido-líquido de los sistemas ternarios {*n*-heptano (1) + tolueno (2) + líquido iónico (3)} se han ajustado haciendo uso del modelo NRTL (Non-Random Two Liquids). Se ha seleccionado este modelo termodinámico basado en coeficientes de actividad, ya que con él se han correlacionado satisfactoriamente los equilibrios líquido-líquido de sistemas que contienen líquidos iónicos (Renon y Prausnitz, 1968; Simoni y col., 2008).

El cálculo de los parámetros del modelo NRTL se ha realizado utilizando el simulador ASPEN Plus. El método de regresión utilizado por el programa de simulación para calcular los parámetros de interacción binaria [$(g_{ij} – g_{ii})/R$] y [$(g_{ij} – g_{ji})/R$] ha sido el método de máxima verosimilitud (*method of maximum likelihood)* aplicando el procedimiento de inicialización de Deming. El algoritmo de Britt-Luecke ha sido seleccionado, al ser válido para el cálculo de parámetros en mezclas. El valor de la tolerancia fijada para la convergencia de la regresión se ha fijado en 0,0001, mientras que el valor de los parámetros de interacción α_{ij} se ha fijado en 0,3, ya que este valor es el más utilizado en el ajuste al modelo NRTL de datos de equilibrio en sistemas formados por hidrocarburos y líquidos iónicos (Marciniak y col., 2012; Krolikowski y col., 2013).

Para comprobar la validez de los resultados predichos por el modelo NRTL, se ha calculado la raíz cuadrada de la media de las desviaciones estándar (σ_x) de las composiciones experimentales (*exptl*) y las calculadas (*calc*):

$$\sigma_x = \left\{ \frac{\sum_i \sum_l \sum_m \left(x_{ilm}^{exptl} - x_{ilm}^{calc} \right)^2}{6k} \right\}^{1/2} \tag{3.4}$$

donde x representa la fracción molar del componente, mientras que *i, l* y *m* hacen referencia al componente, la fase y la recta de reparto, respectivamente. El valor de *k* designa el número de rectas de reparto en el diagrama ternario, que en todos los ensayos fue igual a doce.

Los valores de los parámetros de ajuste del modelo NRTL y de σ_x para los cinco sistemas ternarios se recogen en las publicaciones 1 y 2 del apartado de anexos.

Además del cálculo de la raíz cuadrada de la media de las desviaciones estándar, para comprobar la fiabilidad de los ajustes realizados al modelo NRTL se han representado las composiciones experimentales y ajustadas en forma de diagramas ternarios.

A modo de ejemplo, en la Figura 3.1 se muestran los datos de equilibrio líquido-líquido del sistema ternario {*n*-heptano + tolueno + [emim][TCM]} a 313,2 K. Se puede observar que las composiciones de equilibrio predichas por el modelo NRTL son prácticamente coincidentes con las experimentales tanto en la fase de extracto como en la fase de refinado. Este hecho ocurrió en todos los sistemas ternarios y pseudoternarios determinados en esta tesis doctoral, por lo que se puede concluir que la modelización con NRTL de los datos experimentales fue satisfactoria.

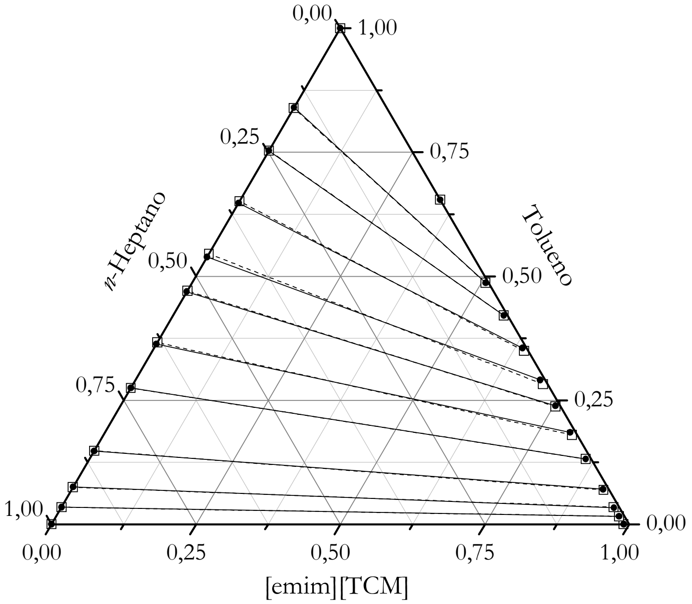


Figura 3.1. Datos de equilibrio líquido-líquido del sistema ternario {*n*-heptano + tolueno + [emim][TCM]} a 313,2 K. Los puntos y las líneas continuas representan los datos experimentales mientras que los cuadrados y las líneas discontinuas hacen referencia a los datos ajustados con el modelo NRTL.

3.1.4. Propiedades físicas de los líquidos iónicos puros

Además de las propiedades extractivas de los seis líquidos iónicos puros en la separación de tolueno de *n*-heptano, se han determinado sus propiedades físicas. En la Tabla 3.3, se muestran los valores de densidad, viscosidad dinámica y tensión superficial de los líquidos iónicos y del sulfolano a la temperatura de 313,2 K.

Los cinco líquidos iónicos basados en el catión imidazolio mostraron una densidad sustancialmente inferior a la del sulfolano, mientras que el [4empy][Tf_2N] exhibió una densidad superior a la del disolvente orgánico convencional. En cuanto a la viscosidad, todos los líquidos iónicos estudiados presentaron una viscosidad superior a la del sulfolano, siendo el [emim][DCA] y el [emim][TCM] los que mostraron un valor más bajo de esta propiedad. Por último, las tensiones superficiales de los líquidos iónicos con catión imidazolio fueron cercanas al valor del sulfolano, mientras que el [4empy][Tf_2N] mostró una tensión superficial considerablemente más baja.

Tabla 3.3. Propiedades físicas de los líquidos iónicos puros utilizados en la tesis doctoral y el sulfolano a 313,2 K.

Líquido iónico	ρ/ g·cm^{-3}	η/ mPa·s	γ/ mN·m^{-1}
[emim][DCA]	1,09144[a]	10,17[a]	54,8[d]
[bmim][DCA]	1,05112[a]	16,72[a]	47,5[e]
[emim][SCN]	1,10795[b]	15,13[b]	52,9[b]
[bmim][SCN]	1,06221[b]	32,20[b]	45,7[b]
[emim][TCM]	1,07106[a]	9,80[a]	49,9[f]
[4empy][Tf_2N]	1,47230[c]	20,70[c]	23,1[d]
Sulfolano	1,25323[a]	8,05[a]	47,2[g]

[a] Publicación 1 del apartado de anexos.
[b] Publicación 2 del apartado de anexos.
[c] Publicación 3 del apartado de anexos.
[d] Navarro y col., 2014a.
[e] Galán Sánchez y col., 2009.
[f] Domanska y col., 2013.
[g] Kelayeh y col., 2011.

Analizando las propiedades físicas de los líquidos iónicos formados por el catión [emim], el orden decreciente de densidad y viscosidad fue el siguiente: [SCN] > [DCA] > [TCM], mientras que el [emim][DCA] fue el que mostró un mayor valor de tensión superficial seguido por el [emim][SCN] y el [emim][TCM].

Considerando exclusivamente las propiedades físicas de los líquidos iónicos puros, para obtener una mezcla de líquidos iónicos con propiedades físicas similares a las mostradas por el sulfolano se puede optar por dos tipos de mezclas. Mezclando el [4empy][Tf_2N], que ha mostrado alta densidad y baja tensión superficial, con uno de los líquidos iónicos formados por el catión [emim], que han exhibido valores de viscosidad y tensión superficial cercanos al sulfolano, se obtendría una mezcla con propiedades similares a las del sulfolano. Asimismo, una mezcla binaria formada por dos líquidos iónicos que contengan el catión [emim] mostraría valores de viscosidad y tensión superficial cercanos al sulfolano, aunque con una densidad ligeramente inferior que podría dificultar la separación de las fases en el extractor.

3.2. Selección de mezclas binarias de líquidos iónicos como potenciales disolventes de extracción de aromáticos

Una vez determinadas las propiedades extractivas de los seis líquidos iónicos puros en la separación de tolueno de *n*-heptano y las propiedades físicas de estos disolventes, se han seleccionado las mezclas binarias de líquidos iónicos con mayor potencial para ser empleadas como disolventes de extracción de hidrocarburos aromáticos. Para realizar esta selección se han tenido en consideración tanto las propiedades físicas como las extractivas, teniendo como objetivo la obtención de una mezcla binaria de líquidos iónicos con propiedades similares a las mostradas por el sulfolano para así garantizar la viabilidad del proceso de extracción a escala industrial.

En la Figura 3.2 se muestran las selectividades tolueno/*n*-heptano y los coeficientes de reparto del tolueno en la separación de tolueno de *n*-heptano de una mezcla con un 10 % en masa de tolueno a una temperatura de 313,2 K. En la misma figura se han incluido las propiedades extractivas del sulfolano como líneas continuas para ser utilizadas como referencia. Para superar los valores del sulfolano las mezclas de líquidos iónicos estarán formadas por un líquido iónico con alto valor de coeficiente de reparto y otro con alta selectividad. El [emim][SCN] y el [emim][DCA] han mostrado valores de selectividad sustancialmente superiores a los del sulfolano, mientras que el [4empy][Tf$_2$N] y el [emim][TCM] han sido los que han exhibido valores más altos del coeficiente de reparto.

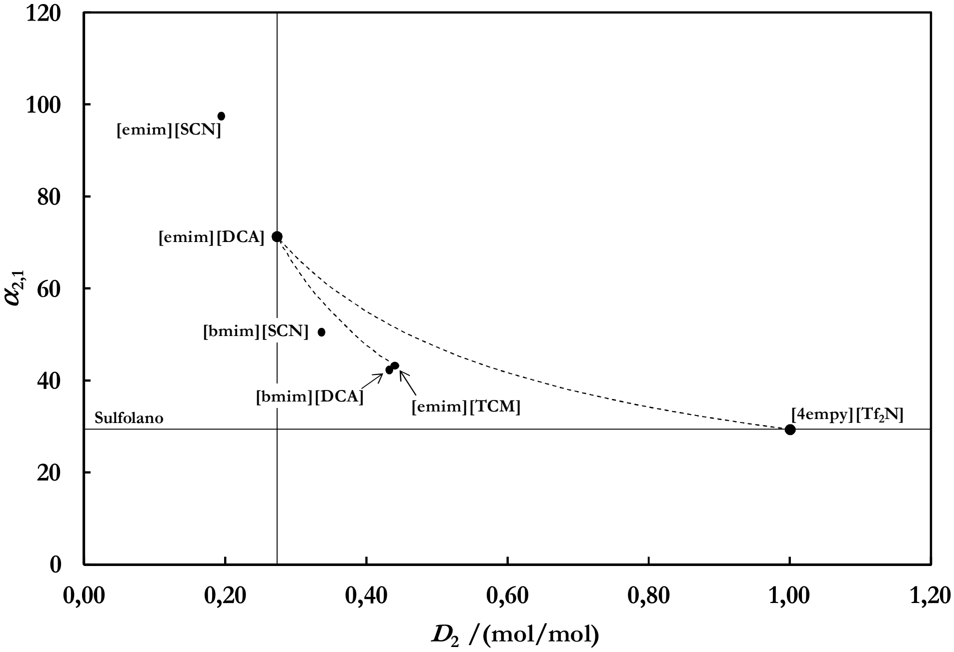


Figura 3.2. Coeficiente de reparto del tolueno y selectividad tolueno/*n*-heptano empleando diferentes líquidos iónicos en la separación de tolueno de *n*-heptano de una mezcla de ambos hidrocarburos con un 10 % en masa de tolueno a 313.2 K. Las líneas continuas representan las propiedades extractivas del sulfolano en las mismas condiciones, mientras que las líneas discontinuas muestran las predicciones realizadas mediante la regla de mezcla de Yalkowsky y Roseman para las mezclas de líquidos iónicos.

El empleo del [emim][SCN] para formar mezclas de líquidos iónicos ha sido descartado frente al [emim][DCA] ya que el primero ha presentado una mayor viscosidad y un coeficiente de reparto sustancialmente más bajo que el segundo. Además, la baja estabilidad térmica del [emim][SCN] condicionaría la estabilidad de la mezcla limitando su empleo a escala industrial (Navarro y col., 2013). Por tanto, considerando tanto las propiedades extractivas como las físicas, se han seleccionado las siguientes dos mezclas de líquidos iónicos: {[emim][TCM] + [emim][DCA]} y {[4empy][Tf_2N] + [emim][DCA]}, como las que presentan un mayor potencial para ser utilizadas a escala industrial en la extracción de hidrocarburos aromáticos.

En la Figura 3.2 se muestran las propiedades extractivas de ambas mezclas binarias predichas por el modelo logarítmico-lineal de Yalkowsky y Roseman (Yalkowsky y Roseman, 1981). Esta ecuación ha sido previamente empleada para predecir satisfactoriamente los resultados obtenidos en la extracción de aromáticos utilizando mezclas de líquidos iónicos (García y col., 2012a). La ecuación de Yalkowsky y Roseman fue aplicada para predecir las composiciones tanto de la fase de refinado como de la fase de extracto usando una mezcla de líquidos iónicos a partir de las composiciones experimentales de ambas fases empleando los líquidos iónicos puros:

$$\ln x_{\mathrm{i,pred}}^{\mathrm{I\ ó\ II}} = \sum_{\mathrm{j}=3}^{4} f_{\mathrm{j}} \cdot \ln x_{\mathrm{i,j}}^{\mathrm{I\ ó\ II}} \qquad \textbf{(3.5)}$$

donde $x_{\mathrm{i,j}}$ es la fracción molar del hidrocarburo i utilizando un líquido iónico puro j en cada una de las fases I y II, f_{j} es la fracción volumétrica inicial del líquido iónico j en la mezcla de líquidos iónicos en ausencia de solutos y $x_{\mathrm{i,pred}}$ es la fracción molar predicha del hidrocarburo i utilizando una mezcla de líquidos iónicos.

A partir de las composiciones estimadas por la ecuación (3.5) se calcularon los valores de selectividad tolueno/*n*-heptano y el coeficiente de reparto del tolueno para las mezclas {[emim][TCM] + [emim][DCA]} y {[4empy][Tf$_2$N] + [emim][DCA]} utilizando las ecuaciones (3.1) y (3.2). Como se puede observar en la Figura 3.2, según las predicciones realizadas, las dos mezclas deberían mostrar valores de ambas propiedades extractivas sustancialmente mayores que los del sulfolano.

3.3. Estudio de las propiedades extractivas y físicas de las mezclas de líquidos iónicos {[emim][TCM] + [emim][DCA]} y {[4empy][Tf$_2$N] + [emim][DCA]}

En una segunda fase de la tesis se ha realizado el estudio del equilibrio líquido-líquido de sistemas pseudoternarios formados por {*n*-heptano (1) + tolueno (2) + mezcla binaria de líquidos iónicos (3)} a 313,2 K. Las mezclas de líquidos iónicos empleadas han sido las dos seleccionadas en el apartado anterior: {[4empy][Tf$_2$N] + [emim][DCA]} y {[emim][TCM] + [emim][DCA]}.

En primer lugar se ha realizado un estudio de la influencia de la composición de la mezcla binaria de líquidos iónicos en las propiedades extractivas. Para ello, se han realizado ensayos de extracción de tolueno de *n*-heptano de sus mezclas con un 10 % en masa de tolueno utilizando la mezcla binaria de líquidos iónicos en todo el intervalo de composiciones.

Asimismo, se ha analizado la influencia de la composición de la mezcla de líquidos iónicos sobre las dos propiedades físicas fundamentales en los procesos de extracción líquido-líquido: la densidad y la viscosidad. La composición óptima en cada una de las mezclas binarias de líquidos iónicos se ha seleccionado considerando tanto las propiedades extractivas como las físicas.

Posteriormente, utilizando como disolvente de extracción la mezcla binaria de líquidos iónicos en su composición óptima se ha determinado el equilibrio pseudoternario de los sistemas {*n*-heptano (1) + tolueno (2) + mezcla binaria de líquidos iónicos (3)} a 313,2 K en todo el intervalo de composiciones, incluyendo los sistemas pseudobinarios formados por cada hidrocarburo con la mezcla de líquidos iónicos. En las Publicaciones 3 y 4 de los anexos se recogen los resultados de estos ensayos de extracción de tolueno de *n*-heptano.

3.3.1. Propiedades extractivas en la separación de tolueno de *n*-heptano

Para seleccionar la composición óptima de la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} se estudió la extracción de tolueno de *n*-heptano de una mezcla de hidrocarburos con un 10 % en masa de tolueno empleando la mezcla en el intervalo completo de composiciones.

Las propiedades extractivas de la mezcla se muestran en la Figura 3.3. Tanto los valores de selectividad tolueno/*n*-heptano como los coeficientes de reparto del tolueno de la mezcla binaria fueron mayores a los del sulfolano e intermedios entre los valores de los líquidos iónicos puros. Atendiendo exclusivamente a las propiedades extractivas, el óptimo en la composición de la mezcla se encuentra en valores de fracción molar de [4empy][Tf_2N] entre 0,2 y 0,4 para superar holgadamente los valores del sulfolano.

En la Figura 3.4 se muestran las propiedades extractivas de la mezcla {[emim][TCM] + [emim][DCA]}. Análogamente a la mezcla anterior, las propiedades de la mezcla fueron intermedias entre los valores utilizando los líquidos iónicos puros y mayores que los del sulfolano. En este caso, se alcanzan propiedades extractivas más altas que las del sulfolano en todo el intervalo de composiciones, pero serán considerablemente mayores que las del sulfolano empleando fracciones molares de [emim][TCM] de entre 0,7 y 0,9.

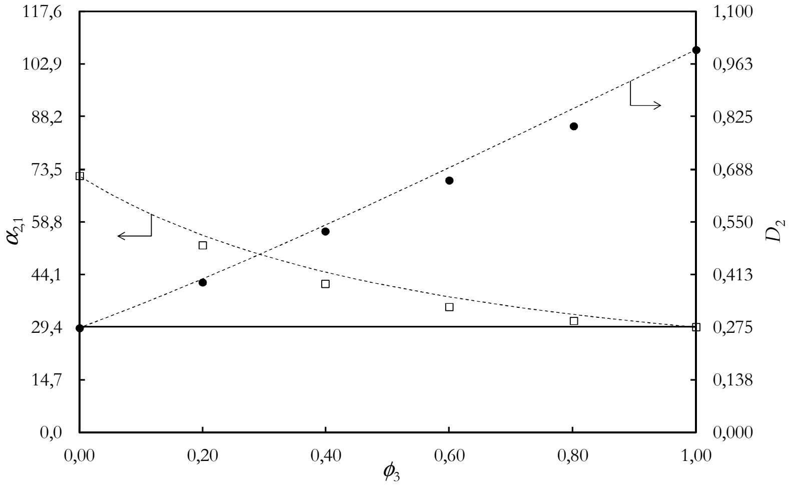


Figura 3.3. Coeficiente de reparto del tolueno (●) y selectividad tolueno/*n*-heptano (□) del sistema *n*-heptano (1) + tolueno (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} a 313,2 K y con un 10 % en masa de tolueno en la mezcla alimentada, en función de la fracción molar de [4empy][Tf_2N] en la mezcla de líquidos iónicos (ϕ_3). Las líneas discontinuas son las predicciones con la ecuación de Yalkowsky y Roseman y la continua los valores del sulfolano.

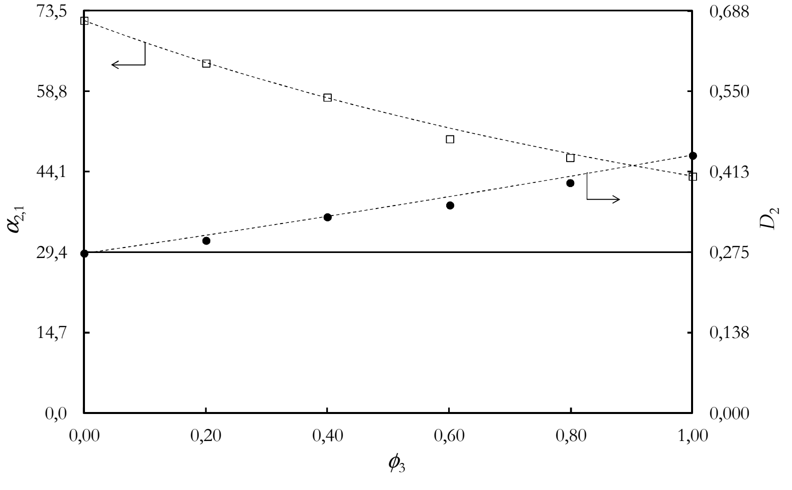


Figura 3.4. Coeficientes de reparto del tolueno (●) y selectividades tolueno/*n*-heptano (□) del sistema *n*-heptano (1) + tolueno (2) + {[emim][TCM] (3) + [emim][DCA] (4)} a 313,2 K y con un 10 % en masa de tolueno en la mezcla alimentada, en función de la fracción molar de [emim][TCM] en la mezcla de líquidos iónicos (ϕ_3). Las líneas discontinuas son las predicciones con la ecuación de Yalkowsky y Roseman y la continua los valores del sulfolano.

Como se comentó en la introducción, debido al gran número de posibles mezclas binarias de líquidos iónicos que pueden formarse a partir de los líquidos iónicos comerciales, el empleo y la validación de ecuaciones que permitan predecir las propiedades de las mezclas es fundamental. Por este motivo, en la tesis doctoral se ha evaluado la validez de diferentes modelos predictivos tanto de las propiedades físicas como de las propiedades extractivas de las mezclas de líquidos iónicos.

La regla de mezcla de Yalkowsky y Roseman fue utilizada para predecir las propiedades extractivas de las dos mezclas de líquidos iónicos a partir de los resultados en la extracción de tolueno utilizando los líquidos iónicos puros que conforman las mezclas. Como se puede observar en las Figuras 3.3 y 3.4, los valores predichos fueron prácticamente coincidentes con los resultados experimentales.

3.3.2. Propiedades físicas de las mezclas de líquidos iónicos

Las densidades y viscosidades de las mezclas de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} y {[emim][TCM] + [emim][DCA]} fueron medidas entre 293,15 K y 353,15 K en todo el intervalo de composiciones. En las Figuras 3.5 y 3.6 se muestran las densidades de las mezclas {[4empy][Tf_2N] + [emim][DCA]} y {[emim][TCM] + [emim][DCA]}, respectivamente, en función de la temperatura y la composición junto con la densidad del sulfolano a 313,2 K. Como se puede comprobar, las densidades de las mezclas fueron intermedias entre las de los líquidos iónicos puros que las forman. La mezcla {[4empy][Tf_2N] + [emim][DCA]} con una fracción molar de [4empy][Tf_2N] de 0,3, mostró una densidad prácticamente igual a la del sulfolano, mientras que los valores de densidad de la mezcla {[emim][TCM] + [emim][DCA]} fueron sustancialmente más bajos.

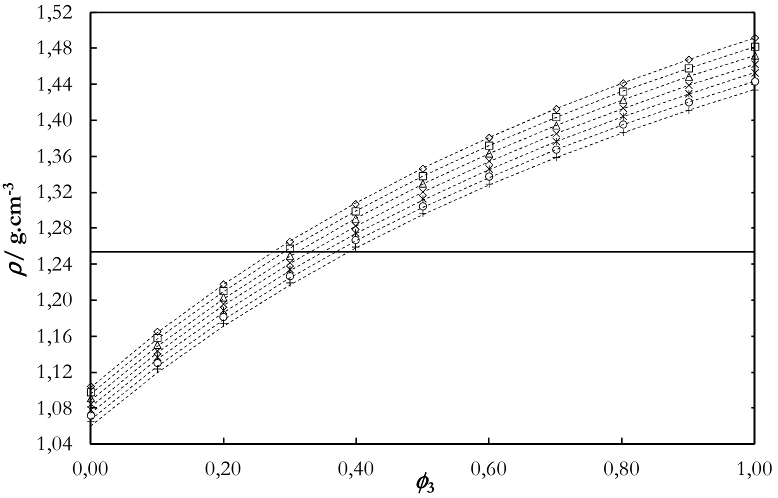


Figura 3.5. Densidades de la mezcla [4empy][Tf$_2$N] (3) + [emim][DCA] (4)} en función de la fracción molar de [4empy][Tf$_2$N] (ϕ_3) a varias temperaturas: ◇, 293,15 K; □, 303,15 K; Δ, 313,15 K; ×, 323,15 K; ∗, 333,15 K; ○, 343,15 K; +, 353,15 K. Las líneas discontinuas son las densidades estimadas mediante el método de contribución de grupos de Ye y Shreeve y la línea continua representa la densidad del sulfolano a 313,15 K.

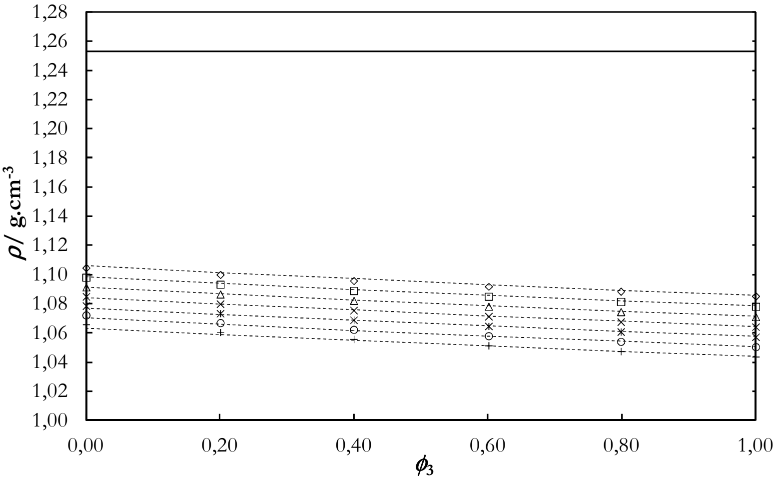


Figura 3.6. Densidades de la mezcla [emim][TCM] (3) + [emim][DCA] (4)} en función de la fracción molar de [emim][TCM] (ϕ_3) a varias temperaturas: ◇, 293,15 K; □, 303,15 K; Δ, 313,15 K; ×, 323,15 K; ∗, 333,15 K; ○, 343,15 K; +, 353,15 K. Las líneas discontinuas son las densidades estimadas mediante el método de contribución de grupos de Ye y Shreeve y la línea continua representa la densidad del sulfolano a 313,15 K.

En las Figuras 3.5 y 3.6 junto con los valores experimentales se muestran también las densidades de las mezclas de líquidos iónicos estimadas mediante el método de contribución de grupos de Ye y Shreeve, que fue ampliado por Gardas y Coutinho (Ye y Shreeve, 2007; Gardas y Coutinho, 2008):

$$\rho = \frac{\sum_{\mathrm{i}=3}^{4} W_{\mathrm{i}}\phi_{\mathrm{i}}}{N\left(\sum_{\mathrm{i}=3}^{4} V_{0,\mathrm{i}}\phi_{\mathrm{i}}\right)\left(a + bT + cP\right)} \qquad \textbf{(3.6)}$$

donde ρ es la densidad de la mezcla de líquidos iónicos in kg·m^{-3}, W_{i} es el peso molecular de cada líquido iónico puro en kg·mol^{-1}, N es el número de Avogadro, $V_{0,\mathrm{i}}$ es el volumen molecular del líquido iónico puro calculado como la suma de los volúmenes del anión y el catión en m^3·molecula^{-1}, T es la temperatura en K y P la presión en MPa. Los parámetros *a*, *b* y *c* obtenidos por Gardas y Coutinho fueron $8.005\cdot10^{-1}$, $6.652\cdot10^{-4}$ K^{-1} y $-5.919\cdot10^{-4}$ MPa^{-1}, respectivamente (Gardas y Coutinho, 2008). Los volúmenes de los iones [emim] (230 Å^3) y [Tf$_2$N] (248 Å^3) fueron obtenidos de la bibliografía (Gardas y Coutinho, 2008), mientras que los volúmenes de los iones [DCA] (86 Å^3), [TCM] (127 Å^3) y [4empy] (202 Å^3) fueron calculados como la diferencia entre el volumen del catión [emim] y el volumen molecular de los líquidos iónicos determinados a partir de las densidades de los líquidos iónicos puros [emim][DCA], [emim][TCM] y [4empy][Tf$_2$N].

Esta ecuación fue inicialmente propuesta para la predicción de las densidades de líquidos iónicos puros, pero también ha demostrado predecir adecuadamente las densidades de mezclas binarias de líquidos iónicos (Larriba y col., 2012 y 2013). Así, como se puede comprobar en las Figuras 3.5 y 3.6, las propiedades experimentales y las estimadas con el método de contribución de grupos fueron prácticamente coincidentes.

Las viscosidades dinámicas en función de la temperatura y la composición de la mezcla {[4empy][Tf_2N] + [emim][DCA]} se muestran en la Figura 3.7, mientras aquellas otras de la mezcla {[emim][TCM] + [emim][DCA]} se representan en la Figura 3.8 conjuntamente con la viscosidad dinámica del sulfolano a 313,2 K. Como se puede observar, las viscosidades de las mezclas fueron intermedias entre aquellas de los líquidos iónicos puros que las forman. La viscosidad de la mezcla {[4empy][Tf_2N] + [emim][DCA]} se incrementó al aumentar el contenido en [4empy][Tf_2N], por lo que considerando exclusivamente esta propiedad convendría emplear bajos contenidos de este líquido iónico en la mezcla para obtener un disolvente de viscosidad similar al sulfolano. Por el contrario, los valores de viscosidad de la mezcla {[emim][TCM] + [emim][DCA]} apenas se vieron afectados por la composición al ser las viscosidades de los líquidos iónicos puros muy similares. La viscosidad de esta mezcla fue muy próxima a la del sulfolano e inferior a la exhibida por la otra mezcla binaria de líquidos iónicos.

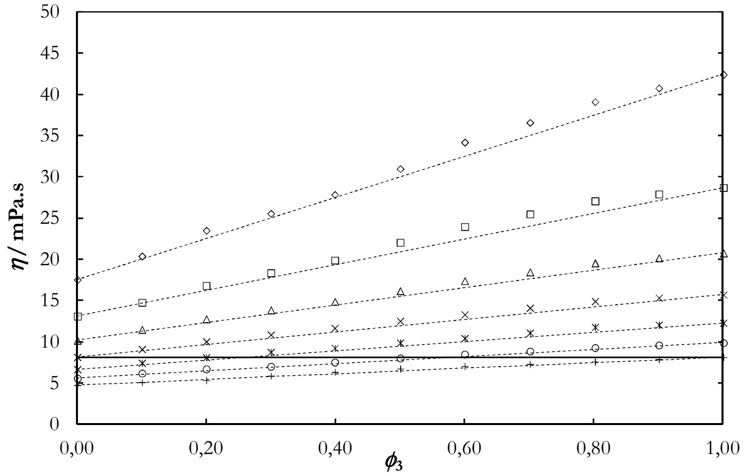


Figura 3.7. Viscosidades de la mezcla {[4empy][Tf_2N] (3) + [emim][DCA] (4)} en función de la fracción molar de [4empy][Tf_2N] (ϕ_3): ◇, 293,15 K; □, 303,15 K; Δ, 313,15 K; ×, 323,15 K; ∗, 333,15 K; ○, 343,15 K; +, 353,15 K. Las líneas discontinuas son las viscosidades estimadas mediante una regla de mezcla lineal y la línea continua es la viscosidad del sulfolano a 313,15 K.

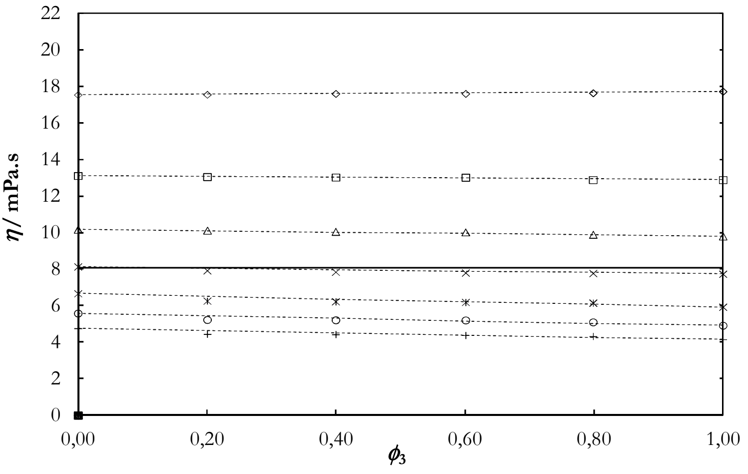


Figura 3.8. Viscosidades de la mezcla {[emim][TCM] (3) + [emim][DCA] (4)} en función de la fracción molar de [emim][TCM] (ϕ_3): ◇, 293,15 K; □, 303,15 K; Δ, 313,15 K; ×, 323,15 K; ∗, 333,15 K; ○, 343,15 K; +, 353,15 K. Las líneas discontinuas son las viscosidades estimadas mediante la regla de Bingham y la línea continua es la viscosidad del sulfolano a 313,15 K.

De forma análoga al estudio de la densidad, se ha analizado la validez de varios métodos de predicción de la viscosidad empleando tres reglas de mezcla para predecir las viscosidades de las mezclas binarias de líquidos iónicos: una regla lineal (ec. 3.7), la regla de mezcla de Bingham (ec. 3.8) y la regla de mezcla de Grunberg-Nissan (ec. 3.9) (Bingham, 1922; Grunberg y Nissan, 1949).

$$\eta = \sum_{\mathrm{i}=3}^{4} \phi_{\mathrm{i}} \eta_{\mathrm{i}} \tag{3.7}$$

$$\frac{1}{\eta} = \sum_{\mathrm{i}=3}^{4} \frac{\phi_{\mathrm{i}}}{\eta_{\mathrm{i}}} \tag{3.8}$$

$$\log_{10}(\eta) = \sum_{\mathrm{i}=3}^{4} \phi_{\mathrm{i}} \log_{10}(\eta_{\mathrm{i}}) \tag{3.9}$$

donde η es la viscosidad dinámica estimada para la mezcla de líquidos iónicos, η_{i} es la viscosidad del líquido iónico puro a la misma temperatura y ϕ_{i} indica la fracción molar de cada líquido iónico en la mezcla de líquidos iónicos.

En las Figuras 3.7 y 3.8 se muestran las viscosidades estimadas mediante reglas de mezcla junto con las viscosidades experimentales de las mezclas de líquidos iónicos. Las viscosidades de la mezcla {[4empy][Tf_2N] + [emim][DCA]} fueron estimadas con mayor precisión empleando la regla de mezcla lineal, mientras que las mejores predicciones para la viscosidad de la mezcla {[emim][TCM] + [emim][DCA]} se alcanzaron con la regla de Bingham.

3.3.3. Selección de la mezcla de líquidos iónicos con mayor potencial para ser empleada como disolvente de extracción de hidrocarburos aromáticos

Considerando las propiedades extractivas de la mezcla {[4empy][Tf_2N] + [emim][DCA]}, la composición óptima de la misma se encontró en valores de fracción molar de [4empy][Tf_2N] de entre 0,2 y 0,4. Evaluando las propiedades físicas, la densidad de esta mezcla fue muy similar a la del sulfolano utilizando una fracción molar de [4empy][Tf_2N] de 0,3, mientras que la viscosidad de la mezcla aumentó con el contenido en el líquido iónico [4empy][Tf_2N]. Por tanto, considerando la influencia de la composición tanto en las propiedades extractivas como físicas se optó por trabajar con un valor de fracción molar de [4empy][Tf_2N] igual a 0,3 en la mezcla binaria {[emim][DCA] + [4empy][Tf_2N]}.

Por otro lado, el óptimo de composición en la mezcla {[emim][TCM] + [emim][DCA]} según sus propiedades extractivas se encontró en fracciones molares de [emim][TCM] entre 0,7 y 0,9. El efecto de la composición de la mezcla sobre los valores de densidad y viscosidad fue muy limitado, ya que las propiedades físicas de ambos líquidos iónicos son similares. Por este motivo, se seleccionó una fracción molar de [emim][TCM] de 0,8 en la mezcla de líquidos iónicos.

Una vez seleccionadas las composiciones óptimas de las dos mezclas de líquidos iónicos empleadas en la separación de tolueno de *n*-heptano, se van a comparar las propiedades extractivas y físicas de ambas mezclas para elegir la que presenta un mayor potencial para ser empleada a escala industrial en un proceso de extracción de hidrocarburos aromáticos.

En la Tabla 3.4 se recogen las propiedades extractivas y termofísicas de las dos mezclas de líquidos iónicos en su composición óptima junto con los valores del sulfolano. Analizando los valores del coeficiente de reparto del tolueno, el valor alcanzado por la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} fue sustancialmente superior al mostrado por la mezcla {[emim][TCM] (0,8) + [emim][DCA] (0,2)} y por el sulfolano. Ambas mezclas de líquidos iónicos alcanzaron valores de selectividad tolueno/*n*-heptano muy similares y mayores que el valor del sulfolano. Por tanto, atendiendo exclusivamente a las propiedades extractivas la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} es la que presenta mejores resultados.

Tabla 3.4. Propiedades extractivas y propiedades termofísicas de las mezclas líquidos iónicos y el sulfolano en la separación de tolueno de *n*-heptano de una mezcla con un 10 % en masa de tolueno a 313.2 K.

Disolvente	D_2	$\alpha_{2,1}$	ρ/g·cm^{-3}	η/mPa·s	γ/mN.m^{-1}	T_{onset}/K
{[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)}	0,471^{a}	47,8^{a}	1,2499^{a}	13,9^{a}	44,1^{d}	560,7^{d}
{[emim][TCM] (0,8) + [emim][DCA] (0,2)}	0,393^{b}	46,6^{b}	1,0745^{b}	9,9^{b}	-	564,7^{e}
Sulfolano	0,275^{a}	29,4^{a}	1,25323^{c}	8,05^{c}	47,2^{f}	-

[a] Publicación 3 del apartado de anexos.
[b] Publicación 4 del apartado de anexos.
[c] Publicación 1 del apartado de anexos.
[d] Navarro y col., 2014a.
[e] Navarro y col., 2014b.
[f] Kelayeh y col., 2011

Por otro lado se han estudiado las propiedades termofísicas de las dos mezclas de líquidos iónicos y se han comparado con las del sulfolano. La mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} mostró una densidad y una tensión superficial muy similares a los valores del sulfolano, mientras que su viscosidad fue ligeramente superior a la exhibida por la otra mezcla y por el disolvente orgánico. Considerando, por tanto, los valores de las propiedades físicas, con el empleo de la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} como disolvente de extracción se produciría una separación entre las fases similar al del sulfolano, aunque esta mezcla ha mostrado una viscosidad ligeramente superior a la de la otra mezcla de líquidos iónicos estudiada.

Además de las propiedades físicas se ha comparado la estabilidad térmica de las mezclas. En la Tabla 3.4 se muestra el valor de la T_{onset} para las dos mezclas de líquidos iónicos (Navarro y col, 2014a y 2014b). Este parámetro es el más utilizado para comparar la estabilidad térmica de los líquidos iónicos, siendo esta temperatura la de descomposición del material determinada mediante TGA dinámico utilizando una rampa de calefacción de 10 $K \cdot min^{-1}$. Analizando los valores de la T_{onset} de las dos mezclas de líquidos iónicos, se puede observar que la estabilidad térmica de las mismas es muy similar, por lo que esta propiedad no ha sido considerada en la selección de la mezcla más adecuada.

Por tanto, considerando los valores de las propiedades físicas de ambas mezclas y que la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} ha mostrado mejores propiedades extractivas, se ha seleccionado esta última como la que presenta un mayor potencial para ser empleada a escala industrial en la extracción líquido-líquido de hidrocarburos aromáticos de corrientes de refinería. Por este motivo, los ensayos de extracción de aromáticos realizados a partir de este punto en la tesis doctoral se han realizado empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]}.

3.4. Extracción de BTEX de alcanos con la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]}

La selección de la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} como la que presenta un mayor potencial para ser empleada en extracción de aromáticos se ha realizado considerando tanto sus propiedades termofísicas como sus propiedades extractivas, obtenidas estas últimas en las separación de tolueno de *n*-heptano. Sin embargo, las corrientes de refinería de las que se obtienen los BTEX están formadas, además de por tolueno y *n*-heptano, por otra serie de compuestos aromáticos y alifáticos.

Por este motivo, se han realizado ensayos de extracción de aromáticos estudiando el equilibrio líquido-líquido de sistemas pseudoternarios formados por un hidrocarburo alifático, un hidrocarburo aromático y la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]}. Se han determinado las propiedades extractivas de la mezcla de líquidos iónicos en la separación de tolueno de *n*-hexano, *n*-heptano, *n*-octano, *n*-nonano, 2,3-dimetilpentano y ciclohexano, y en la extracción líquido-líquido de benceno, etilbenceno, *o*-xileno, *m*-xileno y *p*-xileno de *n*-heptano. De esta forma, se ha comprobado si la composición óptima en la mezcla en la separación de diferentes aromáticos de alifáticos coincide con la seleccionada anteriormente considerando las propiedades físicas y las extractivas en la extracción de tolueno de *n*-heptano; es decir, una fracción molar de [4empy][Tf_2N] de 0,3 en la mezcla.

Asimismo, a partir de los resultados obtenidos en el estudio del equilibrio líquido-líquido de los diferentes sistemas pseudoternarios, se ha analizado la influencia del hidrocarburo aromático y la estructura del hidrocarburo alifático sobre las propiedades extractivas de la mezcla de líquidos iónicos. Estos resultados se recogen en las Publicaciones 3, 5 y 6 del de los anexos.

3.4.1. Influencia de la composición de la mezcla binaria de líquidos iónicos

Para determinar la influencia de la composición de la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} sobre los valores de selectividad aromático/alifático y coeficiente de reparto del hidrocarburo aromático se han realizado ensayos de extracción de aromáticos de una mezcla binaria de hidrocarburos con un 10 % en masa del aromático. En estos ensayos de extracción se han utilizado como disolventes mezclas binarias de líquidos iónicos en su intervalo completo de composiciones y el sulfolano. En la Tabla 3.5 se recoge el intervalo de fracciones molares de [4empy][Tf_2N] en la mezcla de líquidos iónicos que permiten alcanzar valores de selectividad y coeficiente de reparto superiores a los mostrados por el sulfolano.

Tabla 3.5. Intervalo óptimo de composición en la mezcla {[4empy][Tf_2N] + [emim][DCA]} en la separación de aromáticos de alifáticos de mezclas de ambos hidrocarburos con un 10 % en masa del aromático a 313,2 K.

Mezcla de hidrocarburos a separar	Intervalo óptimo de fracción molar de [4empy][Tf_2N] en la mezcla de líquidos iónicos
n-Hexano + Tolueno[b]	0,20 – 0,40
n-Heptano + Tolueno[a]	0,20 – 0,40
n-Octano + Tolueno[b]	0,20 – 0,40
n-Nonano + Tolueno[b]	0,30 – 0,50
2,3-Dimetilpentano + Tolueno[a]	0,30 – 0,50
Ciclohexano + Tolueno[a]	0,30 – 0,60
n-Heptano + Benceno[c]	0,20 – 0,40
n-Heptano + Etilbenceno[c]	0,30 – 0,50
n-Heptano + *o*-Xileno[c]	0,30 – 0,50
n-Heptano + *m*-Xileno[c]	0,20 – 0,50
n-Heptano + *p*-Xileno[c]	0,20 – 0,40

[a] Publicación 3 del apartado de anexos.
[b] Publicación 5 del apartado de anexos.
[c] Publicación 6 del apartado de anexos.

Como se puede comprobar en los valores de la tabla, el intervalo óptimo de fracción molar de [4empy][Tf$_2$N] varió al cambiar los hidrocarburos aromáticos y alifáticos separados. Sin embargo, en los 11 sistemas pseudoternarios el empleo de la mezcla {[4empy][Tf$_2$N] + [emim][DCA]} con fracción molar de [4empy][Tf$_2$N] igual a 0,3 se encontró dentro del intervalo óptimo. Por tanto, se ha comprobado que este valor es la composición más adecuada para realizar la extracción de hidrocarburos aromáticos de alifáticos considerando tanto las propiedades extractivas como las propiedades físicas de la mezcla.

3.4.2. Influencia del hidrocarburo aromático

Una vez determinada la composición óptima de la mezcla de líquidos iónicos se van a analizar los resultados obtenidos en la extracción de benceno, tolueno, etilbenceno, *o*-xileno, *m*-xileno y *p*-xileno de *n*-heptano para estudiar la influencia del hidrocarburo aromático en las propiedades extractivas.

En la Figura 3.9 se muestran los valores del coeficiente de reparto de los hidrocarburos aromáticos obtenidos en la separación de cada aromático de la mezcla binaria con *n*-heptano. Como se puede observar, el valor más alto del coeficiente de reparto se obtuvo en la separación de benceno de *n*-heptano, descendiendo el coeficiente de reparto al incrementarse la longitud de cadena del sustituyente unido al anillo bencénico, alcanzando el valor más bajo en la separación del etilbenceno. Por su parte, los coeficientes de reparto de los tres isómeros del xileno fueron prácticamente coincidentes. En la Figura 3.10 están representados los valores de selectividad aromático/*n*-heptano. Las tendencias observadas para esta propiedad extractiva al modificar la longitud de cadena del sustituyente son análogas a las ya comentadas para los coeficientes de reparto. En relación con los resultados alcanzados en la separación de los isómeros del xileno, la selectividad *p*-xileno/*n*-heptano fue ligeramente inferior a los valores obtenidos en la extracción de los dos isómeros restantes.

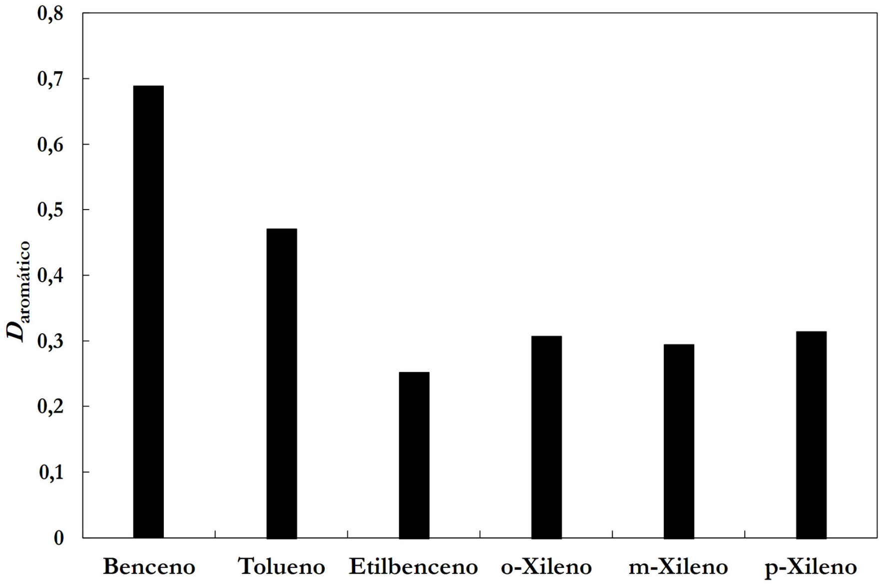


Figura 3.9. Coeficientes de reparto de hidrocarburos aromáticos en la separación del aromático de *n*-heptano de una mezcla con un 10 % en masa de aromático utilizando la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} a 313,2 K.

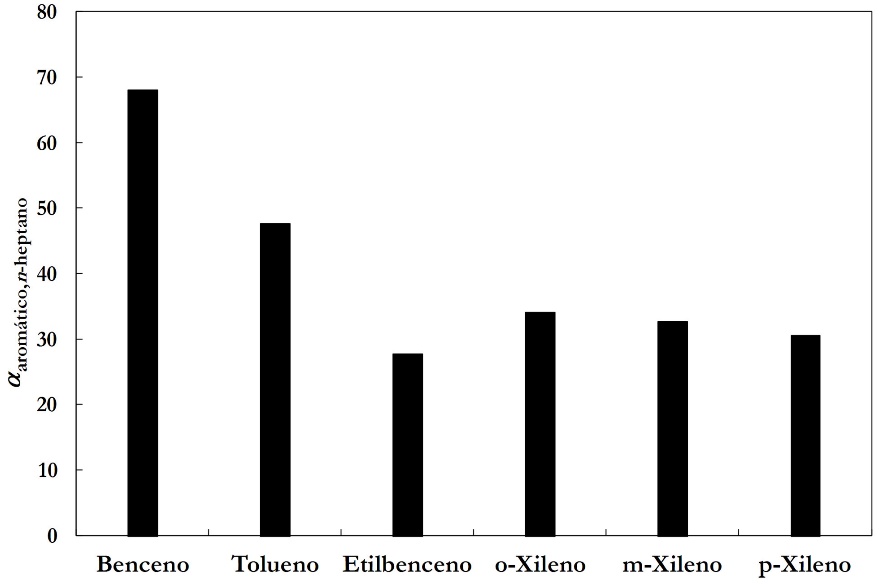


Figura 3.10. Selectividades aromático/*n*-heptano en la separación del aromático de *n*-heptano de una mezcla con un 10 % en masa de aromático utilizando la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} a 313,2 K.

3.4.3. Influencia de la estructura del alcano

Para analizar la influencia de la estructura del alcano sobre las propiedades extractivas de la mezcla de líquidos iónicos se han comparado los valores de selectividad tolueno/alcano obtenidos en la extracción de tolueno de *n*-hexano, *n*-heptano, *n*-octano, *n*-nonano, 2,3-dimetilpentano y ciclohexano. Estos valores se muestran en la Figura 3.11.

Al incrementar del número de carbonos en la cadena del *n*-alcano se produjo un aumento sustancial del valor de selectividad tolueno/alcano. Comparando los valores obtenidos en la separación de tolueno de *n*-hexano y ciclohexano, se observa que la ciclación del alcano provoca un importante descenso en el valor de selectividad. Por su parte, el valor de selectividad obtenido en la separación de tolueno de *n*-heptano fue ligeramente superior al alcanzado en la extracción de aromático de 2,3-dimetilpentano, por lo que la ramificación de la cadena ocasiona un ligero descenso de la selectividad.

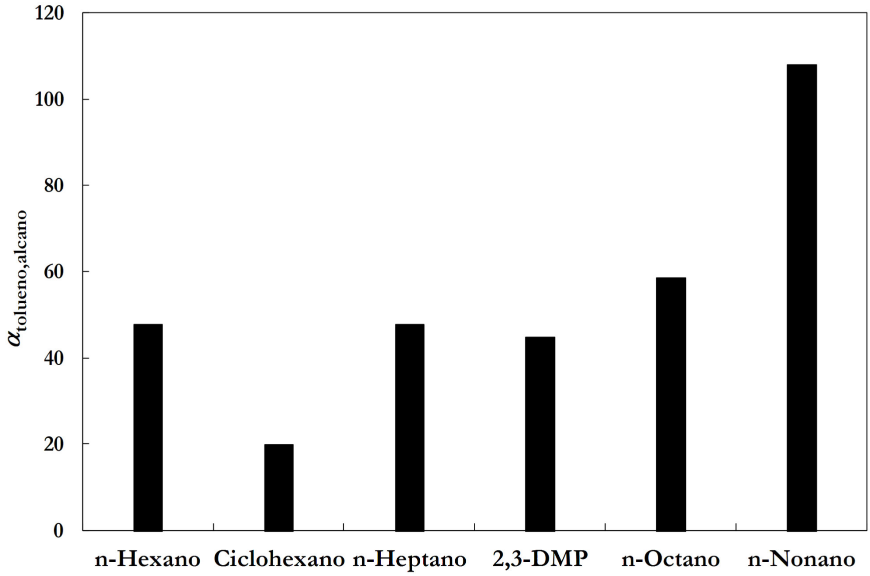


Figura 3.11. Selectividades tolueno/alcano utilizando la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} a 313,2 K y con un 10 % en masa de tolueno en la mezcla de hidrocarburos alimentada.

3.5. Extracción de aromáticos de corrientes de refinería empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)]} y sulfolano

En la última fase experimental de la tesis doctoral se han realizado ensayos de extracción de BTEX de cuatro corrientes de refinería. Estos resultados constituyen el primer trabajo experimental que aborda la extracción simultánea de benceno, tolueno, etilbenceno y *p*-xileno de varios alcanos utilizando líquidos iónicos como disolvente. Las corrientes de refinería empleadas y su contenido en aromáticos fueron las siguientes (Meindersma y de Haan, 2008; Franck y Stadelhofer, 1988):

- Nafta alimentada al cracker de etileno (10 % de aromáticos).
- Gasolina de reformado (55 % de aromáticos con un alto contenido en tolueno).
- Gasolina de pirólisis suave (51 % de aromáticos con un alto contenido en benceno).
- Gasolina de pirólisis severa (66 % de aromáticos con un alto contenido en benceno y tolueno).

Los ensayos de extracción de BTEX de las cuatro corrientes anteriores se realizaron utilizando como disolventes la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} con una fracción molar de [4empy][Tf_2N] igual a 0,3 y sulfolano para comparar las propiedades extractivas de ambos disolventes. Se realizaron ensayos de extracción con valores de relación disolvente/alimento (S/F) en masa de 1,0, 2,0, 3,0, 4,0 y 5,0 para estudiar la influencia de esta variable sobre la extracción de los BTEX. Asimismo, se analizó el efecto de la temperatura a la que se realiza la extracción de los aromáticos sobre las propiedades extractivas comparando los resultados obtenidos a 303,2, 313,2 y 323,2 K.

3.5.1. Cálculo de las propiedades extractivas

Para comparar los resultados obtenidos con la mezcla de líquidos iónicos y con el sulfolano en la extracción de BTEX de las diferentes corrientes de refinería se calcularon cinco propiedades extractivas. A partir de las composiciones experimentales de las fases de extracto y refinado obtenidos en cada uno de los ensayos de extracción de BTEX se calcularon los coeficientes de distribución de los aromáticos en base másica y las selectividades aromáticos/alifáticos empleando las siguientes ecuaciones:

$$D_{\text{aromáticos}} = \frac{w^{\text{II}}_{\text{benc}} + w^{\text{II}}_{\text{tol}} + w^{\text{II}}_{\text{etbenc}} + w^{\text{II}}_{p\text{-xil}}}{w^{\text{I}}_{\text{benc}} + w^{\text{I}}_{\text{tol}} + w^{\text{I}}_{\text{etbenc}} + w^{\text{I}}_{p\text{-xil}}} \qquad \textbf{(3.10)}$$

$$\alpha_{\text{arom,alif}} = \frac{D_{\text{aromáticos}}}{D_{\text{alifáticos}}} \qquad \textbf{(3.11)}$$

Además de las dos propiedades extractivas anteriores, que son las más empleadas en el estudio de los resultados obtenidos en extracción líquido-líquido, se han calculado tres propiedades extractivas adicionales que son fundamentales desde un punto de vista industrial. Así, se han determinado los valores de rendimiento de extracción de hidrocarburos alifáticos ($Yld_{\text{alifáticos}}$) y de hidrocarburos aromáticos ($Yld_{\text{aromáticos}}$) calculados como el cociente porcentual entre la masa de hidrocarburos aromáticos o alifáticos extraídos por el disolvente respecto a la masa total alimentada de estos compuestos:

$$Yld_{\text{alifáticos}}(\%) = \frac{m^{\text{II}}_{\text{hexa}} + m^{\text{II}}_{\text{hepta}} + m^{\text{II}}_{\text{octa}}}{m^{\text{alim}}_{\text{hexa}} + m^{\text{alim}}_{\text{hepta}} + m^{\text{alim}}_{\text{octa}}} \times 100 \qquad \textbf{(3.12)}$$

$$Yld_{\text{aromáticos}}(\%) = \frac{m^{\text{II}}_{\text{benc}} + m^{\text{II}}_{\text{tol}} + m^{\text{II}}_{\text{etbenc}} + m^{\text{II}}_{p\text{-xil}}}{m^{\text{alim}}_{\text{benc}} + m^{\text{alim}}_{\text{tol}} + m^{\text{alim}}_{\text{etbenc}} + m^{\text{alim}}_{p\text{-xil}}} \times 100 \qquad \textbf{(3.13)}$$

Por último, se ha determinado la pureza relativa de los hidrocarburos aromáticos en la fase de extracto ($P_{\text{aromáticos}}$) como el cociente entre la fracción másica de hidrocarburos aromáticos en dicha fase y la suma total de las fracciones másicas de todos los hidrocarburos, tanto aromáticos como alifáticos, en la fase de extracto empleando la siguiente ecuación:

$$P_{\text{aromáticos}}(\%) = \frac{w_{\text{benc}}^{\text{II}} + w_{\text{tol}}^{\text{II}} + w_{\text{etbenc}}^{\text{II}} + w_{p\text{-xil}}^{\text{II}}}{\left(w_{\text{hexa}}^{\text{II}} + w_{\text{hepta}}^{\text{II}} + w_{\text{octa}}^{\text{II}}\right) + \left(w_{\text{benc}}^{\text{II}} + w_{\text{tol}}^{\text{II}} + w_{\text{etbenc}}^{\text{II}} + w_{p\text{-xil}}^{\text{II}}\right)} \times 100 \qquad \textbf{(3.14)}$$

En un proceso industrial de extracción líquido-líquido, el objetivo fundamental es alcanzar el valor máximo tanto de la pureza de los solutos extraídos como del rendimiento de extracción de los mismos. Por este motivo, se han determinado las condiciones de operación de temperatura y relación disolvente/alimento que maximizan ambos parámetros en la extracción de BTEX de las cuatro corrientes de refinería estudiadas.

3.5.2. Simulación y optimización de las columnas de extracción líquido-líquido

Una vez seleccionadas las condiciones óptimas de operación de la columna de extracción considerando las propiedades extractivas a partir de los resultados experimentales, se ha realizado la simulación de la columna de extracción líquido-líquido en contracorriente utilizando la mezcla de líquidos iónicos y el sulfolano mediante la ecuación de Kremser. Utilizando este método se han determinado los caudales y composiciones de las corrientes de extracto y de refinado en el extractor. El método de Kremser permite simular una columna de extracción líquido-líquido si las fases de extracto y refinado son inmiscibles y si los coeficientes de distribución de los solutos son constantes. Ambas condiciones se cumplen en los sistemas estudiados y, por este motivo, se ha podido emplear dicha ecuación (Buchbender y col., 2012).

Todas las simulaciones se han realizado fijando como caudal de alimentación 1000 t/h, calculándose el caudal de disolvente a partir de la relación en masa óptima de disolvente/alimento. A continuación se ha fijado el número de pisos en la columna para realizar la simulación empleando un método iterativo desarrollado en Microsoft Excel. En la Figura 3.12 se muestra la representación de una columna de extracción líquido-líquido en contracorriente con las dos corrientes de entrada, alimentación y disolvente, y las dos corrientes de salida de la columna, extracto y refinado. No se han realizado balances entálpicos en la columna ya que los cambios de temperatura en las columnas de extracción líquido-líquido adiabáticas suelen ser muy pequeños y, por tanto, se han asumido como despreciables en la simulación (Henley y Seader, 1981).

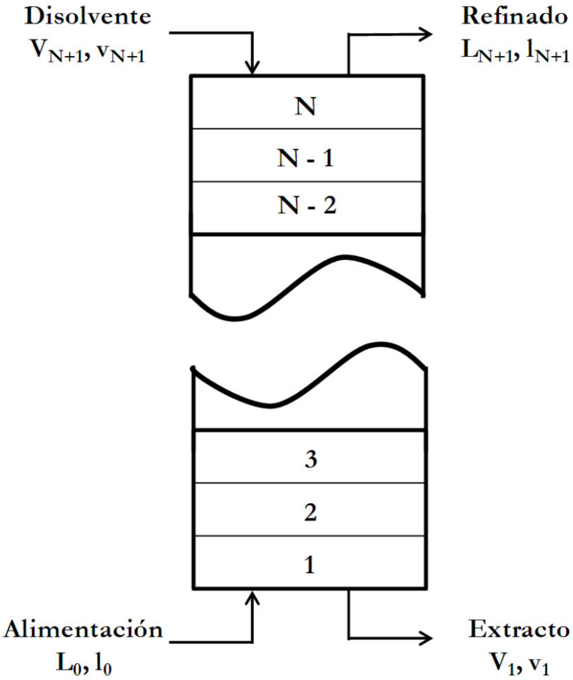


Figura 3.12. Representación de la columna de extracción en contracorriente simulada con el método de Kremser.

El método de Kremser aplicado a la extracción líquido-líquido es análogo al utilizado en absorción. Los parámetros de cálculo del método son el factor de extracción (*E*) y su inverso (*U*) definidos con las siguientes expresiones:

$$E_i = D_i \frac{V}{L} \tag{3.15}$$

$$U_i = \frac{1}{E_i} = \frac{L}{D_i V} \tag{3.16}$$

donde D_i es el coeficiente de reparto del soluto i en base másica determinado a partir de los resultados experimentales en las condiciones de temperatura y relación disolvente/alimento en las que se realiza la simulación, L es el caudal másico de la corriente de refinado y V el caudal másico de la corriente de extracto estimados en la simulación de la columna.

Los caudales totales de las corrientes de extracto y refinado se han calculado a partir de los caudales individuales de cada componente en cada una de las fases obtenidos en la simulación. Para cada componente que se introduce en la columna se han empleado las dos ecuaciones de trabajo que se muestran a continuación:

$$v_1 = v_{N+1}\phi_U + l_0(1-\phi_E) \tag{3.17}$$

$$l_N = l_0 + v_{N+1} - v_1 \tag{3.18}$$

donde v_i es el caudal individual de cada componente en la fase de extracto en cada piso y l_i el caudal individual de cada componente en la fase de refinado. Para realizar el cálculo de los caudales individuales de cada componente se deben determinar los valores de los parámetros ϕ_E y ϕ_U, relacionados con la fracción de componente que entra a la columna y que no es extraída por el disolvente. Estos dos parámetros se calcularon con las siguientes expresiones:

$$\phi_E = \frac{E_e - 1}{E_e^{N+1} - 1} \tag{3.19}$$

$$\phi_U = \frac{U_e - 1}{U_e^{N+1} - 1} \tag{3.20}$$

donde E_e es el factor de extracción efectivo y U_e su inverso, calculados con las siguientes ecuaciones propuestas por Kremser:

$$E_e = [E_1(E_N + 1) + 0,25]^{1/2} - 0,5 \tag{3.21}$$

$$U_e = [U_1(U_N + 1) + 0,25]^{1/2} - 0,5 \tag{3.22}$$

Para comenzar la simulación se deben suponer unos valores aproximados de los caudales individuales de cada componente en las corrientes de extracto y de refinado considerando los caudales alimentados y la solubilidad de cada componente en el disolvente de extracción. Para introducir unos caudales que permitan arrancar la simulación se ha supuesto que el 95 % del caudal de aromáticos alimentados se obtiene por la corriente de extracto y el 95 % de los alifáticos introducidos en la columna salen con la corriente de refinado.

Utilizando un procedimiento de cálculo desarrollado en Microsoft Excel que emplea la función Solver, se han realizado simulaciones iterativas de la columna de extracción líquido-líquido hasta que la función objetivo que compara los caudales supuestos de las corrientes de extracto y refinado en una iteración con los calculados mediante el empleo de las ecuaciones (3.15) a (3.22) cumple con el valor marcado para la tolerancia. A partir de los caudales obtenidos en las simulaciones se han determinado los valores de rendimiento de extracción de hidrocarburos aromáticos ($Yld_{\text{aromáticos}}$) y de la pureza relativa de los hidrocarburos aromáticos en la fase de extracto ($P_{\text{aromáticos}}$) en función del número de pisos utilizado en el extractor.

3.5.3. Extracción de hidrocarburos aromáticos de una nafta alimentada al cracker de etileno

Los resultados experimentales de la extracción líquido-líquido de BTEX de la nafta alimentada al cracker de etileno se recogen en la Publicación 7 del apartado de anexos. Para la selección de las condiciones óptimas de operación en el extractor se han analizado las propiedades extractivas de cada disolvente en función de la temperatura y la relación disolvente/alimento. En el mismo artículo se muestran los resultados obtenidos en la simulación de las columnas de extracción líquido-líquido en las condiciones óptimas utilizando el método de Kremser.

La mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} con una fracción molar de [4empy][Tf_2N] igual a 0,3 mostró valores de selectividad aromáticos/alifáticos sustancialmente superiores a los del sulfolano, mientras que utilizando el disolvente convencional se obtuvieron mayores coeficientes de reparto tanto de aromáticos como de alifáticos. Como consecuencia de estos valores de las propiedades extractivas, la pureza de los hidrocarburos aromáticos extraídos en la fase de extracto fue bastante superior utilizando la mezcla de líquidos iónicos, mientras que el rendimiento de extracción de BTEX fue mayor empleando el sulfolano.

Considerando los resultados obtenidos en función de la temperatura y de la relación disolvente/alimento utilizando la mezcla de líquidos iónicos, se seleccionó una temperatura de 303,2 K como óptima para alcanzar altos valores de rendimiento de extracción de aromáticos y de pureza de los BTEX en la fase de extracto y minimizar el rendimiento de extracción de alifáticos. Por otro lado, una relación disolvente/alimento de 5,0 fue seleccionada como óptima para incrementar el rendimiento de extracción de los BTEX empleando la mezcla de líquidos iónicos.

El método de Kremser fue empleado para simular las columnas de extracción líquido-líquido en las condiciones óptimas citadas anteriormente. Se estudió la influencia del número de pisos en la columna sobre los rendimientos de extracción de los BTEX y la pureza de los aromáticos en el extracto.

Empleando una columna de extracción con 18 etapas de equilibrio que opere a una temperatura de 303,2 K con la mezcla de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} como disolvente, se alcanzaron los siguientes rendimientos de extracción: benceno (> 99,9 %), tolueno (98,4 %), etilbenceno (85,3 %) y *p*-xileno (83,9 %). En las mismas condiciones, el sulfolano mostró unos rendimientos de extracción de aromáticos superiores a los de la mezcla de líquidos iónicos, alcanzando valores de rendimiento de extracción superiores al 99,9 % para el benceno y el tolueno, siendo mayores que 99,0 % en la extracción del etilbenceno, mientras que el rendimiento de extracción del *p*-xileno fue del 96,9 %.

Por tanto, la mezcla binaria de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} podría emplearse para eliminar totalmente el contenido en benceno de la nafta alimentada al cracker de etileno, para reducir casi totalmente el contenido el tolueno y para separar grandes cantidades de etilbenceno y *p*-xileno. Como consecuencia del bajo contenido en aromáticos (10 % en masa) en la corriente de naftas alimentada al cracker de etileno utilizando ambos disolventes se produce la extracción simultánea de ciertas cantidades de hidrocarburos alifáticos que podrían complicar los procesos de purificación de los BTEX extraídos. La pureza relativa de los BTEX extraídos por la mezcla de líquidos iónicos utilizando 18 pisos fue sustancialmente superior (84,9 %) a la alcanzada por el sulfolano (71,9 %), por lo que la purificación de los aromáticos extraídos por la mezcla de líquidos iónicos sería más sencilla que la asociada al empleo del sulfolano.

3.5.4. Extracción de hidrocarburos aromáticos de gasolina de reformado

Los resultados experimentales del estudio de la extracción de BTEX de gasolina de reformado utilizando la mezcla de líquidos iónicos y el sulfolano y las simulaciones de la columna de extracción líquido-líquido utilizando el método de Kremser se muestran en la Publicación 8 de los anexos.

Analizando los valores de las propiedades extractivas de ambos disolventes, la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} mostró valores más elevados de selectividad aromáticos/alifáticos y de pureza relativa de los aromáticos extraídos. Por el contrario, el sulfolano exhibió mayores coeficientes de reparto de los aromáticos y rendimientos de extracción tanto de alifáticos como de BTEX.

Los efectos de la temperatura y la relación disolvente/alimento observados en la extracción de BTEX de gasolina de reformado fueron similares a los comentados para la extracción de aromáticos de la nafta alimentada al cracker de etileno. Se seleccionó trabajar a una temperatura de 303,2 K para incrementar el rendimiento de extracción de BTEX y la pureza de los aromáticos en la fase de extracto, mientras que una relación disolvente/alimento de 5,0 garantizará valores elevados del rendimiento de extracción de los hidrocarburos aromáticos.

De forma análoga a lo explicado para la extracción de BTEX de la nafta alimentada al cracker de etileno, mediante el método de Kremser se simularon las columnas de extracción líquido-líquido en las condiciones óptimas seleccionadas. Realizando las simulaciones se determinó el número de pisos en la columna de extracción que permitía alcanzar los rendimientos individuales de extracción de aromáticos del proceso Sulfolano: benceno (99,9 %), tolueno (99,0 %) y xilenos (97,0 %) (Gary y col., 2007).

Estos valores de rendimiento de extracción fueron alcanzados utilizando sulfolano con 16 etapas de equilibrio, mientras que empleando la mezcla de líquidos iónicos se requirieron 24 pisos de equilibrio en la columna. Por tanto, al reemplazar el proceso Sulfolano por un hipotético proceso empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} se podrían alcanzar los mismos valores de rendimiento de extracción de BTEX pero utilizando una columna con un mayor número de pisos. Analizando los valores de pureza relativa de los BTEX en la corriente de extracto obtenidos en la simulación se puede concluir que trabajar con la mezcla de líquidos iónicos provoca que la pureza de los hidrocarburos aromáticos extraídos (97,7 %) sea sustancialmente superior a la alcanzada utilizando sulfolano (92,1 %).

Tanto los valores de pureza relativa de los BTEX como los rendimientos de extracción de aromáticos fueron sustancialmente superiores en la separación de BTEX de la gasolina de reformado que los valores obtenidos en la extracción de aromáticos de la nafta alimentada al cracker de etileno, debido al mayor porcentaje de aromáticos en la gasolina de reformado.

La mayor pureza de los aromáticos extraídos facilitaría las operaciones posteriores de purificación de los solutos. Hay que tener en cuenta que estos procesos de recuperación y purificación de los aromáticos extraídos también se simplificarían con respecto al proceso Sulfolano debido a la naturaleza no volátil de los líquidos iónicos y a que la presencia de los líquidos iónicos incrementa considerablemente la volatilidad relativa de los alifáticos respecto de los aromáticos (Navarro y col., 2015). Además, debido a la prácticamente nula solubilidad de la mezcla de líquidos iónicos en la corriente de refinado, la columna de lavado de recuperación del disolvente que se emplea en el proceso Sulfolano sería innecesaria en un proceso empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)}.

3.5.5. Extracción de hidrocarburos aromáticos de gasolinas de pirólisis suave y severa

Finalmente se ha estudiado la extracción líquido-líquido de benceno, tolueno y *p*-xileno de dos mezclas representativas de gasolinas de pirólisis suave y severa empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} y el sulfolano. Ambas corrientes de refinería se diferencian en el mayor contenido en aromáticos de la gasolina de pirólisis severa (66,1 % en masa) frente al que presenta la gasolina de pirólisis suave (51,1 % en masa) (Franck y Stadelhofer, 1988). De forma análoga al estudio de las corrientes de refinería anteriores, las simulaciones de las columnas de extracción líquido-líquido se han realizado utilizando el método de Kremser. En la Publicación 9 de los anexos se recogen los resultados experimentales y de las simulaciones de las columnas de extracción líquido-líquido.

La actuación de los disolventes en la separación de BTX de las gasolinas de pirólisis fue similar a las comentadas en las dos corrientes de refinería anteriores. Los valores de selectividad aromáticos/alifáticos y de pureza relativa de los BTX extraídos fueron mayores en el caso del empleo de la mezcla de líquidos iónicos, mientras que el sulfolano mostró mayores coeficientes de reparto de los BTX y rendimientos de extracción de alifáticos y aromáticos.

Comparando las propiedades extractivas mostradas por ambos disolventes en la extracción de BTX de las gasolinas de pirólisis suave y severa se puede observar que empleando tanto el sulfolano como la mezcla de líquidos iónicos se alcanzaron valores mayores de rendimientos de extracción de los aromáticos y de pureza de los aromáticos extraídos en la desaromatización de la gasolina de pirólisis severa como consecuencia del mayor contenido en aromáticos de esta corriente y del mayor porcentaje de benceno en la misma, que es el aromático más soluble en ambos disolventes.

En el estudio de las condiciones óptimas de operación de la columna de extracción líquido-líquido utilizando la mezcla de líquidos iónicos se seleccionó trabajar a una temperatura de 303,2 K y una relación másica de disolvente/alimento igual a 5,0 para garantizar valores elevados del rendimiento de extracción de aromáticos y la pureza relativa de los BTEX en la fase de extracto.

Análogamente a las simulaciones realizadas a partir de los resultados experimentales de la extracción de aromáticos de la gasolina de reformado, se empleó el método de Kremser para determinar el número de pisos en el extractor que permite obtener los rendimientos de extracción de aromáticos del proceso Sulfolano: benceno (99,9 %), tolueno (99,0 %) y xilenos (97,0 %) (Gary y col., 2007).

En la simulación de la columna de extracción de aromáticos de la gasolina de pirólisis suave utilizando la mezcla de líquidos iónicos fueron necesarios 24 etapas de equilibrio para obtener los valores de rendimiento alcanzados por el proceso Sulfolano. En el caso de la simulación utilizando sulfolano, los valores citados de rendimientos de extracción se obtuvieron utilizando 8 etapas de equilibrio. Por tanto, usando la mezcla de líquidos iónicos se podrían alcanzar los mismos rendimientos que los que muestra el sulfolano pero empleando un mayor número de pisos.

Sin embargo, la pureza de los aromáticos extraídos empleando la mezcla de líquidos iónicos (97,2 %) fue considerablemente superior a la alcanzada en la simulación empleando sulfolano (92,1 %), por lo que los procesos de purificación posteriores de los aromáticos obtenidos serían más sencillos en un hipotético proceso empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} que en el proceso Sulfolano.

Por último, en la simulación de la columna de extracción de aromáticos de la gasolina de pirólisis severa utilizando la mezcla de líquidos iónicos se requirieron 14 etapas de equilibrio para alcanzar valores de rendimientos de extracción de BTX superiores a los del proceso Sulfolano: benceno (99,9 %), tolueno (99,0 %) y xilenos (97,0 %). Por el contrario, en la simulación del extractor empleando sulfolano se necesitaron 6 etapas de equilibrio para alcanzar dichos valores. En relación con la pureza de los aromáticos en la corriente de extracto, el valor de pureza obtenido en la simulación de la columna de extracción utilizando la mezcla de líquidos iónicos (98,4 %) fue superior a la obtenida empleando sulfolano (94,2 %).

En resumen, un proceso industrial de extracción líquido-líquido de BTX de gasolinas de pirólisis empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} necesitaría una columna de extracción con un mayor número de pisos para alcanzar los rendimientos de extracción obtenidos con el sulfolano. Sin embargo, debido a que la pureza de los BTX extraídos es considerablemente superior utilizando la mezcla de líquidos iónicos y como consecuencia de la naturaleza no volátil de los líquidos iónicos, el tren de purificación de los aromáticos extraídos sería más sencillo. Además hay que considerar que las condiciones en las que se realizaría tanto la extracción líquido-líquido (30 ºC y 1 atm) en el caso de los líquidos iónicos serían sustancialmente más suaves que las empleadas actualmente en el proceso Sulfolano (100-115 ºC y 2 atm). Por todo ello, los costes de inmovilizado y de operación de este hipotético proceso serían inferiores al proceso convencional empleado actualmente.

4. CONCLUSIONES Y RECOMENDACIONES

4.1. Conclusiones generales

A partir de los resultados experimentales obtenidos en el presente trabajo de investigación y de su discusión se han extraído las siguientes conclusiones.

Extracción de tolueno de n-heptano utilizando líquidos iónicos puros

En la primera etapa experimental se estudió el equilibrio líquido-líquido de sistemas ternarios formados por {*n*-heptano + tolueno + líquido iónico} utilizando seis líquidos iónicos puros: [emim][DCA], [bmim][DCA], [emim][SCN], [bmim][SCN], [emim][TCM] y [4empy][Tf_2N]. La consistencia de los datos experimentales de equilibrio líquido-líquido fue comprobada con la correlación de Othmer-Tobias. Asimismo, los datos de equilibrio líquido-líquido fueron modelados satisfactoriamente empleando el modelo NRTL.

A partir de los datos experimentales se calcularon las propiedades extractivas de los líquidos iónicos. Todos los líquidos iónicos exhibieron selectividades tolueno/*n*-heptano superiores al del sulfolano, además el [bmim][DCA], el [bmim][SCN], el [emim][TCM] y el [4empy][Tf_2N] mostraron también coeficientes de reparto del tolueno mayores que el del sulfolano.

Además de las propiedades extractivas de los seis líquidos iónicos puros, se midieron sus densidades, viscosidades dinámicas y tensiones superficiales. Los líquidos iónicos basados en el catión imidazolio mostraron una densidad inferior a la del sulfolano, mientras que el [4empy][Tf_2N] exhibió una densidad superior. En cuanto a la viscosidad, todos los líquidos iónicos estudiados presentaron una viscosidad superior a la del sulfolano, siendo el [emim][DCA] y el [emim][TCM] los que mostraron una viscosidad más baja. Por último, las tensiones superficiales de los líquidos iónicos con catión imidazolio fueron cercanas al valor del sulfolano, mientras que el [4empy][Tf_2N] mostró una tensión superficial sustancialmente inferior.

Selección de mezclas binarias de líquidos iónicos como potenciales disolventes de extracción de aromáticos

Para realizar la selección de las dos mezclas binarias com mayor potencial para ser empleadas en la extracción de aromáticos de corrientes de refinería, se han tenido en consideración tanto las propiedades físicas como las extractivas de los líquidos iónicos puros, teniendo como objetivo la obtención de una mezcla binaria de líquidos iónicos con propiedades similares a las mostradas por el sulfolano, para así garantizar la viabilidad del proceso de extracción a escala industrial. Para obtener mezclas de líquidos iónicos con elevados valores de las propiedades extractivas se ha decidido seleccionar mezclas formadas por un líquido iónico con alto valor de coeficiente de reparto y otro con alta selectividad. Considerando tanto las propiedades extractivas como las físicas, se seleccionaron las mezclas binarias {[emim][TCM] + [emim][DCA]} y {[4empy][Tf_2N] + [emim][DCA]} como las que presentan un mayor potencial para ser utilizadas a escala industrial.

Estudio de las propiedades extractivas y físicas de las mezclas de líquidos iónicos {[emim][TCM] + [emim][DCA]} y {[4empy][Tf_2N] + [emim][DCA]}

Se estudió el equilibrio líquido-líquido de sistemas pseudoternarios formados por {*n*-heptano + tolueno + mezcla binaria de líquidos iónicos} a 313,2 K empleando las dos mezclas de líquidos iónicos. En primer lugar, se ha estudiado la influencia de la composición de la mezcla de líquidos iónicos en las propiedades extractivas en la separación de tolueno de *n*-heptano. Asimismo se ha considerado la influencia de la composición en la mezcla sobre la densidad y la viscosidad para seleccionar la composición óptima en cada una de las mezclas binarias de líquidos iónicos.

La regla de mezcla de Yalkowsky y Roseman fue utilizada para predecir las propiedades extractivas de las dos mezclas de líquidos iónicos a partir de los resultados obtenidos en la extracción de tolueno utilizando los líquidos iónicos puros que conforman las mezclas. Las densidades de las mezclas binarias fueron predichas de forma satisfactoria con el método de contribución de grupos de Ye y Shreeve, mientras que las viscosidades de las mezclas fueron estimadas adecuadamente empleando diferentes reglas de mezcla como la de de Bingham y la regla de Grunberg-Nissan.

Considerando la influencia de la composición tanto en las propiedades extractivas como físicas se seleccionó como composición óptima un valor de fracción molar de [4empy][Tf_2N] igual a 0,3 en la mezcla {[emim][DCA] + [4empy][Tf_2N]} y una fracción molar de [emim][TCM] de 0,8 en la mezcla de líquidos iónicos {[emim][TCM] + [emim][DCA]}.

Posteriormente, se determinó el equilibrio pseudoternario de los sistemas {*n*-heptano + tolueno + mezcla binaria de líquidos iónicos} en todo el intervalo de composiciones utilizando como disolventes de extracción las dos mezclas binarias de líquidos iónicos en su composición óptima. Atendiendo a las propiedades extractivas en la separación de tolueno de *n*-heptano, la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} mostró mejores resultados que la mezcla {[emim][TCM] (0,8) + [emim][DCA] (0,2)}. Considerando los valores de las propiedades físicas de ambas mezclas, la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} mostró una densidad y una tensión superficial muy similares a los valores del sulfolano, mientras que su viscosidad fue ligeramente superior a la exhibida por la otra mezcla y por el disolvente orgánico. Por tanto, la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} se seleccionó como la que presenta un mayor potencial para ser empleada a escala industrial en la extracción de hidrocarburos aromáticos de corrientes de refinería.

Extracción de BTEX de alcanos con la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]}

En esta etapa se determinó de forma experimental el equilibrio líquido-líquido de sistemas pseudoternarios formados por un hidrocarburo alifático, un hidrocarburo aromático y la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]}. Se estudió la separación de tolueno de *n*-hexano, *n*-heptano, *n*-octano, *n*-nonano, 2,3-dimetilpentano y ciclohexano, y la extracción líquido-líquido de benceno, etilbenceno, *o*-xileno, *m*-xileno y *p*-xileno de *n*-heptano.

Con los resultados obtenidos en estos ensayos de extracción se comprobó que la composición óptima de la mezcla de líquidos iónicos {[4empy][Tf_2N] + [emim][DCA]} para la separación de diferentes aromáticos de alifáticos coincidió con la seleccionada anteriormente considerando las propiedades físicas y las extractivas en la extracción de tolueno de *n*-heptano; es decir, una fracción molar de [4empy][Tf_2N] de 0,3 en la mezcla. Asimismo, se estudió la influencia de la estructura del aromático extraído y de los alcanos sobre las propiedades extractivas de la mezcla de líquidos iónicos.

Extracción de aromáticos de corrientes de refinería empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)]} y sulfolano

Finalmente, se han realizado ensayos experimentales de extracción de BTEX de cuatro corrientes de refinería: la nafta alimentada al cracker de etileno, la gasolina de reformado y las gasolinas de pirólisis suave y severa empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} y el sulfolano como disolventes. Para seleccionar las condiciones óptimas de operación se han realizado ensayos de extracción a temperaturas entre 303,2 K y 323,2 K y a relaciones disolvente/alimento entre 1,0 y 5,0.

A partir de los resultados experimentales se ha realizado la simulación de las columnas de extracción líquido-líquido mediante el método de Kremser, comparándose los resultados obtenidos empleando ambos disolventes.

Extracción de hidrocarburos aromáticos de una nafta alimentada al cracker de etileno

Considerando la influencia de la temperatura y de la relación disolvente/alimento en las propiedades extractivas de la mezcla de líquidos iónicos, se seleccionaron como condiciones óptimas un valor de temperatura de 303,2 K y una relación disolvente/alimento de 5,0. En estas condiciones se maximizaron los rendimientos de extracción de aromáticos y de pureza de los BTEX en el extracto y se minimizó el rendimiento de extracción de alifáticos.

El método de Kremser fue empleado para simular las columnas de extracción líquido-líquido en las condiciones óptimas. Empleando una columna de extracción con 18 etapas de equilibrio se alcanzaron los siguientes rendimientos de extracción utilizando la mezcla de líquidos iónicos: benceno (> 99,9 %), tolueno (98,4 %), etilbenceno (85,3 %) y *p*-xileno (83,9 %), siendo estos valores inferiores a los rendimientos alcanzados por el sulfolano. Por el contrario, la pureza relativa de los BTEX extraídos por la mezcla de líquidos iónicos utilizando fue sustancialmente superior (84,9 %) a la alcanzada por el sulfolano (71,9 %), lo que simplificaría las etapas de purificación posteriores.

Extracción de hidrocarburos aromáticos de gasolina de reformado

Los efectos de la temperatura y la relación S/F sobre las propiedades extractivas de la mezcla de líquidos iónicos en la separación de BTEX de gasolina de reformado fueron análogos a los descritos para la nafta alimentada al cracker de etileno. Por ello, las condiciones óptimas de operación fueron coincidentes: 303,2 K y una relación disolvente/alimento de 5,0.

Mediante las simulaciones empleando el método de Kremser se determinó el número de pisos en el extractor que permitía alcanzar los rendimientos individuales de extracción de aromáticos del proceso Sulfolano: benceno (99,9 %), tolueno (99,0 %) y xilenos (97,0 %). Estos valores de rendimiento de extracción fueron alcanzados utilizando sulfolano con 16 etapas de equilibrio, mientras que empleando la mezcla de líquidos iónicos se requirieron 24 pisos de equilibrio en la columna. La pureza relativa de los BTEX en la corriente de extracto empleando la mezcla de líquidos iónicos (97,7 %) fue sustancialmente superior a la alcanzada utilizando sulfolano (92,1 %).

Extracción de hidrocarburos aromáticos de gasolinas de pirólisis suave y severa

Para garantizar valores elevados del rendimiento de extracción de aromáticos y la pureza relativa de los BTEX se seleccionaron como condiciones óptimas de operación una temperatura de 303,2 K y una relación másica de disolvente/alimento igual a 5,0. Análogamente a las simulaciones realizadas para la gasolina de reformado, se empleó el método de Kremser para determinar el número de pisos en el extractor que permite obtener los rendimientos de extracción de aromáticos del proceso Sulfolano.

En la simulación de las columnas de extracción de aromáticos de las gasolinas de pirólisis suave y severa utilizando la mezcla de líquidos iónicos se alcanzaron los valores de rendimiento de extracción de BTEX que presenta el proceso Sulfolano pero fue necesario un mayor número de pisos. Sin embargo, la pureza de los aromáticos extraídos empleando la mezcla de líquidos iónicos en ambas gasolinas fue considerablemente superior a la alcanzada empleando sulfolano, por lo que los procesos de purificación de los aromáticos obtenidos serían más sencillos en un proceso que utilice la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} que en el proceso Sulfolano.

4.2. Recomendaciones

A partir de las conclusiones obtenidas en esta tesis doctoral se propone la realización de varios trabajos de investigación que completarían las aportaciones presentadas en esta tesis doctoral.

Para garantizar la viabilidad del diseño del proceso de extracción de aromáticos empleando la mezcla de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} se debería realizar un escalado del proceso. Para ello, los ensayos de extracción líquido-líquido realizados en esta tesis doctoral podrían llevarse a cabo en una columna de extracción a escala de planta piloto empleando un mayor volumen de disolvente y de alimento, comprobando que las propiedades extractivas de la mezcla de líquidos iónicos no se ven afectadas. Asimismo, la extracción de BTEX de las gasolinas de reformado y pirólisis y la nafta alimentada al cracker de etileno podría realizarse empleando corrientes reales provenientes de refinería.

En este trabajo de investigación se han estudiado los aspectos termodinámicos de la extracción de BTEX de corrientes de refinería. Sin embargo, para realizar el dimensionado completo de la columna de extracción líquido-líquido se debería también estudiar el proceso de transferencia de materia de los hidrocarburos aromáticos presentes en la corriente al disolvente de extracción, determinando los coeficientes de transferencia de materia.

El proceso industrial de extracción de aromáticos utilizando la mezcla {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} estaría formado por una sección de extracción y una sección de separación de los BTEX extraídos y el disolvente. Por tanto, para realizar el diseño del proceso completo se requeriría también el estudio experimental del equilibrio líquido-vapor existente entre los hidrocarburos que forman la corriente de extracto y el disolvente.

Para asegurar la viabilidad económica del proceso de extracción de aromáticos con la mezcla de líquidos iónicos {[4empy][Tf_2N] (0,3) + [emim][DCA] (0,7)} se debería también estudiar la reutilización de la mezcla de líquidos iónicos mediante ciclos continuos de extracción y separación de los hidrocarburos extraídos. De esta forma, se determinarían los ciclos de servicio y la vida útil del disolvente de extracción.

Por último, una vez conocidos los parámetros de diseño de todos los equipos del proceso de extracción de aromáticos empleando la mezcla de líquidos iónicos, se deberá realizar una estimación del inmovilizado global del proceso y realizar estudios comparativos con los procesos actuales empleados a escala industrial. Asimismo, se deberán calcular los costes energéticos de bombeo y agitación y los servicios de calefacción y enfriamiento requeridos.

BIBLIOGRAFÍA

Al-Jimaz, A.S.; Fandary, M.S.; Alkhaldi, K.H.A.E; Al-Kandary, J.A; Fahim, M.A. Extraction of Aromatics from Middle Distillate Using *N*-Methyl-2-pyrrolidone: Experiment, Modeling, and Optimization. Ind. Eng. Chem. Res. **2007**, 46*,* 5686-5696.

Ali, J. The Hydrogenation of Pyrolysis Gasoline (PyGas) Over Nickel and Palladium Catalysts. PhD Thesis. **2012**. University of Glasgow.

Anjan, S.T. Ionic Liquid for Aromatic Extraction: Are They Ready? Chem. Eng. Prog. **2006**, 102, 30-39.

Anton Paar. Instruction Manual DMA 4100/4500/5000. **2005.**

Arce, A.; Earle, M.J; Rodríguez, H.; Seddon, K.R. Separation of Benzene and Hexane by Solvent Extraction with 1-Alkyl-3-methylimidazolium Bis{(trifluoromethyl)sulfonyl}amide Ionic Liquids: Effect of the Alkyl-Substituent Length. J. Phys. Chem. B **2007**, 111*,* 4732-4736.

Bingham, E.C. Fluidity and Plasticity; McGraw-Hill: New York, **1922**.

Buchbender, F.; Onink, F.; Meindersma, W.; de Haan, A.B.; Pfenning, A. Simulation of Aromatics Extraction with an Ionic Liquid in a Pilot-plant Kühni Extractor Based on Single-Drop Experiments. Chem. Eng. Sci. **2012**, 82, 167-176.

Carvalho, P.J.; Regueira, T.; Santos, L.M.N.B.F.; Fernandez, J.; Coutinho, J.A.P. Effect of Water on the Viscosities and Densities of 1-Butyl-3-methylimidazolium Dicyanamide and 1-Butyl-3-methylimidazolium Tricyanomethane at Atmospheric Pressure. J. Chem. Eng. Data **2010**, 55*,* 645-652.

Chauvel, A.; Lefebvre, G. Petrochemical Processes. Editions Technip. París. **1989.**

Corderi, S. Gonzalez. E.J.; Calvar N.; Dominguez, A. Application of [HMim][NTf2], [HMim][TfO] and [BMim][TfO] Ionic Liquids on the Extraction of Toluene from Alkanes: Effect of the Anion and the Alkyl Chain Length of the Cation on the LLE. J. Chem. Thermodyn. **2012**, 53, 60-66.

Costa, A.J.L; Esperança, J.M.M.; Marrucho, I.M.; Rebelo, L.P.N. Densities and Viscosities of 1-Ethyl-3-methylimidazolium n-Alkyl Sulfates. J. Chem. Eng. Data **2011**, 56, 3433-3441.

Crosthwaite, J.M.; Muldoon, M.J.; Dixon, J.K.; Anderson, J.L.; Brennecke, J.F. Phase Transition and Decomposition Temperatures, Heat Capacities and Viscosities of Pyridinium Ionic Liquids. J. Chem. Thermodyn. **2005**, 37, 559-568.

Dataphysics. Operating Manual OCA 15. **2002.**

DeSimone, J.M. Practical Approaches to Green Solvents. Science **2002**, 297, 799-803.

Domanska, U.; Krolikowska, M.; Walczak, K. Effect of Temperature and Composition on the Density, Viscosity, Surface Tension and Excess Quantities of Binary Mixtures of 1-Ethyl-3-methylimidazolium Tricyanomethanide with Thiophene. Colloids and Surfaces A: Physicochem. Eng. Aspects **2013**, 436, 504-511.

Dominguez, I.; Calvar N.; Gómez, E.; Dominguez, A. Separation of Toluene from Cyclic Hydrocarbons using 1-Butyl-3-methylimidazolium Methylsulfate Ionic Liquid at T = 298.15 K and Atmospheric Pressure. J. Chem. Thermodyn. **2011**, 43, 705-710.

Dominguez, I.; González, E.J.; Dominguez, A. Liquid Extraction of Aromatic/cyclic Aliphatic Hydrocarbon Mixtures using Ionic Liquids as Solvent: Literature Review and New Experimental LLE data. Fuel Process. Technol. **2014**, 125, 207-216.

Esperança, J.M.M.S.; Visak, Z.P.; Plechkova, N.V.: Seddon, K.R.; Guedes, H.J.R.; Rebelo, L.P.N. Density, Speed of Sound, and Derived Thermodynamic Properties of Ionic Liquids over an Extended Pressure Range. 4. [C3mim][NTf2] and [C5mim][NTf2]. J. Chem. Eng. Data **2006**, 51, 2009-2015.

Fahim, M.; Al-Sahhaf, T.; Elkilani, A. Fundamentals of Petroleum Refining. Elsevier. Amsterdam. **2010**.

Firnhaber, B.; Emmerich, G.; Ennenbach, F.; Ranke, U. Separation Processes for the Recovery of Pure Aromatics. Erdol. Erdgas Kohle **2000**, 116, 254-260.

Fletcher, K.A.: Baker, S.N.; Baker, G.A.; Pandey, S. Probing Solute and Solvent Interactions within Binary Ionic Liquid Mixtures, New J. Chem **2003**, 27, 1706-1712.

Franck, H.G.; Staldelhofer, J.W. Industrial Aromatic Chemistry; Springer-Verlag: Berlin, **1988**.

França, J.M.P.; Nieto de Castro, C.A.; Matos Lopes, M.; Nunes, V.M.B. Influence of Thermophysical Properties of Ionic Liquids in Chemical Process Design. J. Eng. Chem. Data **2009**, 54, 2569-2575.

Fredlake, C.P.; Crosthwaite, J.M.; Hert, D.G.; Aki, S.N.V.K.; Brennecke, J.F. Thermophysical Properties of Imidazolium-Based Ionic Liquids. J. Chem. Eng. Data **2004**, 49, 954-964.

Galán Sánchez, L.; Ribé Espel, J.; Onink, F.; Meindersma, G.W.; de Haan, A.B. Density, Viscosity, and Surface Tension of Synthesis Grade Imidazolium, Pyridinium, and Pyrrolidinium Based Room Temperature Ionic Liquids. J. Chem. Eng. Data **2009**, 54, 2803-2812.

García, J.; García, S.; Torrecilla, J.S.; Oliet, M.; Rodríguez, F. Liquid-liquid Equilibria for the Ternary Systems {Heptane + Toluene + *N*-Butylpyridinium Tetrafluoroborate or *N*-Hexylpyridinium Tetrafluoroborate} at T = 313.2 K. J. Chem. Eng. Data **2010**, 55, 2862-2865.

García, S.; Larriba, M.; García, J.; Torrecilla, J.S.; Rodríguez, F. Liquid−Liquid Extraction of Toluene from Heptane Using 1−Alkyl−3−methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids. J. Chem. Eng. Data **2011a**, 56, 113-118.

García, J.; García, S.; Torrecilla, J.S.; Rodríguez, F. N-butylpyridinium bis-(trifluormethylsulfonyl)imide Ionic Liquids as Solvents for the Liquid-liquid Extraction of Aromatic from Their Mixtures with Alkanes: Isomeric Effect of the Cation. Fluid Phase Equilib. **2011b**, 301, 62-66.

García, S.; Larriba, M.; García, J.; Torrecilla, J.S.; Rodríguez, F. Liquid–liquid Extraction of Toluene from Heptane Using Binary Mixtures of *N*–butylpyridinium Tetrafluoroborate and *N*–butylpyridinium Bis(trifluoromethylsulfonyl)imide Ionic Liquids. Chem. Eng. J. **2012a**, 180, 210-215.

García, S.; Larriba, M.; García, J.; Torrecilla, J.S.; Rodríguez, F. Alkylsulfate-based Ionic Liquids in the Liquid-liquid Extraction of Aromatic Hydrocarbons. J. Chem. Thermodyn. **2012b**, 45, 68-74.

García, S.; Larriba, M.; García, J.; Torrecilla, J. S.; Rodríguez, F. Separation of toluene from *n*-heptane by liquid–liquid extraction using binary mixtures of [bpy][BF_4] and [4bmpy][Tf_2N] ionic liquids as solvent. J. Chem. Thermodyn. **2012c**, 53, 119-124.

García, S.; Larriba, M.; Casas, A.; García, J.; Rodríguez, F. Separation of Toluene and Heptane by Liquid−Liquid Extraction Using Binary Mixtures of the Ionic Liquids 1‑Butyl-4-methylpyridinium Bis(trifluoromethylsulfonyl)imide and 1‑Ethyl-3-methylimidazolium Ethylsulfate. J. Chem. Eng. Data **2012d**, 57, 2472-2478.

García, S.; García, J.; Larriba, M.; Casas, A.; Rodríguez, F. Liquid-liquid Extraction of Toluene from Heptane by {[4bmpy][Tf2N] + [emim][CHF2CF2SO3]} Ionic Liquid Mixed Solvents. Fluid Phase Equilib. 2013, 337, 47-52.

Gardas, R.L.; Coutinho, J. A.P. Extension of the Ye and Shreeve Group Contribution Method for Density Estimation of Ionic Liquids in a Wide Range of Temperatures and Pressures. Fluid Phase Equilib. **2008**, 263, 26-32.

Gary, J.; Handwerk, G.; Kaiser, M. Petroleum Refining Technology and Economics, 5th ed.; CRC Press: Boca Raton, FL, **2007**.

Gómez, E.; Domínguez, I.; Calvar, N.; Palomar, J.; Domínguez, A. Experimental Data, Correlation and Prediction of the Extraction of Benzene from Cyclic Hydrocarbons using [Epy][ESO_4] Ionic Liquid. Fluid Phase Equilib. **2014**, 361, 83-92.

González, B.; Calvar, N.; Gómez, E.; Macedo, E.A.; Domínguez, A. Synthesis and Physical Properties of 1-Ethyl-3-methylpyridinium Ethylsulfate and Its Binary Mixtures with Ethanol and Water at Several Temperatures. J. Chem. Eng. Data **2008**, 53, 1824-1828.

González. E.J.; Calvar, N.; González, B.; Domínguez, A. Separation of Toluene from Alkanes using 1-Ethyl-3-methylpyridinium Ethylsulfate Ionic Liquid at T = 298.15 K and Atmospheric Pressure. J. Chem. Thermodyn. **2010**, 42, 752-757.

González. E.J.; González, B.; Calvar, N.; Domínguez, A. Study of [EMim][ESO_4] Ionic Liquid as Solvent in the Liquid-liquid Extraction of Xylenes from their Mixtures with Hexane. Fluid Phase Equilib. **2011**, 305, 227-232.

González, E.J.; Requejo, P.F.; Domínguez, A.; Macedo, E.A. Phase Equilibria of Binary Mixtures (Ionic Liquid + Aromatic Hydrocarbon): Effect of the Structure of the Components on the Solubility. Fluid Phase Equilib. **2013**, 360, 416-422.

Grunberg, L.; Nissan, A.H. Mixture Law for Viscosity. Nature **1949**, 164, 799-800.

Hansmeier, A.R.; Minoves Ruiz, M.; Meindersman, G.W.; de Haan, A.B. Liquid-Liquid Equilibria for the Three Ternary Systems (3-Methyl-*N*-butylpyridinium Dicyanamide + Toluene + Heptane), (1-Butyl-3-methylimidazolium Dicyanamide + Toluene + Heptane) and (1-Butyl-3-methylimidazolium Thiocyanate + Toluene + Heptane) at T = (313.15 and 348.15) K and p = 0.1 MPa. J. Chem. Eng. Data **2010**, 55, 708-713.

Henley, E.J.; Seader, J.D. Equilibrium-Stage Separation Operations in Chemical Engineering; John Wiley and Sons: New York, **1981**.

Hombourger, T.; Gouzien, L.; Mikitenko, P.; Bonfils, P. Solvent Extraction in the Oil Industry. Editions Technip: Paris, **2000**.

HPP Science. Aromatics World Market until 2012. **2013**.

Jacquemin, J.; Husson, P.; Mayer, V.; Cibulka, I. High-Pressure Volumetric Properties of Imidazolium-Based Ionic Liquids: Effect of the Anion. J. Chem. Eng. Data **2007**, 52, 2204-2211.

Kandil, M.E.; Marsh, K.N.; Goodwin, A.R.H. Measurement of the Viscosity, Density, and Electrical Conductivity of 1-Hexyl-3-methylimidazolium Bis(trifluorosulfonyl)imide at Temperatures between (288 and 433) K and Pressures below 50 MPa. J. Chem. Eng. Data **2007**, 52, 2382-2387.

Kelayeh, S.A.; Jalili, A.H.; Ghotbi, C.; Hosseini-Jenab, M.; Taghikhani, V. Densities, Viscosities, and Surface Tensions of Aqueous Mixtures of Sulfolane + Triethanolamine and Sulfolane + Diisopropanolamine. J. Chem. Eng. Data **2011**, 56, 4317-4324.

Kim, M.J.; Shin, S.H.; Kim, Y.J.; Cheong, M.; Lee, J.S.; Kim, H.S. Role of Alkyl Group in the Aromatic Extraction using Pyridinium-Based Ionic Liquids. Phys. Chem B **2013**, 117, 14827-14834.

Kirk, R.E.; Other, D.F. Encyclopaedia of Chemical Technology. Wiley: New York, **1998**.

Kolb, B.; Ettre L.S. Static Headspace-Gas Chromatography: Theory and Practice; Wiley-VCH: New York, **1997**.

Królikowski, M.; Walczak, K.; Domanska, U. Solvent Extraction of Aromatic Sulfur Compounds from n-Heptane using the 1-Ethyl-methylimidazolium Tricyanomethanide Ionic Liquid. J. Chem. Thermodyn. **2013**, 65, 168-173.

Larriba, M.; García, S.; García, J.; Torrecilla, J.S.; Rodríguez, F. Thermophysical Properties of 1-Ethyl-3-methylimidazolium 1,1,2,2-Tetrafluoroethanesulfonate and 1-Ethyl-3-methylimidazolium Ethylsulfate Ionic Liquids as a Function of Temperature. J. Chem. Eng. Data **2011**, 56, 3589-3597.

Larriba, M.; García, S.; Navarro, P.; García, J.; Rodríguez, F. Physical Properties of *N*–butylpyridinium Tetrafluoroborate and *N*–butylpyridinium Bis(trifluoromethylsulfonyl)imide Binary Ionic Liquid Mixtures. J. Chem. Eng. Data **2012**, 57*,* 1318-1325.

Larriba, M.; García, S.; Navarro, P.; García, J.; Rodríguez, F. Physical Physical Characterization of an Aromatic Extraction Solvent Formed by [bpy][BF4] and [4bmpy][Tf2N] Mixed Ionic Liquids. J. Chem. Eng. Data **2013**, 58*,* 1496-1504.

Larriba, M.; Navarro, P.; Beigbeder, J.B.; García, J.; Rodríguez, F. Mixing and Decomposition Behavior of {[4bmpy][Tf_2N] + [emim][$EtSO_4$]} and {[4bmpy][Tf_2N] + [emim][TFES]} Ionic Liquid Mixtures. J. Chem. Thermodyn. **2015**, 82, 58-75.

Marciniak, A.; Krolikowski, M. Ternary (Liquid + liquid) Equilibria of {Trifluorotris(perfluoroethyl)phosphate based Ionic Liquids + Thiophene + Heptane}. J. Chem. Thermodyn. **2012**, 49, 154-158.

Meindersma, G.W.; Podt, A.J.G.; de Haan, A.B. Selection of Ionic Liquids for the Extraction of Aromatic Hydrocarbons from Aromatic/aliphatic Mixtures. Fuel Process. Technol. **2005**, 87, 59-70.

Meindersma, G.W.; de Haan, A.B. Conceptual Process Design for Aromatic/aliphatic Separation with Ionic Liquids. Chem. Eng. Res. Des. **2008**, 86, 745-752.

Meindersma, G.W.; Hansmeier, A.R.; de Haan, A.B. Ionic Liquids for Aromatics Extraction. Present Status and Future Outlook. Ind. Eng. Chem. Res. **2010**, 49, 7530-7540.

Meindersma, G.W.; de Haan, A.B. Cyano-containing Ionic Liquids for the Extraction of Aromatic Hydrocarbons from an Aromatic/aliphatic Mixture. Sci. China Chem. **2012**, 55, 1488-1499.

Meyers, R.A. Handbook of Petroleum Refining Processes, 3rd ed.; McGraw-Hill: New York, **2004**.

Mokhtarani, B.; Musavi, J.; Parvini, M.; Mafi, M.; Sharifi, A.; Mirzaei, M. Ternary (liquid-liquid) Equilibria of Nitrate Based Ionic Liquid + Alkane + Benzene at 298.15 K : Experiments and Correlation. Fluid Phase Equilib. **2013**, 341, 35-41.

Navarro, P.; Larriba, M.; Rojo, E.; García, J.; Rodríguez, F. Thermal Properties of Cyano-based Ionic Liquids. J. Chem. Eng. Data **2013**, 58, 2187-2193.

Navarro, P.; Larriba, M.; García, J.; Rodríguez, F. Thermal Stability, Specific Heats, and Surface Tensions of ([emim][DCA] + [4empy][Tf_2N]) Ionic Liquid Mixtures. J. Chem. Thermodyn. **2014a**, 76, 152-160.

Navarro, P.; Larriba, M.; García, J.; Rodríguez, F. Thermal Stability and Specific Heats of {[emim][DCA] + [emim][TCM]} Mixed Ionic Liquids. Thermochim. Acta **2014b**, 588, 22-27.

Navarro, P.; Larriba, M.; García, J.; González, E.J.; Rodríguez, F. Vapor–liquid Equilibria of {n-Heptane + Toluene + [emim][DCA]} System by Headspace Has Chromatography Fluid Phase Equilib. **2015**, 387, 209-216.

Othmer, D.F.; Tobias, P.E. Toluene and Acetaldehyde Systems, Tie Line Correlation, Partial Pressures of Ternary Liquid Systems and the Prediction of Tie Lines. Ind. Eng. Chem. **1942**, 34, 690-700.

Palomar, J.; Ferro, V.R.; Torrecilla, J.S.; Rodríguez, F. Density and Molar Volume Predictions Using COSMO-RS for Ionic Liquids. An Approach to Solvent Design. Ind. Eng. Chem. Res. **2007**, 46, 6041-6048.

Plechkova, N.V.; Seddon, K.R. Applications of Ionic Liquids in the Chemical Industry. Chem. Soc. Rev. **2008**, 37, 123-150.

Ramos Carpio, M.A. Refino de Petróleo, Gas Natural y Petroquímica. Ed. Ramos Carpio. **1997**.

Renon, H.; Prausnitz, J.M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. AIChE J. **1968**, 14, 135-144.

Rogers, R.D.; Seddon, K.R. Ionic Liquids-Solvents of the Future? Science **2003**, 302, 792-793.

Simoni, L.D.; Lin, Y.; Brennecke, J. F.; Stadtherr, M.A. Modeling Liquid−Liquid Equilibrium of Ionic Liquid Systems with NRTL, Electrolyte−NRTL, and UNIQUAC. Ind. Eng. Chem. Res. **2008**, 47, 256-272.

Sowmiah, S., Srinivasadesikan, V., Tseng, M.C., Chu, Y.H. Review: On the Chemical Stabilities of Ionic Liquids. Molecules **2009**, 14, 3780-3813.

Tokuda, H.; Tsuzuki, S.; Susan, M.A.B.H.; Hayamizu, K.; Watanabe, M. How Ionic Are Room-Temperature Ionic Liquids? An Indicator of the Physicochemical Properties. J. Phys. Chem B **2006**, 110, 19593-19600.

Torrecilla, J.S.; Rafione, T.; García, J.; Rodríguez, F. Effect of Relative Humidity of Air on Density, Apparent Molar Volume, Viscosity, Surface Tension, and Water Content of 1-Ethyl-3-methylimidazolium Ethylsulfate Ionic Liquid. J. Chem. Eng. Data **2008,** 53, 923-928.

ThyssenKrupp. Aromatics, Sources, Demand, and Applications. **2014.**

Wauquier, J.P. Petroleum Refining. Vol. 2. Separation Processes. Editions Technip: Paris, **2000**.

Weissermel, K.; Arpe, H.J. Industrial Organic Chemistry, fourth. ed., Wiley−VCH: New York, **2003**.

Yalkowsky, S.H.; Roseman, T.J. Chapter 3: Solubilization of drugs by cosolvents, in: Techniques of Solubilization of Drugs; Dekker: New York, **1981**.

Ye, C.; Shreeve, J.M. Rapid and Accurate Estimation of Densities of Room-Temperature Ionic Liquids and Salts. J. Phys. Chem. A **2007**, 111, 1456-1461.

Zaiz, T.; Lanez, H.; Kechida, B. Aspen Hysys Simulation and Comparison between Organic Solvents (Sulfolane and DMSO) Used for Benzene Extraction. Int. J. Chem. Petroleum Sci. **2013**, 2, 10-19.

ANEXO: PUBLICACIONES

LISTADO DE PUBLICACIONES

Publicación 1: Liquid−Liquid Extraction of Toluene from Heptane Using [emim][DCA], [bmim][DCA], and [emim][TCM] Ionic Liquids. Ind. Eng. Chem. Res. 2013, 52, 2714-2720.

Publicación 2: Extraction of Toluene from *n*-Heptane using [emim][SCN] and [bmim][SCN] Ionic Liquids as Solvents. J. Chem. Thermodyn. 2014, 79, 266-271.

Publicación 3: Separation of Toluene from *n*-Heptane, 2,3-Dimethylpentane, and Cyclohexane using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids as Extraction Solvents. Sep. Purif. Technol. 2013, 120, 392-401.

Publicación 4: Liquid–liquid Extraction of Toluene from *n*-Heptane by {[emim][TCM] + [emim][DCA]} Binary Ionic Liquid Mixtures. Fluid Phase Equlib. 2014, 364, 48-54.

Publicación 5: Liquid−Liquid Extraction of Toluene from *n*-Alkanes using {[4empy][Tf_2N] + [emim][DCA]} Ionic Liquid Mixtures. J. Chem. Eng. Data 2014, 59, 1692-1699.

Publicación 6: Extraction of Benzene, Ethylbenzene, and Xylenes from *n*-Heptane using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids. Fluid Phase Equilib. 2014, 380, 1-10.

Publicación 7: Separation of BTEX from a Naphtha Feed to Ethylene Crackers using a Binary Mixture of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids. Sep. Purif. Technol. 2015, 144, 54-62.

Publicación 8: Liquid−Liquid Extraction of BTEX from Reformer Gasoline Using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids. Energy Fuels 2014, 28, 6666-6676.

Publicación 9: Dearomatization of Pyrolysis Gasolines from Mild and Severe Cracking by Liquid-Liquid Extraction using a Binary Mixture of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids. Fuel Process. Techol. 2015, DOI: 10.1016/j.fuproc.2015.03.009.

Industrial & Engineering Chemistry Research

Factor de impacto (2013): 2,24

Publicación 1:

Liquid−Liquid Extraction of Toluene from Heptane Using [emim][DCA], [bmim][DCA], and [emim][TCM] Ionic Liquids

Marcos Larriba, Pablo Navarro, Julián García, Francisco Rodríguez

Industrial & Engineering Chemistry Research, 2013, 52, 2714-2720

I&EC research
Industrial & Engineering Chemistry Research

Article
pubs.acs.org/IECR

Liquid−Liquid Extraction of Toluene from Heptane Using [emim][DCA], [bmim][DCA], and [emim][TCM] Ionic Liquids

Marcos Larriba, Pablo Navarro, Julián García,* and Francisco Rodríguez

Department of Chemical Engineering, Complutense University of Madrid, E-28040 Madrid, Spain

ABSTRACT: The performance of the 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]), 1-butyl-3-methylimidazolium dicyanamide ([bmim][DCA]), and 1-ethyl-3-methylimidazolium tricyanomethanide ([emim][TCM]) ionic liquids (ILs) as alternative solvents in the liquid−liquid extraction of toluene from heptane was evaluated at 313.2 K. These ILs were selected due to their low viscosity and their highly aromatic character. Densities and viscosities of the ILs have also been determined over the temperature range from 293.15 to 353.15 K. To analyze the potential of the ILs to be applied in an industrial aromatic extraction process, toluene and heptane distribution ratios, separation factors, and physical properties of the ILs have been compared to the sulfolane values. In addition, the nonrandom two-liquid model successfully correlated the liquid−liquid equilibrium data for the three ternary systems studied.

1. INTRODUCTION

The sulfolane shell UOP is the most widely used process in liquid−liquid extraction of aromatic hydrocarbons from their mixtures with C_4−C_{10} aliphatic hydrocarbons. The main drawbacks of this process are the high energy consumption in regeneration of sulfolane due to its high boiling point (560 K) and the hard recovery of sulfolane dissolved in the raffinate stream.[1] Both problems could be overcome using ILs as solvents. As a result of their practically nonvolatile behavior, the IL recovery could be accomplished by a simple flash distillation or by a stripping.[2,3] In addition, the solubility of ILs in the hydrocarbon rich phase can be considered as negligible, simplifying the purification of the raffinate.[4]

The main drawback of pure ILs and of binary IL mixtures studied so far is their higher viscosity compared to organic solvents used in aromatic extraction.[5−7] Because of this, we have selected two dicyanamide-based ILs and a tricyanomethanide-based IL, since ILs containing these anions have similar viscosities to those of sulfolane. The ILs selected are based on the imidazolium cation due to its aromatic character.

In this work, we have studied the liquid−liquid extraction of toluene from heptane using 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]), 1-butyl-3-methylimidazolium dicyanamide ([bmim][DCA]), and 1-ethyl-3-methylimidazolium tricyanomethanide ([emim][TCM]) ILs. For this purpose, we have determined the LLE for the ternary systems formed by {heptane + toluene + ([emim][DCA], [bmim][DCA], or [emim][TCM])} at 313.2 K and atmospheric pressure. From these results, we have calculated distribution ratios and separation factors for each IL. The reliability of the LLE data has been checked by using the Othmer−Tobias correlation,[8] and the NRTL model[9] has been also used to correlate LLE data. Likewise, densities and viscosities of the ILs and sulfolane have been measured at different temperatures to conduct a comparative analysis of the physical properties of these solvents.

2. EXPERIMENTAL SECTION

2.1. Chemicals. [emim][DCA], [bmim][DCA], and [emim][TCM] ILs were purchased from Iolitec GmbH with mass fraction purities higher than 0.98 and halides and water mass fractions less than 2 × 10^{-2} and 2 × 10^{-3}, respectively. Heptane and toluene, which are over molecular sieves to maintain constant water content, and sulfolane were supplied by Sigma-Aldrich. The specifications of the chemicals used in this paper are listed in Table 1. All chemicals were employed as received without further purification. To prevent water absorption, they were stored inside a desiccator in their original bottles and the handling of ILs was performed inside a glovebox filled with dry nitrogen.

Table 1. Sample Description

chemical name	source	mass fraction purity	analysis method
[emim][DCA][a]	Iolitec GmbH	0.98	NMR[d] and IC[e]
[bmim][DCA][b]	Iolitec GmbH	0.98	NMR[d] and IC[e]
[emim][TCM][c]	Iolitec GmbH	0.98	NMR[d] and IC[e]
Toluene	Sigma−Aldrich	0.995	GC[f]
Heptane	Sigma−Aldrich	0.997	GC[f]
Sulfolane	Sigma−Aldrich	0.99	GC[f]

[a] [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide. [b] [bmim][DCA] = 1-butyl-3-methylimidazolium dicyanamide. [c] [emim][TCM] = 1-ethyl-3-methylimidazolium tricyanomethanide. [d] Nuclear magnetic resonance. [e] Ion chromatography. [f] Gas chromatography.

2.2. Experimental Procedure and Analysis. LLE experiments were gravimetrically prepared in 8 mL vials with screw caps using a Mettler Toledo XS 205 balance with a precision of ±1 × 10^{-5} g. First, known amounts of toluene and

Received: December 5, 2012
Revised: January 23, 2013
Accepted: January 29, 2013
Published: January 30, 2013

Table 2. Experimental LLE Data on Mole Fraction (x), Distribution Ratios (D_i), and Separation Factors ($\alpha_{2,1}$) at T = 313.2 K and Atmospheric Pressure[a]

feed (global composition)		heptane-rich phase (upper layer)		IL-rich phase (lower layer)				
x_1	x_2	x_1^I	x_2^I	x_1^{II}	x_2^{II}	D_1	D_2	$\alpha_{2,1}$
Heptane (1) + Toluene (2) + [emim][DCA] (3)								
0.5050	0.0000	1.0000	0.0000	0.0032	0.0000	0.0032		
0.4924	0.0289	0.9582	0.0418	0.0036	0.0113	0.0038	0.270	72.0
0.4742	0.0582	0.9158	0.0842	0.0035	0.0230	0.0038	0.273	71.5
0.4496	0.1115	0.8320	0.1680	0.0035	0.0466	0.0042	0.277	65.9
0.3992	0.2092	0.6961	0.3039	0.0035	0.0848	0.0050	0.279	55.5
0.3603	0.2903	0.5983	0.4017	0.0030	0.1127	0.0050	0.281	56.0
0.3193	0.3697	0.5029	0.4971	0.0028	0.1395	0.0056	0.281	50.4
0.2814	0.4466	0.4159	0.5841	0.0026	0.1653	0.0063	0.283	45.3
0.2358	0.5358	0.3279	0.6721	0.0024	0.1930	0.0073	0.287	39.2
0.1807	0.6437	0.2338	0.7662	0.0019	0.2216	0.0081	0.289	35.6
0.1300	0.7419	0.1567	0.8433	0.0014	0.2479	0.0089	0.294	32.9
0.0000	0.8532	0.0000	1.0000	0.0000	0.3209		0.321	
Heptane (1) + Toluene (2) + [bmim][DCA] (3)								
0.5009	0.0000	1.0000	0.0000	0.0092	0.0000	0.0092		
0.4889	0.0263	0.9663	0.0337	0.0091	0.0145	0.0094	0.430	45.7
0.4739	0.0581	0.9257	0.0743	0.0094	0.0321	0.0102	0.432	42.5
0.4498	0.1097	0.8509	0.1491	0.0093	0.0644	0.0109	0.432	39.5
0.3957	0.2129	0.7192	0.2808	0.0086	0.1215	0.0120	0.433	36.2
0.3594	0.2869	0.6268	0.3732	0.0087	0.1651	0.0139	0.442	31.9
0.3166	0.3706	0.5282	0.4718	0.0087	0.2099	0.0165	0.445	27.0
0.2864	0.4298	0.4547	0.5453	0.0081	0.2416	0.0178	0.443	24.9
0.2388	0.5250	0.3534	0.6466	0.0071	0.2864	0.0201	0.443	22.0
0.1837	0.6341	0.2513	0.7487	0.0060	0.3445	0.0239	0.460	19.3
0.1289	0.7435	0.1616	0.8384	0.0047	0.3996	0.0291	0.477	16.4
0.0000	0.8521	0.0000	1.0000	0.0000	0.4573		0.457	
Heptane (1) + Toluene (2) + [emim][TCM] (3)								
0.4974	0.0000	1.0000	0.0000	0.0091	0.0000	0.0091		
0.4824	0.0283	0.9655	0.0345	0.0094	0.0158	0.0097	0.458	47.0
0.5167	0.0634	0.9247	0.0753	0.0094	0.0332	0.0102	0.441	43.4
0.4356	0.1172	0.8528	0.1472	0.0099	0.0702	0.0116	0.477	41.1
0.3900	0.2176	0.7252	0.2748	0.0089	0.1315	0.0123	0.479	39.0
0.3532	0.2984	0.6365	0.3635	0.0097	0.1851	0.0152	0.509	33.4
0.3089	0.3809	0.5312	0.4688	0.0084	0.2386	0.0158	0.509	32.2
0.2793	0.4396	0.4611	0.5389	0.0083	0.2906	0.0180	0.539	30.0
0.2297	0.5401	0.3519	0.6481	0.0073	0.3551	0.0207	0.548	26.4
0.1755	0.6470	0.2469	0.7531	0.0066	0.4208	0.0267	0.559	20.9
0.1256	0.7504	0.1597	0.8403	0.0049	0.4865	0.0307	0.579	18.9
0.0000	0.8419	0.0000	1.0000	0.0000	0.6545		0.655	

[a] Standard uncertainties (u) are $u(T)$ = 0.1 K, $u(x_i)$ = 0.0007, $u(x_i^I)$ = 0.0006; $u(x_1^{II})$ = 0.0009; $u(x_2^{II})$ = 0.0020.

heptane binary mixtures over the whole range of composition were added to tared vials. Subsequently, [emim][DCA], [bmim][DCA], or [emim][TCM] ILs were gravimetrically added. The estimated uncertainty in feed mole fraction was lower than 0.0007. The LLE was reached using a Labnet Vortemp 1550 shaking incubator at (313.2 ± 0.1) K for 5 h with a shaking speed of 800 rpm. Then, vials were placed in a Labnet Accublock dry bath for 12 h at a controlled temperature of (313.2 ± 0.1) K to ensure a complete separation of layers.

The compositions of the heptane-rich phase (raffinate) were determined using an Agilent 7890A gas chromatograph. This GC is provided with a flame ionization detector (FID), and with a HP-5 Agilent column whose dimensions are 30 m × 0.320 mm × 0.25 μm. The temperature of the injection port was 523 K, the oven temperature was 348 K, and the FID temperature was set at 573 K, whereas the helium carrier flow was controlled to 2 mL·min^{-1}. Three samples from each raffinate were injected three times in the GC using an autosampler Agilent 7693, and the results shown here are the average compositions. To determine the composition, an area normalization method was performed employing toluene and heptane gravimetrically prepared mixtures. For this purpose, toluene was chosen as the standard and its response factor was fixed to 1.0, and the heptane response factor was determined from obtained areas for the standard mixtures. To check that the presence of IL in the heptane-rich phases can be considered negligible, samples from the raffinate were analyzed by a Bruker Avance 500 MHz NMR spectrometer. This fact was confirmed as none of the samples analyzed showed signals corresponding to ILs in the ^{1}H NMR spectra.

To analyze the composition of the IL-rich phase (extract), the technique of multiple headspace extraction (MHE) was used. The basis of this quantitative technique consists of consecutive extractions from the headspace of the same vial to determine the amount of volatile analytes as the sum of the peak areas obtained until full exhaustion. To promote the evaporation of volatiles, the vial containing the sample is heated in an oven before performing the extractions with a headspace sampler. In practice, the amount of analyte present in a sample is calculated from peak areas of a limited number of extractions based on mathematical relationships. A more detailed description of the MHE technique can be found elsewhere.[10]

This technique has the advantage that the IL is not introduced to the chromatographic column as a result of its nonvolatile behavior, and the amount of IL present in the sample can be easily calculated as the difference between the weight of the sample added to the vial and the weight of the volatile compounds determined by the MHE technique.

Triplicate samples from the IL-rich phase were analyzed using an Agilent 7890A Gas Chromatograph equipped with a Headspace Sampler Agilent 7697A. Approximately 100 μL of IL-rich phase was added to 20 mL tared vials using Pasteur micropipets, and the exact amount added was measured using the balance described above. Then, the tightly sealed vials were introduced to the oven of the headspace sampler at 393 K for 1 h and shaken at 100 rpm. From each vial were made five consecutive extractions. This number of extractions is enough to obtain correlation coefficients higher than 0.999 for the semilogarithmic relationship between peak areas and the number of extraction. Kolb and Ettre suggested in their work that the correlation coefficient should be at least 0.998 for an MHE successful measurement.[10] To determine the relationship between the sum of the peak areas and the amount of analyte present, external standards of pure toluene and heptane were analyzed by MHE under the same conditions. Other variables of the analytical method (injection port, oven, and FID temperatures, chromatographic column used, and flow carrier) have already been described in the analysis of the heptane-rich phase.

On the other hand, densities of the ILs at temperatures between 293.15 and 353.15 K were measured with an Anton Paar DMA−5000 oscillating U−tube density meter, whereas dynamic viscosities were determined at the same temperature range using an Anton Paar automated micro viscometer (AMVn) based on the falling ball principle. Densities and viscosities of sulfolane were measured with the same instruments over the temperature range from (303.15 to 353.15) K to be used as benchmarks. The reliability of the physical properties measurement methods was assessed in previous works by comparing experimental densities and viscosities with available data for several pure ILs in the literature.[7,11,12]

3. RESULTS AND DISCUSSION

3.1. Experimental LLE Data. Experimental compositions of the heptane-rich (raffinate) and IL-rich (extract) phases in equilibrium for the ternary systems {heptane (1) + toluene (2) + ([emim][DCA], [bmim][DCA], or [emim][TCM]) (3)} at 313.2 K and atmospheric pressure are listed in Table 2. The LLE data are also plotted in ternary diagrams in Figure 1. As discussed in the Experimental Section, the presence of IL in the raffinate was not detected by ^{1}H NMR. This is an important advantage of ILs as solvents compared to sulfolane, since this fact could reduce the number of purification steps in the aromatic extraction unit, reducing its operating costs.

The reliability of the LLE results gathered in this work has been confirmed by the Othmer−Tobias correlation[8]

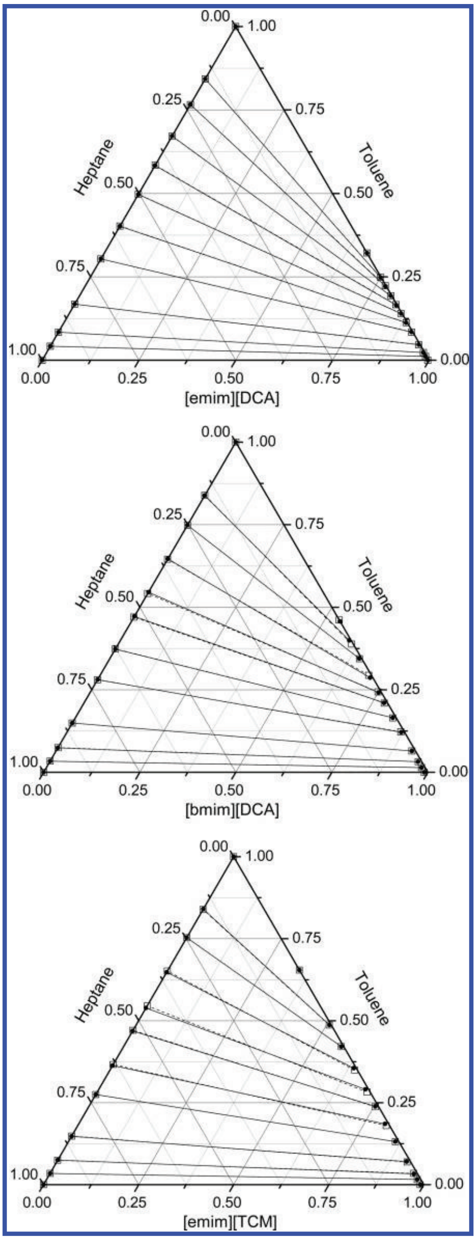


Figure 1. Experimental and calculated LLE for the ternary systems heptane (1) + toluene (2) + IL (3) at T = 313.2 K. Solid lines and full points represent experimental tie−lines, and dashed lines and empty squares indicate calculated data by the NRTL model.

$$\ln\left(\frac{1 - w_3^{\mathrm{II}}}{w_3^{\mathrm{II}}}\right) = a + b\ \ln\left(\frac{1 - w_1^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right) \tag{1}$$

where w_3^{II} indicates the IL mass fraction in the extract phase, w_1^{I} is the mass fraction of heptane in the raffinate phase, and a and

b are the fitted parameters of the eq 1. As can be observed in Figure 2, the plots for the three ternary systems studied have a high linearity, and this fact highlights the quality of the experimental LLE data. Also, the degree of consistency of the experimental results can be ascertained by the regression coefficients (R^2) for the Othmer–Tobias correlations close to 1, and the small values of the standard deviation (σ) presented in Table 3.

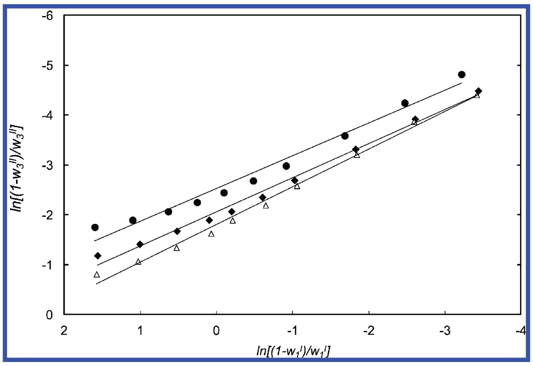


Figure 2. Othmer–Tobias plot for the ternary systems at T = 313.2 K and atmospheric pressure: ●, heptane (1) + toluene (2) + [emim][DCA] (3); ♦, heptane (1) + toluene (2) + [bmim][DCA] (3); Δ, heptane (1) + toluene (2) + [emim][TCM] (3). Solid lines represent the linear Othmer–Tobias fit.

Table 3. Constants of the Othmer–Tobias Correlation (a, b), Regression Coefficients (R^2), and Standard Deviations (σ)

a	b	R^2	σ
Heptane (1) + Toluene (2) + [emim][DCA] (3)			
−2.5286	0.6577	0.9758	0.2082
Heptane (1) + Toluene (2) + [bmim][DCA] (3)			
−2.0581	0.6848	0.9900	0.0961
Heptane (1) + Toluene (2) + [emim][TCM] (3)			
−1.8098	0.7536	0.9925	0.0878

3.2. Correlation of LLE Data.

The nonrandom two-liquid (NRTL) model[9] was used to fit the LLE experimental data, because this model has been successfully employed to correlate LLE of systems containing ILs.[13] The two binary interaction parameters $\Delta g_{ij}/R$ and $\Delta g_{ji}/R$ were determined using the ASPEN Plus simulator. The value of the third nonrandomness parameter (α_{ij}) in the NRTL model was fixed to 0.3, since this value is widely used in systems formed by organic solvents and ILs.[14–16]

The values of parameters of the NRTL model for ternary systems are given in Table 4 along with the root-mean-square deviation of the fits (σ_x) calculated using

$$\sigma_x = \left\{ \frac{\sum_i \sum_l \sum_m (x_{ilm}^{\text{exptl}} - x_{ilm}^{\text{calc}})^2}{6k} \right\}^{1/2} \tag{2}$$

where x is mole fraction and the subscripts i, l, and m denote the component, phase, and the tie lines, respectively. The parameter k is the number of tie lines in the LLE ternary diagram.

Table 4. Values of the NRTL Parameters Obtained from LLE Data by Regression at 313.2 K

component	NRTL parameters			
i–j	$(\Delta g_{ij}/R)$/K	$(\Delta g_{ji}/R)$/K	α_{ij}	σ_x
Heptane (1) + Toluene (2) + [emim][DCA] (3)				
1–2	459.28	−634.73	0.30	0.0009
1–3	2075.3	−987.06	0.30	
2–3	3558.4	−1652.1	0.30	
Heptane (1) + Toluene (2) + [bmim][DCA] (3)				
1–2	−165.56	234.10	0.30	0.0026
1–3	−189.73	294.08	0.30	
2–3	4179.2	−2079.7	0.30	
Heptane (1) + Toluene (2) + [emim][TCM] (3)				
1–2	−325.68	336.45	0.30	0.0024
1–3	−487.07	553.46	0.30	
2–3	4156.8	−2237.8	0.30	

Predicted tie lines by the NRTL model are plotted in Figure 1 together with the experimental data as dashed lines and empty squares. As seen, the experimental LLE data of the ternary systems {heptane (1) + toluene (2) + [emim][DCA], [bmim][DCA], or [emim][TCM] (3)} at 313.2 K were correctly correlated to the NRTL equation.

3.3. Distribution Ratios and Separation Factor.

To perform a comparative analysis between the extractive capacity and the selectivity of the ILs and those of sulfolane, the heptane and toluene distribution ratios (D_i) and the separation factor ($\alpha_{2,1}$) were calculated using the following equations from the experimental LLE data

$$D_1 = \frac{x_1^{\text{II}}}{x_1^{\text{I}}} \tag{3}$$

$$D_2 = \frac{x_2^{\text{II}}}{x_2^{\text{I}}} \tag{4}$$

$$\alpha_{2,1} = \frac{x_2^{\text{II}} x_1^{\text{I}}}{x_2^{\text{I}} x_1^{\text{II}}} = \frac{D_2}{D_1} \tag{5}$$

where x denotes the mole fraction of the compound, and subscripts 1 and 2 refer to heptane and toluene, respectively. The superscript I indicates the heptane-rich phase (raffinate) and the superscript II the IL-rich phase (extract).

Heptane distribution ratios (D_1) for the three systems studied are plotted in Figure 3 along with heptane distribution ratios of sulfolane[17] and together with the literature data for the [bmim][DCA] at 303.2 K.[18] As seen, the values of D_1 for the three ILs have been substantially lower than those of sulfolane, being the [emim][DCA] the IL with the lowest values of D_1. The experimental values of D_1 for the [bmim][DCA] at 313.2 K have been slightly higher than those reported by Hansmeier et al. at 303.2 K.[18] This small difference can be because the heptane distribution coefficient in ILs increases with increasing temperature.[19]

In Figure 4, experimental toluene distribution ratios (D_2) at 313.2 K are represented. Among the ILs studied in this work, only the [emim][TCM] has shown D_2 higher than the sulfolane values over the whole range of compositions of toluene in raffinate. By contrast, the values of D_2 for the [emim][DCA] have been lower than those of sulfolane.

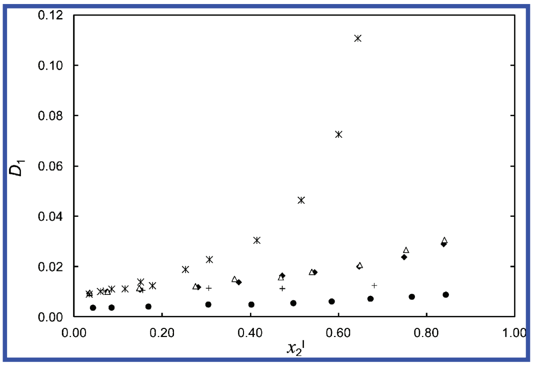


Figure 3. Heptane distribution ratios for the ternary systems at T = 313.2 K: ●, heptane (1) + toluene (2) + [emim][DCA] (3); ♦, heptane (1) + toluene (2) + [bmim][DCA] (3); Δ, heptane (1) + toluene (2) + [emim][TCM] (3); *, heptane (1) + toluene (2) + sulfolane (3) (from ref 17); +, heptane (1) + toluene (2) + [bmim][DCA] (3) at T = 303.2 K (from ref 18).

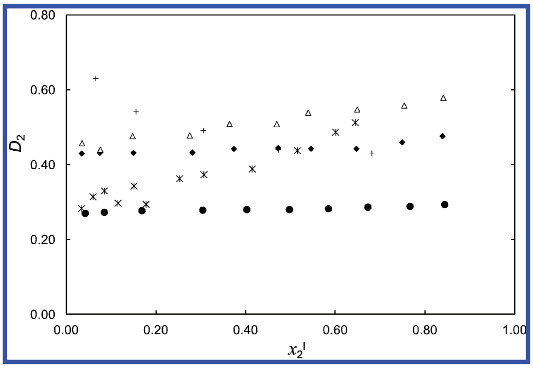


Figure 4. Toluene distribution ratios for the ternary systems at T = 313.2 K: ●, heptane (1) + toluene (2) + [emim][DCA] (3); ♦, heptane (1) + toluene (2) + [bmim][DCA] (3); Δ, heptane (1) + toluene (2) + [emim][TCM] (3); *, heptane (1) + toluene (2) + sulfolane (3) (from ref 17); +, heptane (1) + toluene (2) + [bmim][DCA] (3) at T = 303.2 K (from ref 18).

Therefore, the substitution of the [TCM] anion for the [DCA] anion causes a significant decrease in solubility of toluene in the IL. On the other hand, the [bmim][DCA] has shown D_2 higher than those of sulfolane for toluene mole fractions in the hydrocarbon-rich phase lower than 0.50. Hence, the replacement of the [emim] cation by the [bmim] cation increases the amount of toluene dissolved in the IL. This trend is the same as that observed in [xmim][Tf_2N],[4] [xdmim][Tf_2N],[20] and [xmim][TfO] ILs,[21] and it is agreed with predictions using COSMO-RS.[22,23] Lastly, our values of D_2 at 313.2 K for the [bmim][DCA] have been somewhat lower than the literature values at 303.2 K.[18] This fact could be because toluene distribution ratios for ILs decrease as temperature increases.[19,23]

The experimental values of the separation factor ($\alpha_{2,1}$) at 313.2 K for [emim][DCA], [bmim][DCA], and [emim][TCM] ILs are plotted in Figure 5. As can be observed, the three ILs have shown $\alpha_{2,1}$ values substantially higher than those of sulfolane over the whole range of compositions. This fact proves that the extracted toluene using these ILs has a higher purity than that using sulfolane, being the [emim][DCA] the most selective IL studied here. A higher purity of toluene obtained could simplify the further purifications of aromatic hydrocarbons extracted.[5]

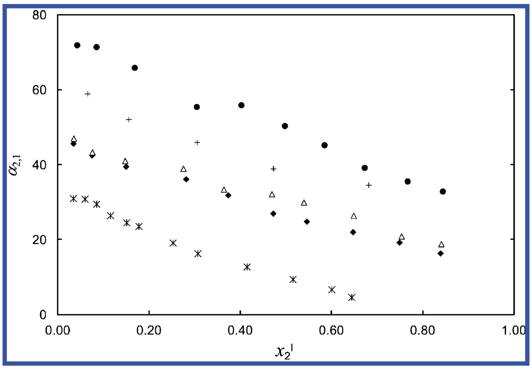


Figure 5. Separation factors for the ternary systems at T = 313.2 K: ●, heptane (1) + toluene (2) + [emim][DCA] (3); ♦, heptane (1) + toluene (2) + [bmim][DCA] (3); Δ, heptane (1) + toluene (2) + [emim][TCM] (3); *, heptane (1) + toluene (2) + sulfolane (3) (from ref 17); +, heptane (1) + toluene (2) + [bmim][DCA] (3) at T = 303.2 K (from ref 18).

3.4. Physical Properties. To complete the study on the potential use of the ILs studied here in industrial scale, we have performed a brief analysis of their physical properties. Densities and dynamic viscosities of [emim][DCA], [bmim][DCA], and [emim][TCM] ILs at the temperature range of (293.15 to 353.15) K are shown in Table 5. Both physical properties of sulfolane are also listed in Table 5, but only at temperatures between 303.15 and 353.15 K because the melting point of this compound is 300 K.

As seen, densities of the ILs are substantially lower than that of sulfolane. However, the density of a solvent is not a key property in extraction, only its density must be sufficiently different from the density of the feed to have a correct hydrodynamic behavior in the extraction column.[5,24] Taking into account that the density at 313.15 K of heptane is 0.659 g cm^{-3} and of toluene is 0.850 g cm^{-3}, there is enough difference between the densities of these hydrocarbons and those of ILs studied in this work.

On the other hand, [emim][DCA] and [emim][TCM] have shown dynamic viscosities similar that those of sulfolane, whereas the viscosity of [bmim][DCA] was almost double that of the viscosity of sulfolane. This fact could be an important drawback in the application of the [bmim][DCA] at industrial scale.

In addition to comparing with sulfolane, it is important to note that the viscosity at 313.15 K of [emim][DCA] (10.2 mPa s) and of [emim][TCM] (9.8 mPa s) ILs are quite lower than that of other promising pure ILs in aromatic extraction at the same temperature: [4bmpy][BF_4] (92.4 mPa s),[19] [emim][$EtSO_4$] (50.1 mPa s),[25,26] [3bmpy][TCM] (23.3 mPa s),[19] and [3bmpy][DCA] (21.3 mPa s).[19] Also, the viscosities of both ILs are much lower than that of the binary {[bpy][BF_4] + [bpy][Tf_2N]} IL mixture with a [bpy][BF_4] mole fraction of 0.7 (53.1 mPa s).[6,7] Therefore, the pumping and mixing costs of a process using [emim][DCA] or [emim][TCM] ILs as aromatic extraction solvent would be similar to the costs of the

Table 5. Densities (ρ) and Dynamic Viscosities (η) of [emim][DCA], [bmim][DCA], and [emim][TCM] ILs and of Sulfolane as a Function of Temperature[a]

	ρ/g cm^{-3}			
T/K	[emim][DCA]	[bmim][DCA]	[emim][TCM]	sulfolane
293.15	1.10464	1.06396	1.08517	
298.15	1.10132	1.06076	1.08162	
303.15	1.09800	1.05757	1.07808	1.26202
313.15	1.09144	1.05112	1.07106	1.25323
323.15	1.08494	1.04494	1.06411	1.24445
333.15	1.07852	1.03873	1.05722	1.23567
343.15	1.07215	1.03257	1.05041	1.22689
353.15	1.06584	1.02646	1.04365	1.21810
	η/mPa s			
	[emim][DCA]	[bmim][DCA]	[emim][TCM]	sulfolane
293.15	17.54	33.15	17.72	
298.15	15.08	27.34	15.02	
303.15	13.11	22.92	12.88	10.84
313.15	10.17	16.72	9.80	8.05
323.15	8.13	12.74	7.73	6.38
333.15	6.66	10.04	5.93	5.15
343.15	5.58	8.12	4.91	4.24
353.15	4.75	6.72	4.15	3.54

[a] Standard uncertainties u are $u(\rho) = 0.00008$ g cm^{-3}, $u(\eta) = 0.8\%$.

sulfolane process, and much lower than those using other IL-based solvents.

4. CONCLUSIONS

The aim of this paper was to study the liquid−liquid extraction of toluene from heptane using [emim][DCA], [bmim][DCA], and [emim][TCM] ILs as solvents at 313.2 K. The reliability of the LLE data was assessed by using the Othmer−Tobias correlation, and the experimental results were successfully fitted to the NRTL model.

Among the ILs studied in this work, [emim][TCM] was the one that showed the highest potential to be considered as an alternative solvent for aromatics extraction. This IL has shown separation factors and molar-based toluene distribution ratios higher than the sulfolane values. In addition, the [emim][TCM] has proper densities and viscosities to be used in an industrial process.

Separation factors of [emim][DCA] were double than that of sulfolane, but it showed lower toluene distribution ratios. Hence, this IL could be applied in a highly selective process of extraction of aromatic hydrocarbons, because it also has exhibited adequate physical properties. Finally, although the extractive properties of [bmim][DCA] have been similar to those of [emim][TCM], its higher dynamic viscosity represents a significant drawback.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +34 91 394 51 19. Fax: +34 91 394 42 43. E-mail: jgarcia@quim.ucm.es.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to the Ministerio de Economía y Competitividad (MINECO) of Spain and the Comunidad Autónoma de Madrid for financial support of Projects CTQ2011-23533 and S2009/PPQ-1545, respectively. M.L. thanks Ministerio de Educación, Cultura y Deporte for awarding him an FPU grant (Reference AP-2010-0318), and P.N. also thanks MINECO for awarding him an FPI grant (Reference BES-2012-052312).

■ REFERENCES

(1) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Selection of Ionic Liquids for the Extraction of Aromatic Hydrocarbons from Aromatic/aliphatic Mixtures. *Fuel Process. Technol.* **2005**, *87*, 59.

(2) Anjan, S. T. Ionic Liquid for Aromatic Extraction: Are They Ready? *Chem. Eng. Prog.* **2006**, *102*, 30.

(3) Meindersma, G. W.; Hansmeier, A. R.; de Haan, A. B. Ionic Liquids for Aromatics Extraction. Present Status and Future Outlook. *Ind. Eng. Chem. Res.* **2010**, *49*, 7530.

(4) García, S.; Larriba, M.; García, J.; Torrecilla, J. S.; Rodríguez, F. Liquid−Liquid Extraction of Toluene from Heptane Using 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids. *J. Chem. Eng. Data* **2011**, *56*, 113.

(5) Meindersma, G. W.; de Haan, A. B. Cyano-containing Ionic Liquids for the Extraction of Aromatic Hydrocarbons from an Aromatic/aliphatic Mixture. *Sci. Chin. Chem.* **2012**, *55*, 1488.

(6) García, S.; Larriba, M.; García, J.; Torrecilla, J. S.; Rodríguez, F. Liquid-liquid Extraction of Toluene from n-Heptane Using Binary Mixtures of *N*-Butylpyridium Tetrafluoroborate and N-Butylpyridinium Bis(trifluoromethylsulfonyl)imide Ionic Liquids. *Chem. Eng. J.* **2012**, *180*, 210.

(7) Larriba, M.; García, S.; Navarro, P.; García, J.; Rodríguez, F. Physical Properties of *N*-butylpyridinium Tetrafluoroborate and *N*−butylpyridinium Bis(trifluoromethylsulfonyl)imide Binary Ionic Liquid Mixtures. *J. Chem. Eng. Data* **2012**, *57*, 1318.

(8) Othmer, D. F.; Tobias, P. E. Toluene and Acetaldehyde Systems, Tie Line Correlation, Partial Pressures of Ternary Liquid Systems and the Prediction of Tie Lines. *Ind. Eng. Chem.* **1942**, *34*, 693.

(9) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135.

(10) Kolb, B.; Ettre, L. S. *Static Headspace-Gas Chromatography: Theory and Practice*; Wiley-VCH: New York, 1997.

(11) Larriba, M.; García, S.; García, J.; Torrecilla, J. S.; Rodríguez, F. Thermophysical Properties of 1-Ethyl-3-methylimidazolium 1,1,2,2-Tetrafluoroethanesulfonate and 1-Ethyl-3-methylimidazolium Ethylsulfate Ionic Liquids as a Function of Temperature. *J. Chem. Eng. Data* **2011**, *56*, 3589.

(12) Navarro, P.; Larriba, M.; García, S.; García, J.; Rodríguez, F. Physical Properties of Binary and Ternary Mixtures of 2-Propanol, Water, and 1-Butyl-3-methylimidazolium Tetrafluoroborate Ionic Liquid. *J. Chem. Eng. Data* **2012**, *57*, 1165.

(13) Simoni, L. D.; Lin, Y.; Brennecke, J. F.; Stadtherr, M. A. Modeling Liquid−Liquid Equilibrium of Ionic Liquid Systems with NRTL, Electrolyte−NRTL, and UNIQUAC. *Ind. Eng. Chem. Res.* **2008**, *47*, 256.

(14) Pereiro, A. B.; Rodriguez, A. Thermodynamic Properties of Ionic Liquids in Organic Solvents from (293.15 to 303.15) K. *J. Chem. Eng. Data* **2007**, *52*, 600.

(15) Marciniak, A.; Krolikowski, M. Ternary (Liquid + liquid) Equilibria of {Trifluorotris(perfluoroethyl)phosphate based Ionic Liquids + Thiophene + Heptane}. *J. Chem. Thermodyn.* **2012**, *49*, 154.

(16) Gutiérrez, J. P.; Meindersma, G. W.; de Haan, A. B. COSMO-RS-Based Ionic-Liquid Selection for Extractive Distillation Processes. *Ind. Eng. Chem. Res.* **2012**, *51*, 11518.

(17) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Ternary Liquid−Liquid Equilibria for Mixtures of Toluene + n−Heptane + an Ionic Liquid. *Fluid Phase Equilib.* **2006**, *247*, 158.

(18) Hansmeier, A. R.; Minoves Ruiz, M.; Meindersma, G. W.; de Haan, A. B. Liquid-Liquid Equilibria for the Three Ternary Systems (3-Methyl-*N*-butylpyridinium Dicyanamide + Toluene + Heptane), (1-Butyl-3-methylimidazolium Dicyanamide + Toluene + Heptane)

and (1-Butyl-3-methylimidazolium Thiocyanate + Toluene + Heptane) at T = (313.15 and 348.15) K and p = 0.1 MPa. *J. Chem. Eng. Data* **2010**, *55*, 708.

(19) Meindersma, G. W.; Simons, B. T. J.; de Haan, A. B. Physical Properties of 3-Methyl-N-butylpyridinium Tetracyanoborate and 1-Butyl-1-methylpyrrolidinium Tetracyanoborate and Ternary LLE Data of [3-mebupy]B(CN)4 with an Aromatic and an Aliphatic Hydrocarbon at T = 303.2 and 328.2 K and p = 0.1 MPa. *J. Chem. Thermodyn.* **2011**, *43*, 1628.

(20) García, S.; Larriba, M.; García, J.; Torrecilla, J. S.; Rodríguez, F. 1−Alkyl− 2,3−dimethylimidazolium Bis(trifluoromethylsulfonyl)-imide Ionic Liquids for the Liquid−Liquid Extraction of Toluene from Heptane. *J. Chem. Eng. Data* **2011**, *56*, 3468.

(21) Corderí, S.; González, E. J.; Calvar, N.; Domínguez, A. Application of [HMim][NTf_2], [HMim][TfO] and [BMim][TfO] Ionic Liquids on the Extraction of Toluene from Alkanes: Effect of the Anion and the Alkyl Chain Length of the Cation on the LLE. *J. Chem. Thermodyn.* **2012**, *53*, 60.

(22) Ferreira, A. R.; Freire, M. G.; Ribeiro, J. C.; Lopes, F. M; Crespo, J. G.; Coutinho, J. A. P. An Overview of the Liquid−Liquid Equilibria of (Ionic Liquid + Hydrocarbon) Binary Systems and Their Modeling by the Conductor−like Screening Model for Real Solvents. *Ind. Eng. Chem. Res.* **2011**, *50*, 5279.

(23) Ferreira, A. R.; Freire, M. G.; Ribeiro, J. C.; Lopes, F. M.; Crespo, J. G.; Coutinho, J. A. P. Overview of the Liquid−Liquid Equilibria of Ternary Systems Composed of Ionic Liquid and Aromatic and Aliphatic Hydrocarbons, and Their Modeling by COSMO-RS. *Ind. Eng. Chem. Res.* **2012**, *51*, 3483.

(24) Onink, F.; Drumm, C.; Meindersma, G. W.; Bart, H. J.; de Haan, A. B. Hydrodynamic Behavior Analysis of a Rotating Disc Contactor for Aromatics Extraction with 4-Methyl-butyl-pyridinium·BF4 by CFD. *Chem. Eng. J.* **2010**, *160*, 511.

(25) González, E. J.; Calvar, N.; Domínguez, I.; Domínguez, A. Extraction of toluene from aliphatic compounds using an ionic liquid as solvent: Influence of the alkane on the (liquid + liquid) equilibrium. *J. Chem. Thermodyn.* **2011**, *43*, 562.

(26) González, E. J.; González, B.; Calvar, N.; Domínguez, A. Physical Properties of Binary Mixtures of the Ionic Liquid 1-Ethyl-3-methylimidazolium Ethyl Sulfate with Several Alcohols at T = (298.15, 313.15, and 328.15) K and Atmospheric Pressure. *J. Chem. Eng. Data* **2007**, *52*, 1641.

Journal of Chemical Thermodynamics

Factor de impacto (2013): 2,42

Publicación 2:

Selective Extraction of Toluene from *n*-Heptane using [emim][SCN] and [bmim][SCN] Ionic Liquids as Solvents

Marcos Larriba, Pablo Navarro, Julián García, Francisco Rodríguez

Journal of Chemical Thermodynamics, 2014, 79, 266-271

J. Chem. Thermodynamics 79 (2014) 266–271

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Selective extraction of toluene from *n*-heptane using [emim][SCN] and [bmim][SCN] ionic liquids as solvents

Marcos Larriba, Pablo Navarro, Julián García *, Francisco Rodríguez

Department of Chemical Engineering, Complutense University of Madrid, E-28040 Madrid, Spain

ARTICLE INFO

Article history:
Available online 16 November 2013

Keywords:
Aromatic/aliphatic separation
Liquid–liquid extraction
Toluene
n-Heptane
Ionic liquids
Thiocyanate

ABSTRACT

Among the ionic liquids (ILs) studied so far in the liquid–liquid extraction of aromatic hydrocarbons, only a few of them have shown aromatic distribution ratios and aromatic/aliphatic selectivities considerably higher than those of conventional organic solvents, such as sulfolane. Moreover, these ILs had high dynamic viscosities that could limit their application at industrial scale. In this work, we have studied the performance of 1-ethyl-3-methylimidazolium thiocyanate ([emim][SCN]) and 1-butyl-3-methylimidazolium thiocyanate ([bmim][SCN]) ILs in the liquid–liquid extraction of toluene from *n*-heptane at 313.2 K. Densities, dynamic viscosities, and surface tensions of the ILs were also measured to evaluate their suitability as aromatic extraction solvents. In spite of the high selectivities and toluene distribution ratios of [bmim][SCN], its high dynamic viscosity could imply an important drawback. By contrast, the [emim][SCN] shown toluene/*n*-heptane selectivities three times higher of the sulfolane values and also substantially higher than those of other promising ILs. Futhermore, densities, viscosities, and surface tensions of [emim][SCN] were also appropriate to consider this IL as an alternative to organic solvents.

1. Introduction

Ionic liquids (ILs) have been revealed as potential solvents to replace organic solvents in the liquid–liquid extraction of aromatic hydrocarbons from aliphatic hydrocarbons, according to numerous studies [1,2]. Conventional processes, such as sulfolane Shell-UOP, have the disadvantage of a high energy consumption in solvent recovery due to the high boiling point of the organic solvents used. The most notable characteristic of ILs is their practically negligible vapor pressure [3]. As a result of their exceptional nonvolatile nature, ILs would simplify the aromatic extraction unit, since the separation of hydrocarbons extracted from the IL-based solvent could be performed by a simple flash distillation or by stripping [2,4].

Among ILs applied in the liquid–liquid extraction of aromatics from aliphatics, a limited number of them had simultaneously values of aromatic distribution ratios and aromatic/aliphatic selectivities higher than those of sulfolane [2]. Because of this, in our recent works we have proposed the use of binary mixtures of ILs formed by an IL with high aromatic/aliphatic selectivities mixed with other IL with high aromatic distribution ratios. These binary IL mixtures shown extractive and physical properties intermediate between the values of pure ILs [5–8].

However, highly selective ILs studied so far have presented high dynamic viscosities, and this property limits their potential use at industrial scale. For instance, ILs such as 1-ethyl-3-methylimidazolium ethylsulfate ([emim][$EtSO_4$]) [9,10], 1-butyl-4-methylpyridinium tetrafluoroborate ([4bmpy][BF_4]) [11,12], or butylpyridinium tetrafluoroborate ([bpy][BF_4]) [7,13] had selectivities considerably higher than the sulfolane values, but viscosities several times higher than that of sulfolane.

For that reason, the aim of this work was to find an IL with high values of toluene/*n*-heptane selectivity and adequate physical properties. We have selected the 1-ethyl-3-methylimidazolium thiocyanate ([emim][SCN]) and the 1-butyl-3-methylimidazolium thiocyanate ([bmim][SCN]), since the 1-alkyl-3-methylimidazolium cations have a high aromatic character and the SCN-based ILs have low values of viscosity [14]. In this paper, we have studied the liquid–liquid equilibrium (LLE) of the {*n*-heptane + toluene + [emim][SCN]} and {*n*-heptane + toluene + [bmim][SCN]} ternary systems at 313.2 K. From LLE data, we have calculated toluene and *n*-heptane distribution ratios and toluene/*n*-heptane selectivity. Using these results, a comparative analysis between extractive properties of both ILs and those of sulfolane was performed. Likewise, densities, dynamic viscosities, and surface tensions of [emim][SCN] and [bmim][SCN] ILs were measured as a function of temperature, and their physical properties were compared with the values of sulfolane and other highly selective ILs.

2. Experimental

2.1. Chemicals

[emim][SCN] and [bmim][SCN] ILs were supplied by Iolitec GmbH with water content in mass fraction less than $2 \cdot 10^{-3}$,

---

* Corresponding author. Tel.: +34 91 394 51 19; fax: +34 91 394 42 43.
E-mail address: jgarcia@quim.ucm.es (J. García).

0021-9614/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jct.2013.11.005

halides mass fraction less than $2 \cdot 10^{-2}$, and IL purities higher than 0.98. Toluene and *n*-heptane, over molecular sieves to remove dissolved water, were purchased from Sigma–Aldrich. The specifications of the chemicals employed in this work are summarized in table 1. All chemicals were used as received, and they were stored in a desiccator in their original tightly closed bottles to avoid water hydration. Due to the same reason, ILs were handled in a glove box under an atmosphere of dry nitrogen.

2.2. Experimental procedure and analysis

LLE experiments were performed in 8 mL vials with screw caps. Hydrocarbons and ILs were gravimetrically added to vials using a Mettler Toledo XS 205 balance with a precision of $\pm 1 \cdot 10^{-5}$ g. Filled vials were shaken in a Labnet Vortemp 1550 shaking incubator for 5 h at $T = (313.2 \pm 0.1)$ K and 800 rpm to reach the LLE. Then, vials were located in a Labnet Accublock dry bath at $T = (313.2 \pm 0.1)$ K for 12 h to achieve the separation of layers in equilibrium. Shaking and settling times were optimized to guarantee that the LLE was reached and the complete separation of layers was achieved.

An Agilent 7890A gas chromatograph (GC) provided with a liquid autosampler Agilent 7693 and a flame ionization detector (FID) was used to determine the composition of the raffinate (hydrocarbon-rich) phases. Samples from the raffinate phases were analyzed in triplicate, being the results gathered in this paper the average compositions. A normalization method was used, employing mixtures of toluene and *n*-heptane gravimetrically prepared. Toluene was selected as the standard and its response factor was set to 1.0, whereas the *n*-heptane response factor was obtained from GC peak areas of the standard mixtures. A more detailed description, including the variables of the analytical method, can be found elsewhere [15]. To verify that ILs were not dissolved in the raffinate phases, samples from these phases were analyzed in a Bruker Avance 500 MHz NMR spectrometer. The presence of ILs in raffinate was considered as negligible, since ^{1}H NMR spectra did not shown signals corresponding to [emim][SCN] and [bmim][SCN] ILs. To confirm the total absence of ILs in raffinate, an analytical technique with a lower detection limit than NMR spectroscopy could be used. The absence of IL in the hydrocarbon-rich phase is one of the main advantages of ILs compared to sulfolane as aromatic extraction solvents, because this fact would simplify the purification of this phase in an industrial process [15,16].

Samples from the extract (IL-rich) phases were analyzed by a multiple headspace extraction (MHE) method in an Agilent 7890A GC provided with a Headspace Sampler Agilent 7697A. Approximately 100 μL of IL-rich phase were added to closed vials of 20 mL, heated at $T = 393$ K, and agitated at 100 rpm for 1 h to facilitate the evaporation of the dissolved hydrocarbons from the IL. The amounts of toluene and *n*-heptane in the sample were calculated from the sum of peak areas of five consecutive extractions from the same vial according to mathematical relationships proposed by Kolb and Ettre [17]. Correlation coefficients higher than 0.999 for the semi-logarithmic relationship between peak areas and the number of extraction were obtained, complying with the recommendations of Kolb and Ettre that suggested correlation coefficients higher than 0.998 for an MHE successful quantitative determination. As a result of its non-volatile behavior, the IL amount was determined as the difference between the weight of the extract phase sample added to the vial and the mass of hydrocarbons in the sample determined by MHE. Samples were taken in triplicate and the average compositions are reported here. A detailed description of the MHE technique used can be found elsewhere [15].

Finally, a physical characterization of the ILs was performed by measuring their densities, dynamic viscosities, and surface tensions as a function of temperature. Densities of [emim][SCN] and [bmim][SCN] ILs were determined in an Anton Paar DMA-5000 oscillating U-tube density meter over the temperature range from 293.15 K to 353.15 K. An Anton Paar Automated Micro Viscometer (AMVn) based on the falling ball principle was used to measure dynamic viscosities at the same temperature range. Surface tensions were determined in a Dataphysics OCA 15 plus pendant drop tensiometer at temperatures between 298.15 K and 323.15 K controlled by a Julabo F12-EC bath. The shape of the IL pendant drop was determined by a charge-coupled device (CCD) camera and the IL surface tension was calculated by the software SCA 20 OCA using the Young–Laplace equation. The reliability of measurement methods was checked in our previous papers by comparative analysis between experimental densities, dynamic viscosities, and surface tensions with published data for different pure ILs [7,8,10,18].

TABLE 1
Suppliers and purities of chemicals.

Chemical	Supplier	Mass fraction purity	Analysis method
[emim][SCN][a]	Iolitec GmbH	0.98	NMR[c] and IC[d]
[bmim][SCN][b]	Iolitec GmbH	0.98	NMR[c] and IC[d]
Toluene	Sigma–Aldrich	0.995	GC[e]
n-Heptane	Sigma–Aldrich	0.997	GC[e]

[a] [emim][SCN] = 1-ethyl-3-methylimidazolium thiocyanate.
[b] [bmim][SCN] = 1-butyl-3-methylimidazolium thiocyanate.
[c] Nuclear Magnetic Resonance.
[d] Ion Chromatography.
[e] Gas Chromatography.

3. Results and discussion

3.1. Experimental LLE data

Experimental LLE for the ternary systems {*n*-heptane (1) + toluene (2) + [emim][SCN] (3)} and {*n*-heptane (1) + toluene (2) + [bmim][SCN] (3)} at $T = 313.2$ K and atmospheric pressure are summarized in table 2. Compositions of the raffinate and extract phases in LLE are also graphically shown in figure 1 as ternary diagrams.

The Othmer–Tobias correlation is usually employed to check the reliability of LLE data [19]:

$$\ln\left(\frac{1 - w_3^{\mathrm{II}}}{w_3^{\mathrm{II}}}\right) = a + b\ln\left(\frac{1 - w_1^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right), \tag{1}$$

where w_3^{II} is the IL mass fraction in the IL-rich phase, w_1^{I} denotes the *n*-heptane mass fraction in the hydrocarbon-rich phase, and *a* and *b* are fitting parameters. In table 3, constants of Othmer–Tobias correlation, regression coefficients (R^2), and standard deviations (σ) of the fit of experimental LLE data are listed. As observed, the reliability of the LLE gathered in this work can be confirmed by the high values of regression coefficients ($R^2 > 0.97$) together with low standard deviations.

3.2. Correlation of LLE using NRTL model

Experimental LLE data of systems containing ILs are frequently fitted to the nonrandom two-liquid (NRTL) model [20,21]. From LLE compositions, the binary interaction parameters $\Delta g_{ij}/R$ and $\Delta g_{ji}/R$ were calculated using ASPEN Plus process simulator software. The value of the nonrandomness parameter (α_{ij}) of the NRTL model was set to 0.30, as this value is widely employed in the correlation of LLE data of systems composed of organic compounds and ILs [15,22–25]. Correlation parameters of the NRTL model for the {*n*-heptane + toluene + [emim][SCN]} and {*n*-heptane + tolu-

TABLE 2
Experimental LLE data on mole fraction (x_i), distribution ratios (D_i), and toluene/n-heptane selectivities ($\alpha_{2,1}$) for the ternary systems {n-heptane (1) + toluene (2) + IL (3)} at T = 313.2 K and atmospheric pressure.[a]

Feed (global composition)		Hydrocarbon-rich phase (raffinate phase)		IL-rich phase (extract phase)		D_1	D_2	$\alpha_{2,1}$
x_1	x_2	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}			
				n-Heptane (1) + toluene (2) + [emim][SCN] (3)				
0.5052	0.0000	1.0000	0.0000	0.0017	0.0000	0.0017		
0.5012	0.0262	0.9541	0.0459	0.0018	0.0088	0.0019	0.192	101.6
0.4718	0.0570	0.9108	0.0892	0.0018	0.0173	0.0020	0.194	98.1
0.4464	0.1175	0.8162	0.1838	0.0018	0.0365	0.0022	0.199	90.0
0.4097	0.1893	0.7154	0.2846	0.0016	0.0563	0.0022	0.198	88.5
0.3525	0.3018	0.5667	0.4333	0.0015	0.0850	0.0026	0.196	74.1
0.3161	0.3730	0.4772	0.5228	0.0015	0.1076	0.0031	0.206	65.5
0.2858	0.4325	0.4094	0.5906	0.0013	0.1216	0.0032	0.206	64.8
0.2297	0.5451	0.3079	0.6921	0.0011	0.1448	0.0036	0.209	58.6
0.1798	0.6447	0.2261	0.7739	0.0010	0.1692	0.0044	0.219	49.4
0.1262	0.7500	0.1447	0.8553	0.0007	0.1922	0.0048	0.225	46.5
0.0000	0.8523	0.0000	1.0000	0.0000	0.2056		0.206	
				n-Heptane (1) + toluene (2) + [bmim][SCN] (3)				
0.5035	0.0000	1.0000	0.0000	0.0062	0.0000	0.0062		
0.4901	0.0287	0.9607	0.0393	0.0063	0.0137	0.0066	0.349	53.2
0.4765	0.0576	0.9211	0.0789	0.0061	0.0265	0.0066	0.336	50.7
0.4465	0.1133	0.8430	0.1570	0.0059	0.0533	0.0070	0.339	48.5
0.4004	0.2056	0.7171	0.2829	0.0064	0.0985	0.0089	0.348	39.0
0.3551	0.2968	0.5936	0.4064	0.0063	0.1409	0.0106	0.347	32.7
0.3120	0.3826	0.4945	0.5055	0.0060	0.1822	0.0121	0.360	29.7
0.2805	0.4430	0.4233	0.5767	0.0057	0.2119	0.0135	0.367	27.3
0.2477	0.5073	0.3668	0.6332	0.0054	0.2346	0.0147	0.370	25.2
0.1898	0.6254	0.2496	0.7504	0.0046	0.2842	0.0184	0.379	20.6
0.1272	0.7473	0.1558	0.8442	0.0035	0.3383	0.0225	0.401	17.8
0.0000	0.8529	0.0000	1.0000	0.0000	0.3804		0.380	

[a] Standard uncertainties (u) are: u(T) = 0.1 K, $u(x_i)$ = 0.0007, $u(x_i^{I})$ = 0.0008; $u(x_1^{II})$ = 0.0009; $u(x_2^{II})$ = 0.0020.

ene + [bmim][SCN]} ternary systems at T = 313.2 K are listed in Table 4 together with the root mean square deviation (*rmsd*) of the correlations calculated as follows:

$$rmsd = \left\{ \frac{\sum_i \sum_l \sum_m \left(x_{ilm}^{exptl} - x_{ilm}^{calc} \right)^2}{6k} \right\}^{1/2}, \tag{2}$$

where the subscripts i, l, and m indicate the component, phase, and tie line, respectively, x denotes mole fraction, whereas k indicates the number of tie lines in the LLE ternary diagram.

Predicted LLE by NRTL model are plotted in figure 1 as empty squares and dashed lines along with experimental tie lines. As can be observed, LLE data of {n-heptane + toluene + [emim][SCN]} and {n-heptane + toluene + [bmim][SCN]} systems were satisfactorily correlated to the NRTL model.

3.3. Distribution ratios and toluene/n-heptane selectivities

To evaluate the behavior of [emim][SCN] and [bmim][SCN] ILs as toluene extraction solvents, we have calculated n-heptane and toluene distribution ratios (D_i) and toluene/n-heptane selectivity ($\alpha_{2,1}$) from the experimental compositions of the raffinate and extract phases in LLE using:

$$D_1 = \frac{x_1^{II}}{x_1^{I}}, \tag{3}$$

$$D_2 = \frac{x_2^{II}}{x_2^{I}}, \tag{4}$$

$$\alpha_{2,1} = \frac{x_2^{II} x_1^{I}}{x_2^{I} x_1^{II}} = \frac{D_2}{D_1}, \tag{5}$$

where x is the mole fraction of the hydrocarbons and subscripts 1 and 2 refer to n-heptane and toluene, respectively. The superscript I denotes the raffinate (hydrocarbon-rich) phase, whereas the superscript II refers to the extract (IL-rich) phase.

In figure 2, experimental n-heptane distribution ratios (D_1) at 313.2 K for [emim][SCN] and [bmim][SCN] are graphically shown along with the n-heptane distribution ratios of sulfolane at the same temperature [12], and literature data for [bmim][SCN] at T = 303.2 K [26].

As can be observed, the values of D_1 employing both SCN-based ILs have been much lower than the sulfolane values. This result demonstrates the low solubility of n-heptane in [emim][SCN] and [bmim][SCN] ILs, and it will cause high values of toluene/n-heptane selectivities. n-Heptane distribution ratios of [emim][SCN] have been substantially lower than those of [bmim][SCN] because an increase in the length of the alkyl chain in the cation causes an increase in hydrocarbon solubility [27]. Finally, experimental D_1 of [bmim][SCN] at T = 313.2 K have been very close to the values reported by Hansmeier *et al.* at T = 303.2 K [26]. This fact shows the reliability of LLE data for the {n-heptane + toluene + [emim][SCN]} and {n-heptane + toluene + [bmim][SCN]} systems presented in this paper, and the slight influence of temperature on hydrocarbon solubility in ILs [28,29].

Experimental toluene distribution ratios (D_2) using [emim][SCN] and [bmim][SCN] at T = 313.2 K are plotted in figure 3 together with literature data of sulfolane [12] and [bmim][SCN] at T = 303.2 K [26]. As seen, D_2 employing both ILs have been lower than those of sulfolane, except for the [bmim][SCN] at mole fractions of toluene in the raffinate phase lower than 0.1. As explained in the introduction section, this important drawback could be solved by mixing [emim][SCN] or [bmim][SCN] ILs with other IL with high values of toluene distribution ratios, such as the 1-ethyl-3-methylimidazolium tricyanomethanide ([emim][TCM]) [15], the 1-butyl-3-methylimidazolium dicyanamide ([bmim][DCA]), [15] or the 4-methyl-N-butylpyridinium bis(trifluoromethylsulfonyl)imide ([4bmpy][Tf$_2$N]) [30] to obtain a binary IL mixture with intermediate values of D_2. However, to select the most

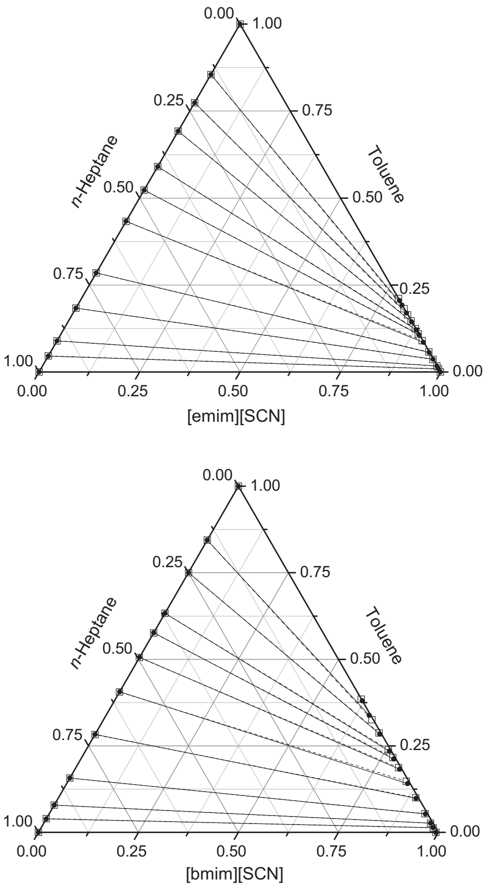


FIGURE 1. Experimental and calculated LLE for the ternary systems {*n*-heptane (1) + toluene (2) + IL (3)} at $T = 313.2$ K. Solid lines and full points represent experimental tie-lines, and dashed lines and empty squares indicate calculated data by the NRTL model.

TABLE 3
Constants of the Othmer–Tobias Correlation (*a*,*b*), Regression Coefficients (R^2), and Standard Deviations (σ).

a	*b*	R^2	σ
	n-Heptane (1) + toluene (2) + [emim][SCN] (3)		
−2.8708	0.6588	0.9747	0.2179
	n-Heptane (1) + toluene (2) + [bmim][SCN] (3)		
−2.2949	0.6866	0.9877	0.1155

appropriate binary mixture of ILs their physical properties, in particular their dynamic viscosity, must also be considered.

Toluene distribution ratios of [bmim][SCN] have been higher than the [emim][SCN] values. This result is in agreement with the trend observed in imidazolium-based ILs formed by dicyanamide [15] and by bis(trifluoromethylsulfonyl)imide anions [16], and with predictions obtained using COSMO-RS [28]. This increase of toluene solubility with the length of the alkyl chain in imidazolium-based ILs was extensively studied by Lachwa *et al.* [31]. Lastly, our values of D_2 for [bmim][SCN] at $T = 313.2$ K were very close to the published values at $T = 303.2$ K [26] as a result of the low effect of temperature on toluene solubility in ILs [28].

TABLE 4
Values of the NRTL parameters regressed from LLE data at $T = 313.2$ K and atmospheric pressure.

Component *i*–*j*	NRTL parameters			*rmsd*
	$(\Delta g_{ij}/R)$/K	$(\Delta g_{ji}/R)$/K	α_{ij}	
	n-Heptane (1) + toluene (2) + [emim][SCN] (3)			
1–2	60.036	16.767	0.30	0.0025
1–3	−0.4643	627.36	0.30	
2–3	3596.0	−1536.8	0.30	
	n-Heptane (1) + toluene (2) + [bmim][SCN] (3)			
1–2	63.111	151.31	0.30	0.0030
1–3	−483.33	681.19	0.30	
2–3	3759.9	−1834.0	0.30	

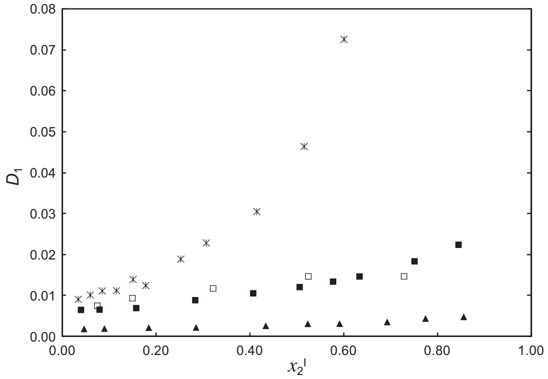


FIGURE 2. Distribution ratios of *n*-heptane for the ternary systems at $T = 313.2$ K against toluene mole fraction in the raffinate phase: ▲, *n*-heptane (1) + toluene (2) + [emim][SCN] (3); ■, *n*-heptane (1) + toluene (2) + [bmim][SCN] (3); ∗, *n*-heptane (1) + toluene (2) + sulfolane (3) [12]; □, *n*-heptane (1) + toluene (2) + [bmim][SCN] (3) at $T = 303.15$ K [26].

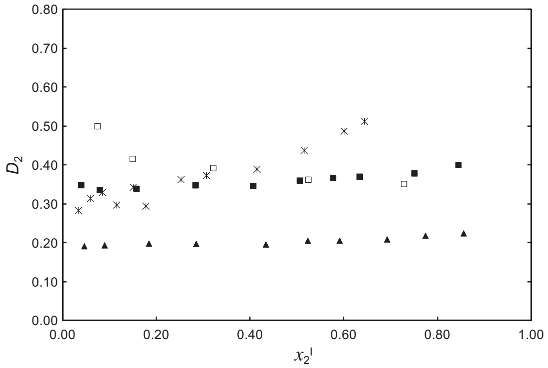


FIGURE 3. Distribution ratios of toluene for the ternary systems at $T = 313.2$ K against toluene mole fraction in the raffinate phase: ▲, *n*-heptane (1) + toluene (2) + [emim][SCN] (3); ■, *n*-heptane (1) + toluene (2) + [bmim][SCN] (3); ∗, *n*-heptane (1) + toluene (2) + sulfolane (3) [12]; □, *n*-heptane (1) + toluene (2) + [bmim][SCN] (3) at $T = 303.15$ K [26].

In figure 4, experimental toluene/*n*-heptane selectivities ($\alpha_{2,1}$) for [emim][SCN] and [bmim][SCN], and literature values for sulfolane [12] and [bmim][SCN] are plotted [26]. Selectivities of

[emim][SCN] have been approximately three times higher than the sulfolane values, whereas selectivities using [bmim][SCN] have been almost double than those of sulfolane. As Revelli *et al.* suggested, the selectivity has decreased with increasing length of the alkyl chain in the cation [32]. In addition, the maximum $\alpha_{2,1}$ using [emim][SCN] was 101.6, and this value was substantially higher than that of other highly selective ILs: [emim][EtSO$_4$] (68.1) [9], [4bmpy][BF$_4$] (53.1) [12], and [bpy][BF$_4$] (74.4) [13]. Hence, toluene obtained using [emim][SCN] is more pure than toluene extracted by sulfolane and other promising ILs. This higher purity of the toluene in the IL-rich phase would simplify its purification, reducing operating costs [33]. To conclude the analysis of extractive properties, toluene/*n*-heptane selectivities of [bmim][SCN] at $T = 313.2$ K were in agreement with values published by Hansmeier *et al.* at $T = 303.2$ K [26].

3.4. Physical characterization of IL-based solvents

In addition to the extractive properties of [emim][SCN] and [bmim][SCN] in the liquid–liquid extraction of toluene from *n*-heptane, we have also measured densities, dynamic viscosities, and surface tensions of the ILs as a function of temperature. In table 5, physical properties of both SCN-based ILs are listed together with literature properties of sulfolane [15,34] to facilitate the comparative analysis between physical properties of the solvents.

As can be seen, densities of [emim][SCN] and [bmim][SCN] have been somewhat lower than those of sulfolane. However, density is not a key property to select a solvent in an extraction process, but its density should permit a correct hydrodynamic behavior in the extractor [33,35]. In this case, densities of both ILs seem to be sufficiently higher than those of the hydrocarbon-rich phase (i.e. mixtures of *n*-heptane and toluene) with densities between 0.659 and 0.850 $g \cdot cm^{-3}$ at $T = 313.2$ K.

Surface tension of a solvent also affects to the hydrodynamic performance of an extraction column [33]. As observed in table 5, surface tensions of [emim][SCN] and [bmim][SCN] have been quite close to the literature data of sulfolane. Therefore, taking into account the values of densities and surface tensions, the hydrodynamic characteristics of an aromatic extraction column using both SCN-based would be moderately similar to the behavior using sulfolane.

On the other hand, dynamic viscosities at $T = 313.2$ K of [emim][SCN] (15.1 $mPa \cdot s$) and [bmim][SCN] (32.2 $mPa \cdot s$) have been higher than that of sulfolane (8.1 $mPa \cdot s$). Nevertheless, the [emim][SCN] have shown a dynamic viscosity at $T = 313.2$ K much lower than that of other ILs that also had high toluene/*n*-heptane selectivities, such as the [emim][EtSO$_4$] (49.8 $mPa \cdot s$) [9,10], the [4bmpy][BF$_4$] (92.4 $mPa \cdot s$) [11,12], or the [bpy][BF$_4$] (74.8 $mPa \cdot s$) [7,13].

TABLE 5
Densities (ρ), dynamic viscosities (η), and surface tensions (γ) of [emim][SCN] and [bmim][SCN] ILs[a] and literature data of sulfolane[b,c] as a function of temperature and atmospheric pressure.

T/K		$\rho/g \cdot cm^{-3}$	
	[emim][SCN]	[bmim][SCN]	Sulfolane[b]
293.15	1.12002	1.07399	
298.15	1.11697	1.07104	
303.15	1.11391	1.06808	1.26202
313.15	1.10795	1.06221	1.25323
323.15	1.10184	1.05639	1.24445
333.15	1.09589	1.05061	1.23567
343.15	1.08998	1.04487	1.22689
353.15	1.08412	1.03917	1.21810
		$\eta/mPa \cdot s$	
	[emim][SCN]	[bmim][SCN]	Sulfolane[b]
293.15	28.27	76.08	
298.15	23.79	59.81	
303.15	20.25	47.84	10.84
313.15	15.13	32.20	8.05
323.15	11.73	22.97	6.38
333.15	9.36	17.12	5.15
343.15	7.65	13.20	4.24
353.15	6.38	10.50	3.54
		$\gamma/mN \cdot m^{-1}$	
	[emim][SCN]	[bmim][SCN]	Sulfolane[c]
298.15	54.1	47.0	
303.15	53.6	46.6	47.95
313.15	52.9	45.7	47.22
323.15	52.1	44.8	46.61

[a] Standard uncertainties u are $u(\rho) = 0.00008$ $g \cdot cm^{-3}$, $u(\eta) = 0.8\%$, $u(\gamma) = 0.10$ $mN \cdot m^{-1}$.
[b] from Larriba *et al.* [15].
[c] from Kelayeh *et al.* [34].

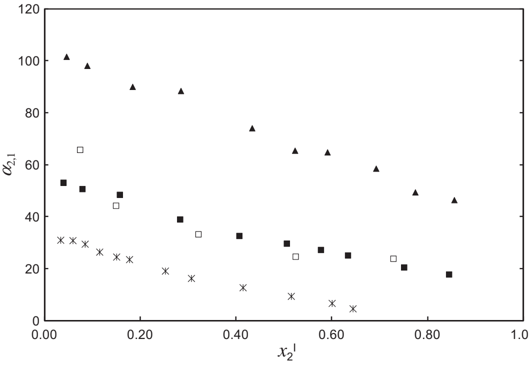


FIGURE 4. Toluene/*n*-heptane selectivities for the ternary systems at $T = 313.2$ K against toluene mole fraction in the raffinate phase: ▲, *n*-heptane (1) + toluene (2) + [emim][SCN] (3); ■, *n*-heptane (1) + toluene (2) + [bmim][SCN] (3); ⁎, *n*-heptane (1) + toluene (2) + sulfolane (3) [12]; □, *n*-heptane (1) + toluene (2) + [bmim][SCN] (3) at $T = 303.15$ K [26].

As a result of its adequate physical properties and its high toluene/*n*-heptane selectivity, the pure [emim][SCN] IL could be applied in a highly selective process of liquid–liquid extraction of aromatics from aliphatic hydrocarbons. Moreover, [emim][SCN] could be mixed with [bmim][DCA] [15], [emim][TCM] [15], or [4bmpy][Tf$_2$N] ILs [8,30] to increase the values of toluene distribution ratios, forming a binary IL mixture with low viscosity and good extractive properties.

4. Conclusions

In this paper, the performance of [emim][SCN] and [bmim][SCN] ILs as toluene extraction solvents was analyzed. For this purpose, the LLE of {*n*-heptane + toluene + [emim][SCN]} and {*n*-heptane + toluene + [bmim][SCN]} systems was performed at $T = 313.2$ K, and from these LLE data, *n*-heptane and toluene distribution ratios and toluene/*n*-heptane selectivities were calculated. To complete the study, densities, dynamic viscosities, and surface tension of the ILs were also determined as a function of temperature to evaluate the potential use of these solvents.

Results obtained for [emim][SCN] indicated that this IL could be considered as a promising IL to replace organic solvents, such as sulfolane, in the liquid–liquid extraction of aromatic hydrocarbons. Toluene/*n*-heptane selectivities using [emim][SCN] were three times higher than the sulfolane values, and their physical properties were appropriate to be applied in an industrial process. In addition, dynamic viscosities of [emim][SCN] were substantially lower than those of other highly selective ILs. The main drawback of [emim][SCN] was the low values of toluene distribution ratios. However, this problem could be overcome mixing this IL-based solvent with other IL with high values of toluene distribution ratios and low dynamic viscosity. By contrast, [bmim][SCN] shown adequate values of toluene distribution ratios and toluene/*n*-heptane selectivities, but its high dynamic viscosity could limit its industrial use.

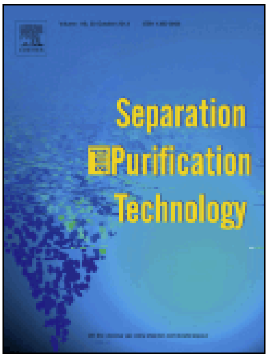
Acknowledgments

The authors are grateful to the Ministerio de Economía y Competitividad (MINECO) of Spain and the Comunidad Autónoma de Madrid for financial support of Projects CTQ2011-23533 and S2009/PPQ-1545, respectively. Marcos Larriba thanks Ministerio de Educación, Cultura y Deporte for awarding him an FPU Grant (Reference AP-2010-0318), and Pablo Navarro also thanks MINECO for awarding him an FPI Grant (Reference BES-2012-052312).

References

[1] G.W. Meindersma, A.J.G. Podt, A.B. de Haan, Fuel Process. Technol. 87 (2005) 59–70.
[2] G.W. Meindersma, A.R. Hansmeier, A.B. de Haan, Ind. Eng. Chem. Res. 49 (2010) 7530–7540.
[3] R.D. Rogers, K.R. Seddon, Science 302 (2003) 792–793.
[4] S.T. Anjan, Chem. Eng. Prog. 102 (2006) 30–39.
[5] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, J. Chem. Thermodyn. 53 (2012) 119–124.
[6] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, Chem. Eng. J. 180 (2012) 210–215.
[7] M. Larriba, S. García, P. Navarro, J. García, F. Rodríguez, J. Chem. Eng. Data 57 (2012) 1318–1325.
[8] M. Larriba, S. García, P. Navarro, J. García, F. Rodríguez, J. Chem. Eng. Data 58 (2013) 1496–1504.
[9] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, J. Chem. Thermodyn. 45 (2012) 68–74.
[10] M. Larriba, S. García, J. García, J.S. Torrecilla, F. Rodríguez, J. Chem. Eng. Data 56 (2011) 3589–3597.
[11] G.W. Meindersma, B.T.J. Simons, A.B. de Haan, J. Chem. Thermodyn. 43 (2011) 1628–1640.
[12] G.W. Meindersma, A.J.G. Podt, A.B. de Haan, Fluid Phase Equilib. 247 (2006) 158–168.
[13] J. García, S. García, J.S. Torrecilla, M. Oliet, F. Rodríguez, J. Chem. Eng. Data 55 (2010) 2862–2865.
[14] U. Domanska, M. Krolikowska, J. Chem. Eng. Data 55 (2010) 2994–3004.
[15] M. Larriba, P. Navarro, J. García, F. Rodríguez, Ind. Eng. Chem. Res. 52 (2013) 2714–2720.
[16] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, J. Chem. Eng. Data 56 (2011) 113–118.
[17] B. Kolb, L.S. Ettre, Static Headspace-Gas Chromatography: Theory and Practice, Wiley-VCH, 1997.
[18] P. Navarro, M. Larriba, S. García, J. García, F. Rodríguez, J. Chem. Eng. Data 57 (2012) 1165–1173.
[19] D.F. Othmer, P.E. Tobias, Ind. Eng. Chem. 34 (1942) 693–696.
[20] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135–144.
[21] L.D. Simoni, Y. Lin, J.F. Brennecke, M.A. Stadtherr, Ind. Eng. Chem. Res. 47 (2008) 256–272.
[22] A. Marciniak, M. Królikowski, J. Chem. Thermodyn. 49 (2012) 154–158.
[23] J.P. Gutiérrez, G.W. Meindersma, A.B. de Haan, Ind. Eng. Chem. Res. 51 (2012) 11518–11529.
[24] M. Królikowski, K. Walczak, U. Domanska, J. Chem. Thermodyn. 65 (2013) 168–173.
[25] A.L. Revelli, F. Mutelet, J.N. Jaubert, J. Phys. Chem. B 114 (2010) 4600–4608.
[26] A.R. Hansmeier, M. Minoves Ruiz, G.W. Meindersma, A.B. de Haan, J. Chem. Eng. Data 55 (2010) 708–713.
[27] A. Arce, M.J. Earle, H. Rodríguez, K.R. Seddon, J. Phys. Chem. B 111 (2007) 4732–4736.
[28] A.R. Ferreira, M.G. Freire, J.C. Ribeiro, F.M. Lopes, J.G. Crespo, J.A.P. Coutinho, Ind. Eng. Chem. Res. 51 (2012) 3483–3507.
[29] E.J. González, N. Calvar, E. Gómez, A. Domínguez, J. Chem. Thermodyn. 42 (2010) 104–109.
[30] J. García, S. García, J.S. Torrecilla, F. Rodríguez, Fluid Phase Equilib. 301 (2011) 62–66.
[31] J. Lachwa, J. Szydlowski, A. Makowska, K.R. Seddon, J.M.S.S. Esperança, H.J.R. Guedes, L.P.N. Rebelo, Green Chem. 8 (2006) 262–267.
[32] A.L. Revelli, F. Mutelet, J.N. Laubert, J. Chromatogr. A 1216 (2009) 4775–4786.
[33] G.W. Meindersma, A.B. de Haan, Sci. China Chem. 55 (2012) 1488–1499.
[34] S.A. Kelayeh, A.H. Jalili, C. Ghotbi, M. Hosseini-Jenab, V. Taghikhani, J. Chem. Eng. Data 56 (2011) 4317–4324.
[35] F. Onink, C. Drumm, G.W. Meindersma, H.J. Bart, A.B. de Haan, Chem. Eng. J. 160 (2010) 511–521.

JCT 13-372



Separation and Purification Technology

Factor de impacto (2013): 3,07

Publicación 3:

Separation of Toluene from *n*-Heptane, 2,3-Dimethylpentane, and Cyclohexane using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids as Extraction Solvents

Marcos Larriba, Pablo Navarro, Julián García, Francisco Rodríguez

Separation and Purification Technology, 2013, 120, 392-401.

Separation and Purification Technology 120 (2013) 392–401

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Separation of toluene from *n*-heptane, 2,3-dimethylpentane, and cyclohexane using binary mixtures of [4empy][Tf_2N] and [emim][DCA] ionic liquids as extraction solvents

Marcos Larriba, Pablo Navarro, Julián García *, Francisco Rodríguez

Department of Chemical Engineering, Complutense University of Madrid, E-28040 Madrid, Spain

A R T I C L E I N F O

Article history:
Received 5 September 2013
Received in revised form 4 October 2013
Accepted 8 October 2013
Available online 18 October 2013

Keywords:
Aromatic/alkane separation
Liquid–liquid extraction
Ionic liquids
Mixed solvents

A B S T R A C T

The use of ionic liquids (ILs) in the separation of aromatic hydrocarbons from alkanes could decrease the environmental impact of the aromatic extraction units, reducing the number of steps and simplifying the solvent recovery. Mixing ILs has been also revealed as a useful tool to tune the extractive and physical properties of IL-based solvents. In this work, the suitability of binary mixtures of 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf_2N]) and 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) ILs as aromatic extraction solvent has been evaluated. For this purpose, we have studied the liquid–liquid extraction of toluene from a straight-chain alkane (*n*-heptane), a branched-chain alkane (2,3-dimethylpentane), and a cycloalkane (cyclohexane) at 313.2 K, using {[4empy][Tf_2N] + [emim][DCA]} mixed IL solvents. A physical characterization of the IL mixtures has also been performed by measuring their densities and dynamic viscosities as a function of temperature. Extractive and physical properties of the mixed IL solvents have been intermediate between the values of pure ILs. A {[4empy][Tf_2N] + [emim][DCA]} mixture with a 0.3 mole fraction of [4empy][Tf_2N] has shown extractive properties better than those of sulfolane for the extraction of toluene from alkanes and adequate densities and viscosities. Finally, a log-linear mixing rule has successfully estimated the extractive properties of the mixed ILs, and the use of predictive models of densities and viscosities of binary IL mixtures has also been studied.

1. Introduction

In the last few years, ionic liquids (ILs) have been proposed as extraction solvents in a wide variety of separation processes [1–7]. The main advantage of ILs with respect to conventional extraction organic solvents is their nonvolatile behavior. As a result of this unusual property, ILs have been considered as environmentally-friendly solvents that could be applied in green technologies. Specifically, ILs could be used in the separation of aromatics from their homogeneous mixtures with aliphatic hydrocarbons, reducing the environmental impact and energy consumption [8].

The separation of aromatic hydrocarbons from aliphatic presents significant challenges due to the proximity of the boiling points of the hydrocarbons, and because of the formation of multiple azeotropic mixtures [9,10]. Liquid–liquid extraction is usually employed to separate the aromatics from aromatic/aliphatic mixtures with aromatic content between 20 and 65 wt%, being the sulfolane the most widely used solvent at industrial scale [11].

In a hypothetical aromatic extraction process using ILs, the solvent recovery could be done by a simple flash distillation or stripping at moderate temperatures due to their negligible vapor pressure [8,12,13]. By contrast, in the Shell-UOP sulfolane process the solvent recovery is accomplished by stripping followed by a distillation at temperatures higher than the sulfolane boiling point (560 K) with the consequent high energy consumption [14]. Moreover, ILs could be used to extract the aromatics from streams with aromatic content lower than 20 wt%, such as the ethylene cracker feeds [14]. However, only a small number of ILs have shown simultaneously aromatic distribution ratios and aromatic/aliphatic selectivities higher than the sulfolane values, and the high viscosity of the ILs could also limit their application in industry [9,15,16].

In our recent researches, we have studied the potential use of binary IL mixtures as aromatic extraction solvents [17,18]. Mixing ILs, we obtained solvents with intermediate extractive properties between those of the pure ILs, and their physical properties were also between the values of pure ILs [19,20].

Therefore, we have studied in this work the performance of binary IL mixtures formed by the 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf_2N]) and the 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) ILs as

---

* Corresponding author. Tel.: +34 91 394 51 19; fax: +34 91 394 42 43.
E-mail address: jgarcia@quim.ucm.es (J. García).

1383-5866/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.seppur.2013.10.017

extraction solvents. The [4empy][Tf_2N] was selected since this IL showed toluene distribution ratios considerably higher than the sulfolane values [21]. Pyridinium Tf_2N-based ILs also show appropriate values of density and high thermal stabilities [22,23]. By contrast, the [emim][DCA] showed toluene/*n*-heptane selectivities substantially higher than those of sulfolane, low dynamic viscosities [24], and adequate thermal stability [25]. Hence, the {[4empy][Tf_2N] + [emim][DCA]} binary IL mixtures should have extractive properties comparable to those of sulfolane and proper thermophysical properties.

The aim of this paper was to study the liquid–liquid extraction of toluene from *n*-heptane, 2,3-dimethylpentane, and cyclohexane using {[4empy][Tf_2N] + [emim][DCA]} mixed IL solvents. These aliphatic hydrocarbons were chosen to study the separation of toluene from a straight-chain alkane, a branched-chain alkane, and a cycloalkane.

To select the most appropriate composition in the IL mixture, liquid–liquid equilibrium (LLE) screening experiments were performed using binary IL mixtures with different compositions as solvents in the liquid–liquid extraction of toluene from {(*n*-heptane, 2,3-dimethylpentane, or cyclohexane) + toluene} mixtures with 10% of toluene in mass basis. LLE experiments using sulfolane as solvent were made under the same conditions to be used as benchmarks. The fixed percentage of toluene in the hydrocarbon mixtures is the usual percentage of aromatics in the feed stream to ethylene crackers [14]. In addition, densities and viscosities of the binary IL mixtures were also measured as a function of temperature and composition. Bearing in mind the results of the LLE screening and the physical properties of the mixtures, a {[4empy][Tf_2N] + [emim][DCA]} mixture with a [4empy][Tf_2N] mole fraction of 0.3 was selected. To conclude, the LLE data of the pseudoternary systems (*n*-heptane, 2,3-dimethylpentane, or cyclohexane) (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at 313.2 K and atmospheric pressure were obtained.

2. Materials and methods

2.1. Materials

[4empy][Tf_2N] and [emim][DCA] ILs were purchased from Iolitec GmbH with mass fraction purities higher than 0.99 and 0.98, respectively. Water content in the ILs in mass fractions were less than 2×10^{-3} and their halides mass fractions were less than 2×10^{-2}. Toluene, *n*-heptane, 2,3-dimethylpentane, cyclohexane, and sulfolane were supplied by Sigma–Aldrich with the specifications shown in Table 1. Chemicals were used as received without further purification, and to avoid water absorption they were placed in a desiccator in their original tightly closed bottles during the period of the experimentation. In addition, the IL handling was made in a glovebox filled with dry nitrogen to maintain constant their water content.

2.2. Liquid–liquid extraction. Experimental procedure and analysis

LLE experiments were prepared in 8 mL vials with screw caps employing a Mettler Toledo XS 205 balance with a precision of $\pm 1 \times 10^{-5}$ g to determine gravimetrically the global composition of feeds. To reach the LLE, vials were shaken in a Labnet Vortemp 1550 shaking incubator at (313.2 ± 0.1) K and 800 rpm for 5 h. To ensure the separation of layers in equilibrium, vials were then placed in a Labnet Accublock dry bath at (313.2 ± 0.1) K for 12 h.

To select the most appropriate composition of the mixed IL solvent, a screening was performed using {[4empy][Tf_2N] + [emim][DCA]} binary mixtures over the whole range of compositions as solvents. In the LLE screening experiments, 2 mL of the mixed solvent or sulfolane was added to the vials together with the same volume of a binary mixture formed by {(*n*-heptane, 2,3-dimethylpentane, or cyclohexane) + toluene} with 10% of toluene in mass basis. Finally, LLE data of the pseudoternary systems (*n*-heptane, 2,3-dimethylpentane, or cyclohexane) (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at 313.2 K and atmospheric pressure were obtained.

To determine the composition of the hydrocarbon-rich (raffinate) phases and the sulfolane-rich phases, an Agilent 7890A gas chromatograph (GC) with a liquid autosampler Agilent 7693 and a flame ionization detector (FID) was employed. Samples from the phases were taken in triplicate, showing in this paper the average compositions. A more detailed description of the analytical method can be found elsewhere [24].

A Bruker Avance 500 MHz NMR spectrometer was used to check the IL absence in the raffinate phases. ^1H NMR spectra did not show signals corresponding to ILs; therefore, the presence of ILs in hydrocarbon-rich phases was considered as negligible. The absence of ILs in the raffinate phase would facilitate its purification at industrial scale. This is an important advantage of ILs with respect to sulfolane, since this organic solvent is partially soluble in aromatic and aliphatic hydrocarbons.

A multiple headspace extraction (MHE) method was employed to determine the composition of the IL-rich phases using an Agilent 7890A GC provided with a Headspace Sampler Agilent 7697A. Approximately 100 μL of extract phases were placed in closed 20 mL vials, shaken at 100 rpm and 393 K for 1 h to promote the evaporation of the dissolved hydrocarbons from the IL-based solvents. The hydrocarbon amounts in samples were determined as the sum of peak areas of consecutive extractions from the same vial. Due to its nonvolatile nature, the IL amount was easily calculated as the difference between the weight of the sample added to the vial and the mass of hydrocarbons determined by MHE. Samples were taken in triplicate and the average compositions are

Table 1
Suppliers and purities of chemicals.

Chemical	Supplier	Mass fraction purity	Analysis method
[4empy][Tf_2N][a]	Iolitec GmbH	0.99	NMR[c] and IC[d]
[emim][DCA][b]	Iolitec GmbH	0.98	NMR[c] and IC[d]
Toluene	Sigma–Aldrich	0.995	GC[e]
n-Heptane	Sigma–Aldrich	0.997	GC[e]
2,3-Dimethylpentane	Sigma–Aldrich	0.99	GC[e]
Cyclohexane	Sigma–Aldrich	0.995	GC[e]
Sulfolane	Sigma–Aldrich	0.99	GC[e]

[a] [4empy][Tf_2N] = 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide.

[b] [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide.

[c] Nuclear magnetic resonance.

[d] Ion chromatography.

[e] Gas chromatography.

the results gathered in this paper. A detailed description of the MHE method used can be found elsewhere [24].

2.3. Physical characterization of the mixed IL solvents

Densities and viscosities of the pure [4empy][Tf_2N] and [emim][DCA] ILs and their binary IL mixtures over the whole range of composition were measured from 293.15 K to 353.15 K. An Anton Paar DMA-5000 oscillating U-tube density meter was used to determine the densities of the IL-based solvents, and an Anton Paar Automated Micro Viscometer (AMVn) based on the falling ball principle was employed to measure their dynamic viscosities. The reliability of both measurement methods was confirmed in our previous papers by comparing experimental densities and dynamic viscosities with literature data for different pure ILs [19,20,26,27].

3. Results and discussion

3.1. Screening LLE experiments with {[4empy][Tf_2N] + [emim][DCA]} mixed ILs

The experimental LLE data of the pseudoternary systems alkane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at 313.2 K as a function of the [4empy][Tf_2N] mole fraction in the mixed solvent (ϕ_3) are listed in Table 2 along with the standard uncertainties of the compositions. As explained in the experimental section, all hydrocarbon feeds employed in this screening were formed by binary mixtures of an alkane hydrocarbon and toluene with 10% of toluene in mass basis. In Table 3, the experimental LLE for the systems alkane (1) + toluene (2) + sulfolane (3) under the same conditions are also shown.

To evaluate the results obtained for the different extraction solvents used in the screening, we have calculated alkane and toluene distribution ratios (D_i) and toluene/alkane selectivities ($\alpha_{2,1}$) from the LLE data using the following expressions:

$$D_1 = \frac{x_1^{II}}{x_1^{I}} \tag{1}$$

$$D_2 = \frac{x_2^{II}}{x_2^{I}} \tag{2}$$

$$\alpha_{2,1} = \frac{x_2^{II}x_1^{I}}{x_2^{I}x_1^{II}} = \frac{D_2}{D_1} \tag{3}$$

where x is the mole fraction of the hydrocarbon and subscripts 1 and 2 refer to the alkane hydrocarbon and toluene, respectively.

Table 2

Experimental LLE data on mole fraction (x), distribution ratios (D_i), and toluene/alkane selectivities ($\alpha_{2,1}$) of the pseudoternary systems as a function of [4empy][Tf_2N] mole fraction in the mixed IL solvent (ϕ_3) at 313.2 K and 10% of toluene in mass basis in hydrocarbon feeds.[a]

[4empy][Tf_2N] In solvent	Hydrocarbon-rich phase (Upper layer)		IL-rich phase (Lower layer)			D_1	D_2	$\alpha_{2,1}$
ϕ_3	x_1^I	x_2^I	x_1^{II}	x_2^{II}	x_{3+4}^{II}			
n-Heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}								
0.00	0.9158	0.0842	0.0035	0.0230	0.9735	0.004	0.273	71.5
0.20	0.9189	0.0811	0.0069	0.0318	0.9613	0.008	0.392	52.2
0.40	0.9231	0.0769	0.0117	0.0405	0.9478	0.013	0.527	41.6
0.60	0.9261	0.0739	0.0174	0.0487	0.9339	0.019	0.659	35.1
0.80	0.9294	0.0706	0.0238	0.0566	0.9196	0.026	0.802	31.3
1.00	0.9475	0.0525	0.0321	0.0525	0.9154	0.034	1.000	29.5
2,3-Dimethylpentane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}								
0.00	0.9143	0.0857	0.0043	0.0258	0.9699	0.005	0.301	64.3
0.20	0.9207	0.0793	0.0088	0.0362	0.9550	0.010	0.456	47.8
0.40	0.9238	0.0762	0.0135	0.0446	0.9419	0.015	0.585	40.1
0.60	0.9284	0.0716	0.0214	0.0550	0.9236	0.023	0.768	33.3
0.80	0.9301	0.0699	0.0303	0.0643	0.9054	0.033	0.920	28.2
1.00	0.9342	0.0658	0.0401	0.0732	0.8867	0.043	1.112	26.0
Cyclohexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}								
0.00	0.9226	0.0774	0.0124	0.0236	0.9640	0.013	0.305	22.7
0.20	0.9269	0.0731	0.0224	0.0349	0.9427	0.024	0.477	19.8
0.40	0.9298	0.0702	0.0305	0.0441	0.9254	0.033	0.628	19.2
0.60	0.9339	0.0661	0.0436	0.0537	0.9027	0.047	0.812	17.4
0.80	0.9362	0.0638	0.0556	0.0614	0.8830	0.059	0.962	16.2
1.00	0.9384	0.0616	0.0697	0.0689	0.8614	0.074	1.118	15.1

[a] Standard uncertainties (u) are: $u(T)$ = 0.1 K, $u(x_i^I)$ = 0.0008; $u(x_1^{II})$ = 0.0009; $u(x_2^{II})$ = 0.0020.

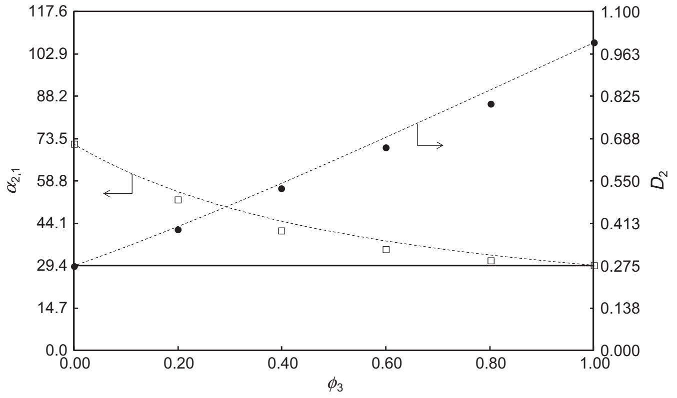
Table 3

Experimental LLE data on mole fraction (x), distribution ratios (D_i), and toluene/alkane selectivities ($\alpha_{2,1}$) of ternary systems alkane (1) + toluene (2) + sulfolane (3) at 313.2 K and 10% of toluene in mass basis in feeds.[a]

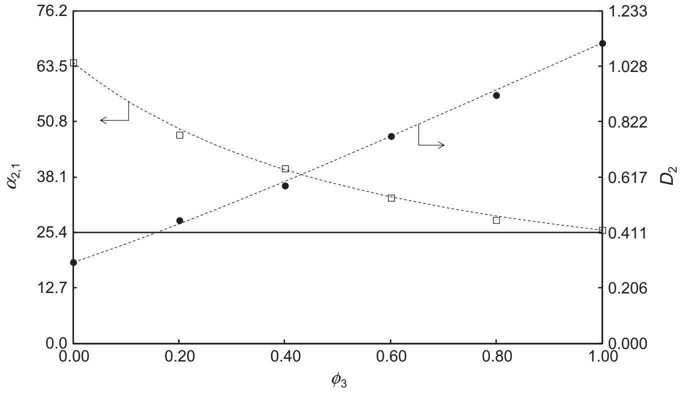
Hydrocarbon-rich phase (upper layer)			Sulfolane-rich phase (lower layer)			D_1	D_2	$\alpha_{2,1}$
x_1^I	x_2^I	x_3^I	x_1^{II}	x_2^{II}	x_3^{II}			
n-Heptane (1) + toluene (2) + sulfolane (3)								
0.9293	0.0666	0.0041	0.0087	0.0183	0.9730	0.009	0.275	29.4
2,3-Dimethylpentane (1) + toluene (2) + sulfolane (3)								
0.9275	0.0684	0.0041	0.0150	0.0281	0.9569	0.016	0.411	25.4
Cyclohexane (1) + toluene (2) + sulfolane (3)								
0.9295	0.0654	0.0051	0.0393	0.0252	0.9355	0.042	0.386	9.1

[a] Standard uncertainties (u) are: $u(T)$ = 0.1 K, $u(x_i^I)$ = 0.0008; $u(x_i^{II})$ = 0.0015.

(a) *n*-heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}



(b) 2,3-dimethylpentane(1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}



(c) cyclohexane(1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}

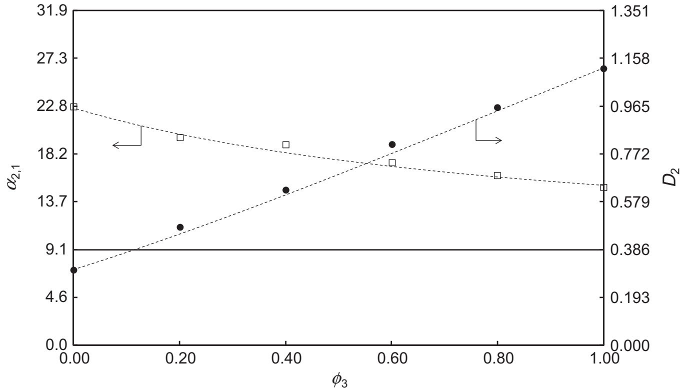


Fig. 1. Toluene distribution ratios (●) and toluene/alkane selectivities (□) of the pseudoternary systems: (a) *n*-heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}; (b) 2,3-dimethylpentane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}; (c) cyclohexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $T = 313.2$ K and 10% of toluene in mass basis in hydrocarbon feeds, as a function of [4empy][Tf_2N] mole fraction in the mixed IL solvent (ϕ_3). Dashed lines were calculated using Yalkowsky and Roseman model and solid lines represent sulfolane values at $T = 313.2$ K and 10% of toluene in mass basis in hydrocarbon feeds.

The superscript I denotes the raffinate phase, whereas the superscript II refers to the extract phase. Values of distribution ratios and toluene/alkane selectivities of IL-based solvents and sulfolane are listed in Tables 2 and 3 together with the experimental LLE.

To perform a comparison between the extractive properties of sulfolane and those of {[4empy][Tf_2N] + [emim][DCA]} IL mixtures, values of D_2 and $\alpha_{2,1}$ of the extraction solvents are graphically shown in Fig. 1. Experimental values for IL-based solvents are

Table 4
Densities ρ and dynamic viscosities η of the {[4empy][Tf_2N] (3) + [emim][DCA] (4)} mixed solvent, as a function of [4empy][Tf_2N] mole fraction (ϕ_3) at several temperatures[a].

ϕ_3	T/K						
	293.15	303.15	313.15	323.15	333.15	343.15	353.15
ρ/g cm^{-3}							
0.00	1.1046	1.0980	1.0914	1.0849	1.0785	1.0721	1.0658
0.10	1.1654	1.1584	1.1508	1.1441	1.1372	1.1306	1.1239
0.20	1.2180	1.2107	1.2034	1.1961	1.1890	1.1818	1.1746
0.30	1.2654	1.2576	1.2499	1.2422	1.2346	1.2271	1.2196
0.40	1.3072	1.2991	1.2910	1.2830	1.2751	1.2672	1.2594
0.50	1.3466	1.3383	1.3300	1.3208	1.3130	1.3047	1.2967
0.60	1.3809	1.3722	1.3635	1.3549	1.3463	1.3379	1.3295
0.70	1.4128	1.4039	1.3947	1.3855	1.3767	1.3678	1.3591
0.80	1.4415	1.4322	1.4230	1.4138	1.4047	1.3957	1.3867
0.90	1.4677	1.4581	1.4487	1.4393	1.4299	1.4204	1.4112
1.00	1.4919	1.4821	1.4723	1.4626	1.4530	1.4435	1.4340
η/mPa s							
0.00	17.5	13.1	10.2	8.1	6.7	5.6	4.8
0.10	20.4	14.8	11.5	9.1	7.4	6.2	5.1
0.20	23.5	16.8	12.8	10.0	8.1	6.7	5.3
0.30	25.6	18.4	13.9	10.9	8.8	7.0	5.9
0.40	27.8	19.9	14.9	11.7	9.2	7.5	6.3
0.50	31.0	22.0	16.2	12.5	9.9	8.0	6.7
0.60	34.2	24.0	17.4	13.3	10.4	8.5	7.1
0.70	36.6	25.5	18.5	14.1	11.1	8.9	7.3
0.80	39.1	27.1	19.6	14.9	11.8	9.3	7.6
0.90	40.8	27.9	20.2	15.3	12.1	9.6	7.9
1.00	42.4	28.7	20.7	15.7	12.3	9.9	8.1

[a] Standard uncertainties u are, $u(T) = 0.01$ K, $u(\rho) = 0.0006$ g cm^{-3}, $u(\eta) = 1.3\%$.

plotted as symbols, whereas the sulfolane values are plotted as solid lines to be used as a benchmark. Additionally, toluene distribution ratios and toluene/alkane selectivities using mixed ILs were predicted from the LLE data for the pure [emim][DCA] and [4empy][Tf_2N] ILs. These values are plotted in Fig. 1 as dashed lines and they were calculated using the Yalkowsky and Roseman log-linear mixing rule [28]:

$$\ln\, x_{\mathrm{i,predicted}}^{\mathrm{I\ or\ II}} = \sum_{\mathrm{j}=3}^{4} f_{\mathrm{j}} \cdot \ln x_{\mathrm{i,j}}^{\mathrm{I\ or\ II}} \tag{4}$$

where $x_{\mathrm{i,j}}$ is the hydrocarbon mole fraction using a pure IL, j refers to the pure ILs, f_{j} denotes the initial volume fraction of IL in the mixed IL solvent in the absence of solutes, and $x_{\mathrm{i,predicted}}$ is the hydrocarbon mole fraction predicted using the mixed IL solvent. Eq. (4) was applied to both raffinate and extract phases to predict the compositions in LLE for the different mixed solvents. As observed in Fig. 1, predicted D_2 and $\alpha_{2,1}$ were in agreement with the experimental values. The maximum average deviation between the experimental values of D_2 and those predicted by Eq. (4) was 4.08% for the cyclohexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} system, whereas the maximum average deviation of predicted toluene/alkane selectivities was found in the *n*-heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} system with a value of 6.82%. Therefore, the Yalkowsky and Roseman equation seems to be a useful tool to predict the extractive properties of binary IL mixtures from experimental data of LLE employing pure ILs.

On the other hand, binary IL mixtures have shown intermediate toluene distribution ratios and toluene/alkane selectivities between the values of the pure [4empy][Tf_2N] and [emim][DCA] ILs as seen in Fig. 1. Therefore, the extractive properties of the solvent composed of two mixed ILs can be changed by modifying the composition of the IL mixture. By analyzing the results plotted in Fig. 1, binary IL mixtures with [4empy][Tf_2N] mole fractions between 0.2 and 0.6 simultaneously showed values of D_2 and $\alpha_{2,1}$ considerably higher than those of sulfolane in the three ternary systems studied. To select the most appropriate composition in the mixed solvent, its physical properties must also be considered.

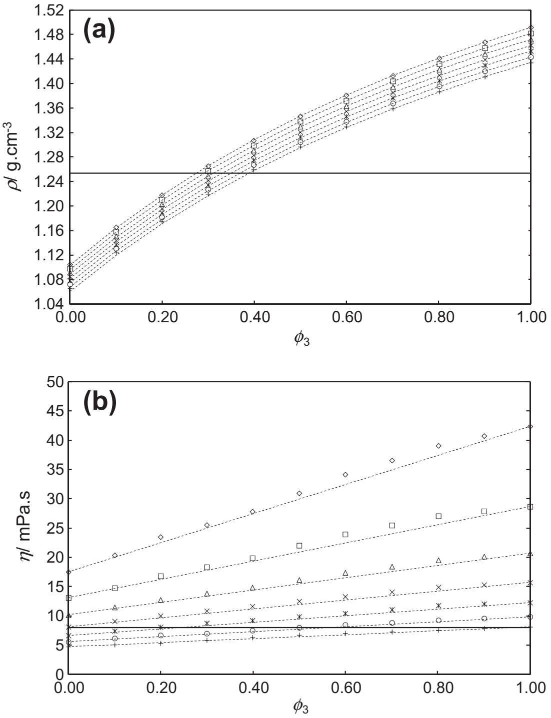


Fig. 2. (a) Densities and (b) dynamic viscosities of the {[4empy][Tf_2N] (3) + [emim][DCA] (4)} mixed solvent, as a function of [4empy][Tf_2N] mole fraction (ϕ_3) at several temperatures: ◇ 293.15 K; □ 303.15 K; Δ 313.15 K; ×, 323.15 K; ⋇, 333.15 K; ○ 343.15 K; + 353.15 K. Dashed lines in (a) are densities estimated from the group contribution model of Ye and Shreeve (Eq. (5)), whereas dashed lines in Fig. 2b are viscosities estimated from a linear mixing rule (Eq. (6)). Solid lines represent densities and dynamic viscosities of sulfolane at 313.15 K from Ref. [24].

3.2. Physical characterization of {[4empy][Tf_2N] + [emim][DCA]} IL mixtures

Densities and dynamic viscosities of {[4empy][Tf_2N] + [emim][DCA]} IL mixture as a function of temperature and [4empy][Tf_2N] mole fraction (ϕ_3) are listed in Table 4. These properties are also graphically shown in Fig. 2 along with the literature properties of sulfolane at 313.2 K [24], since it is the temperature used in the liquid–liquid extraction of toluene in this paper.

As seen in Fig. 2, densities and dynamic viscosities of the binary IL mixtures were intermediate between the physical properties of pure ILs. This fact also confirms the possibility of fine tuning the physical properties of a mixed IL solvent in addition to the extractive properties by changing the composition of the IL mixture.

From the results of the screening performed using {[4empy][Tf_2N] + [emim][DCA]} IL mixtures in the liquid–liquid extraction of toluene from alkane hydrocarbons, and taking also into account the physical properties of the IL-based solvents, we have decided to select a binary mixture with a [4empy][Tf_2N] mole fraction of 0.3. This mixed IL solvent has shown a density at 313.2 K (1.250 g cm^{-3}) very close to the sulfolane density at the same temperature (1.253 g cm^{-3}) [24]. This guarantees that the difference between the density of the hydrocarbon feed and that of the mixed IL solvent is suitable to be used in an industrial process of liquid–liquid extraction of aromatic hydrocarbons. Moreover, the IL mixture with a ϕ_3 of 0.3 had a dynamic viscosity (13.9 mPa s at 313.2 K) slightly higher than the sulfolane value

Table 5
Experimental LLE data of the pseudoternary systems alkane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3 on mole fraction (x), distribution ratios (D_i), and toluene/alkane selectivities ($\alpha_{2,1}$) at T = 313.2 K and atmospheric pressure.[a]

Feed (global composition)			Hydrocarbon-rich phase (upper layer)		IL-rich phase (lower layer)			D_1	D_2	$a_{2,1}$
x_1	x_2	x_{3+4}	x_1^I	x_2^I	x_1^{II}	x_2^{II}	x_{3+4}^{II}			
n-Heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3										
0.5082	0.0000	0.4918	1.0000	0.0000	0.0090	0.0000	0.9910	0.009		
0.4906	0.0291	0.4803	0.9635	0.0365	0.0089	0.0173	0.9738	0.009	0.474	51.3
0.4757	0.0590	0.4653	0.9254	0.0746	0.0091	0.0351	0.9558	0.010	0.471	47.8
0.4432	0.1178	0.4390	0.8461	0.1539	0.0093	0.0708	0.9199	0.011	0.460	41.9
0.4044	0.1929	0.4027	0.7499	0.2501	0.0094	0.1163	0.8743	0.013	0.465	37.1
0.3788	0.2568	0.3644	0.6730	0.3270	0.0088	0.1532	0.8380	0.013	0.469	35.8
0.3274	0.3563	0.3163	0.5496	0.4504	0.0088	0.2103	0.7809	0.016	0.467	29.2
0.2912	0.4271	0.2817	0.4668	0.5332	0.0080	0.2499	0.7421	0.017	0.469	27.3
0.2358	0.5386	0.2256	0.3465	0.6535	0.0071	0.3070	0.6859	0.020	0.470	22.9
0.1800	0.6464	0.1736	0.2428	0.7572	0.0063	0.3778	0.6159	0.026	0.499	19.2
0.1290	0.7466	0.1244	0.1578	0.8422	0.0049	0.4288	0.5663	0.031	0.509	16.4
0.0000	0.8526	0.1474	0.0000	1.0000	0.0000	0.5419	0.4581		0.542	
2,3-Dimethylpentane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3										
0.5003	0.0000	0.4997	1.0000	0.0000	0.0115	0.0000	0.9885	0.012		
0.4877	0.0285	0.4838	0.9643	0.0357	0.0118	0.0204	0.9678	0.012	0.571	46.7
0.4693	0.0573	0.4734	0.9282	0.0718	0.0115	0.0400	0.9485	0.012	0.557	45.0
0.4381	0.1247	0.4372	0.8403	0.1597	0.0114	0.0845	0.9041	0.014	0.529	39.0
0.4009	0.1955	0.4036	0.7500	0.2500	0.0112	0.1285	0.8603	0.015	0.514	34.4
0.3647	0.2704	0.3649	0.6562	0.3438	0.0108	0.1738	0.8154	0.016	0.506	30.7
0.3063	0.3871	0.3066	0.5157	0.4843	0.0107	0.2424	0.7469	0.021	0.501	24.1
0.2742	0.4492	0.2766	0.4419	0.5581	0.0098	0.2796	0.7106	0.022	0.501	22.6
0.2250	0.5507	0.2243	0.3354	0.6646	0.0080	0.3274	0.6646	0.024	0.493	20.7
0.1728	0.6540	0.1732	0.2364	0.7636	0.0073	0.3774	0.6153	0.031	0.494	16.0
0.1227	0.7551	0.1222	0.1536	0.8464	0.0058	0.4105	0.5837	0.038	0.485	12.8
0.0000	0.8526	0.1474	0.0000	1.0000	0.0000	0.5419	0.4581		0.542	
Cyclohexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3										
0.5046	0.0000	0.4954	1.0000	0.0000	0.0272	0.0000	0.9728	0.027		
0.4927	0.0239	0.4834	0.9705	0.0295	0.0264	0.0164	0.9572	0.027	0.556	20.4
0.4804	0.0491	0.4705	0.9393	0.0607	0.0263	0.0340	0.9397	0.028	0.560	20.0
0.4589	0.0955	0.4456	0.8772	0.1228	0.0266	0.0656	0.9078	0.030	0.534	17.6
0.4198	0.1647	0.4155	0.7902	0.2098	0.0255	0.1115	0.8630	0.032	0.531	16.5
0.3736	0.2563	0.3701	0.6558	0.3442	0.0235	0.1743	0.8022	0.036	0.506	14.1
0.3359	0.3315	0.3326	0.5765	0.4235	0.0219	0.2082	0.7699	0.038	0.492	12.9
0.3137	0.3756	0.3107	0.5142	0.4858	0.0202	0.2332	0.7466	0.039	0.480	12.2
0.2617	0.4797	0.2586	0.4031	0.5969	0.0179	0.2823	0.6998	0.044	0.473	10.7
0.2055	0.5921	0.2024	0.2895	0.7105	0.0148	0.3379	0.6473	0.051	0.476	9.3
0.1489	0.7029	0.1482	0.1899	0.8101	0.0105	0.3872	0.6023	0.055	0.478	8.6
0.0000	0.8526	0.1474	0.0000	1.0000	0.0000	0.5419	0.4581		0.542	

[a] Standard uncertainties (u) are: $u(T)$ = 0.1 K, $u(x_i)$ = 0.0007, $u(x_i{}^I)$ = 0.0008; $u(x_1^{II})$ = 0.0009; $u(x_2^{II})$ = 0.0020.

(8.1 mPa s at 313.2 K). This value is also much lower than the viscosities at the same temperature of pure ILs or binary IL mixtures that also showed better extractive properties than those of sulfolane, such as the [4bmpy][BF_4] (92.4 mPa s) [29], the {[bpy][BF_4] (0.7) + [bpy][Tf_2N] (0.3)} IL mixture (53.1 mPa s) [17,19], or the {[bpy][BF_4] (0.7) + [4bmpy][Tf_2N] (0.3)} IL mixture (56.6 mPa s) [18,20].

Due to the numerous binary IL mixtures that can be formed by mixing commercially available ILs, models to predict the properties of IL mixtures are absolutely necessary. The group contribution method proposed by Ye and Shreeve [30] and extended by Gardas and Coutinho [31] has been revealed as an appropriate method to predict densities of binary mixtures of pyridinium-based ILs [19,20]. In this paper, we have studied the reliability of the method in the prediction of densities of {[4empy][Tf_2N] + [emim][DCA]} mixtures using the next equation:

$$\rho = \frac{\sum_{i=3}^{4} W_i \phi_i}{N\left(\sum_{i=3}^{4} V_{0,i}\phi_i\right)(a + bT + cP)} \tag{5}$$

where ρ is the density of the IL mixture in kg m^{-3}, W_i denotes the molecular weight of the pure IL in kg mol^{-1}, N is the Avogadro constant, $V_{0,i}$ is the molecular volume of the pure IL calculated as the sum of the volumes of anion and cation in m^3 mol^{-1}, T indicates the temperature in K, and P is the pressure in MPa. The parameters a, b, and c obtained by Gardas and Coutinho were 8.005×10^{-1}, 6.652×10^{-4} K^{-1}, and -5.919×10^{-4} MPa^{-1}, respectively [31]. Volumes of [emim] (230 $Å^3$) and [Tf_2N] (248 $Å^3$) ions were obtained from literature [31], whereas the volumes of [DCA] (86 $Å^3$) and [4empy] (202 $Å^3$) ions were estimated as the difference between the volume of [emim] cation and the molecular volume of [emim][DCA], and as the difference between the volume of [Tf_2N] anion and the molecular volume of [4empy][Tf_2N], respectively, from experimental densities of pure ILs gathered in this work. Estimated densities using Eq. (5) are plotted in Fig. 2 together with the experimental densities of the IL mixtures. The average deviation between the experimental and predicted values was 0.11%; therefore, the method proposed by Ye and Shreeve has very accurately predicted the densities of {[4empy][Tf_2N] + [emim][DCA]} IL mixtures.

On the other hand, a linear mixing rule has been employed to estimate the dynamic viscosities of the binary IL mixtures from viscosities of pure ILs:

$$\eta = \sum_{i=3}^{4} \phi_i \eta_i \tag{6}$$

where η is the estimated dynamic viscosity of the binary IL mixture, η_i is the viscosity of the pure IL at the same temperature and ϕ_i indicates the IL mole fraction in the mixed solvent. As observed in Fig. 2, estimated viscosities were in agreement with experimental properties. The average deviation of the predictions was 2.99%. Hence, dynamic viscosities of {[4empy][Tf_2N] + [emim][DCA]} IL mixtures have shown a quasi-ideal behavior.

3.3. LLE of the pseudoternary systems alkane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3 and 313.2 K

3.3.1. Validation of experimental LLE data

The experimental LLE data for the pseudoternary systems (*n*-heptane, 2,3-dimethylpentane, or cyclohexane) (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3, 313.2 K, and atmospheric pressure are listed in Table 5 and plotted as ternary diagrams in Fig. 3.

To check the reliability of the LLE data, the Othmer–Tobias correlation was used [32]:

$$\ln\left(\frac{1-w^{\mathrm{II}}_{(3+4)}}{w^{\mathrm{II}}_{(3+4)}}\right) = a + b\ln\left(\frac{1-w^{\mathrm{I}}_{1}}{w^{\mathrm{I}}_{1}}\right) \quad (7)$$

where $w^{\mathrm{II}}_{(3+4)}$ is the mixed IL solvent mass fraction in the extract phase, w^{I}_{1} is the mass fraction of the alkane hydrocarbon in the raffinate phase, and *a* and *b* are the fitted parameters presented in Table 6 together with the values of regression coefficients (R^2) and standard deviations (σ). The values of R^2 higher than 0.985 and the low values of σ indicate the high degree of consistency of the experimental results.

3.3.2. Correlation of LLE using NRTL model

The nonrandom two-liquid (NRTL) model has been successfully employed in the fitting of LLE data of ternary systems containing ILs [33,34]. From LLE results of Table 5 for each pseudoternary system, the binary interaction parameters $\Delta g_{ij}/R$ and $\Delta g_{ji}/R$ were estimated using ASPEN Plus simulator. The third nonrandomness parameter (α_{ij}) of the NRTL equation was set to 0.30, since this is the usual value in the correlation of LLE of systems formed by organic compounds and ILs [24,35–37]. Parameters of the NRTL model for the three pseudoternary systems at 313.2 K are presented in Table 7 along with the root mean square deviation (*rmsd*) of the correlations estimated with the following expression:

$$rmsd = \left\{\frac{\sum_{\mathrm{i}}\sum_{\mathrm{l}}\sum_{\mathrm{m}}\left(x^{\mathrm{exptl}}_{\mathrm{ilm}} - x^{\mathrm{calc}}_{\mathrm{ilm}}\right)^2}{6k}\right\}^{1/2} \quad (8)$$

where the subscripts i, l, and m refer to the component, phase, and tie line, respectively, *x* is mole fraction of the compound, and *k* is the number of tie lines in the LLE ternary diagram.

Predicted tie lines by the NRTL model of the pseudoternary systems are graphically shown in Fig. 3 as empty squares and dashed lines along with experimental LLE data. As seen, predicted LLE of the three systems were highly similar to the experimental results. Hence, LLE data presented in this paper have been satisfactorily fitted to the NRTL model.

3.3.3. Distribution ratios and toluene/alkane selectivities

To make a comparative study on the performance of the {[4empy][Tf_2N] + [emim][DCA]} mixed IL solvent with a [4empy][Tf_2N] mole fraction of 0.3 for the liquid–liquid extraction of toluene from alkanes, we have calculated distribution ratios and toluene/alkane selectivities for the pseudoternary systems using Eqs. (1)–(3). Calculated values of D_i and $\alpha_{2,1}$ are listed in Table 5 together with the LLE data.

In Fig. 4, alkane distribution ratios of the three pseudoternary systems at 313.2 K are plotted together with literature data for the {*n*-heptane + toluene + sulfolane} system at the same temperature [38] and the {cyclohexane + toluene + sulfolane} system at 303.2 K [39].

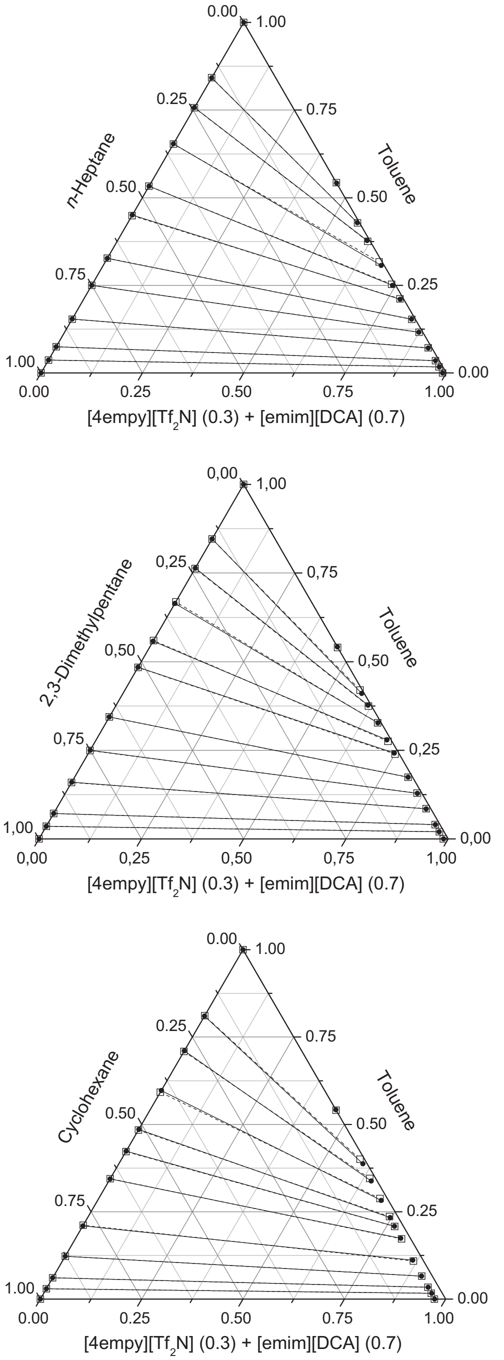


Fig. 3. LLE for the pseudoternary systems alkane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3, *T* = 313.2 K, and atmospheric pressure. Full points and solid lines are experimental tie lines, and empty squares and dashed lines represent calculated LLE by the NRTL model.

Table 6
Constants of the Othmer–Tobias correlation (*a*, *b*), regression coefficients (R^2), and standard deviations (σ) for the LLE data of the pseudoternary systems alkane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$, $T = 313.2$ K, and atmospheric pressure.

a	*b*	R^2	σ
n-Heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$			
−2.1595	0.6922	0.9923	0.0749
2,3-Dimethylpentane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$			
−2.1026	0.6372	0.9857	0.1239
Cyclohexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$			
−2.1558	0.5778	0.9950	0.0343

Table 7
Values of the NRTL parameters obtained from LLE data by regression for the pseudoternary systems alkane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$, $T = 313.2$ K, and atmospheric pressure.

Component	NRTL parameters			
i–j	$(\Delta g_{ij}/R)/K$	$(\Delta g_{ji}/R)/K$	α_{ij}	*rmsd*
n-Heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$				
1–2	−45.960	−17.547	0.30	0.0018
1–(3 + 4)	772.02	−469.81	0.30	
2–(3 + 4)	3789.9	−1989.6	0.30	
2,3-Dimethylpentane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$				
1–2	413.18	−632.75	0.30	0.0013
1–(3 + 4)	2226.7	−1431.9	0.30	
2–(3 + 4)	3871.8	−2002.6	0.30	
Cyclohexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$				
1–2	267.46	−424.55	0.30	0.0017
1–(3 + 4)	2240.3	−1692.3	0.30	
2–(3 + 4)	3704.5	−1930.9	0.30	

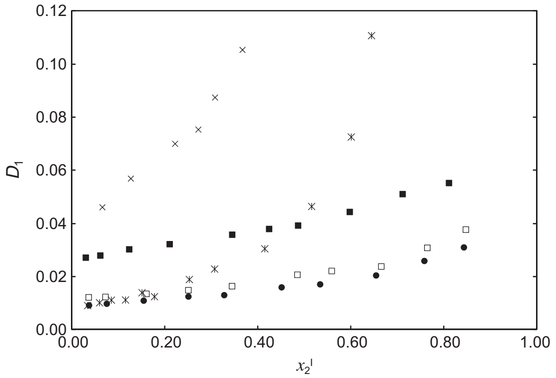


Fig. 4. Alkane distribution ratios (D_1) at $T = 313.2$ K for the systems: ●, *n*-heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; □ 2,3-dimethylpentane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; ■ cyclohexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; ⁎, *n*-heptane (1) + toluene (2) + sulfolane (3) from Ref. [38]. × Cyclohexane (1) + toluene (2) + sulfolane (3) at $T = 303.2$ K from Ref. [39].

n-Heptane distribution ratios using {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} IL mixture were very closed to the published values of sulfolane at low mole fractions of toluene in raffinate, whereas D_1 values at high contents of toluene in raffinate using the mixed IL solvent were considerably lower than those of sulfolane. Cyclohexane distribution ratios employing the IL mixture were substantially lower than the literature values of sulfolane and therefore, the solubility of this cycloalkane was lower in the IL-based solvent than in sulfolane.

Analyzing the values of D_1 for the three pseudoternary systems studied in this work, we can order the alkane hydrocarbons according to their solubility in the mixed IL solvent. The *n*-heptane was the least soluble in the IL mixture and the 2,3-dimethylpentane showed a solubility slightly higher than that of *n*-heptane. Hence, the branching of the alkane chain caused a small increase in the affinity of the hydrocarbon for the mixed ILs. Finally, values of cyclohexane distribution ratios were approximately double than those of *n*-heptane and 2,3-dimethylpentane. So, the cyclohexane solubility was the highest in the IL-based solvent. The same trend was observed by Corderí et al. in the solubility of cyclohexane and *n*-heptane in pure imidazolium-based ILs [40].

Experimental values of toluene distribution ratios and toluene/*n*-heptane selectivities for the *n*-heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} pseudoternary system at $\phi_3 = 0.3$ and 313.2 K are shown in Fig. 5. In the same figure, literature values for the liquid–liquid extraction of toluene from *n*-heptane using sulfolane and [emim][DCA] and [4empy][Tf_2N] pure ILs are also plotted [21,24,38]. As can be observed, toluene/*n*-heptane selectivities using {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} were considerably higher than the sulfolane values; thus, toluene extracted by the IL mixture had a higher purity than that employing sulfolane. In addition, toluene distribution ratios for the mixed IL solvent were higher than those of sulfolane at toluene mole fraction in raffinate phase lower than 0.6. To conclude the analysis of Fig. 5, values of both extractive properties of the binary IL mixture were between those corresponding to the pure [emim][DCA] and [4empy][Tf_2N] ILs. This fact supports that mixing ILs can be considered as an appropriate way to tune the distribution ratios and selectivities of IL-based solvents in the liquid–liquid extraction of hydrocarbons.

In Fig. 6, toluene distribution ratios and toluene/alkane selectivities for the pseudoternary systems: 2,3-dimethylpentane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} and cyclohexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$ and 313.2 K are plotted along with published values for the {cyclohexane + toluene + sulfolane} system at 303.2 K [39]. Values of D_2 for the {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} sol-

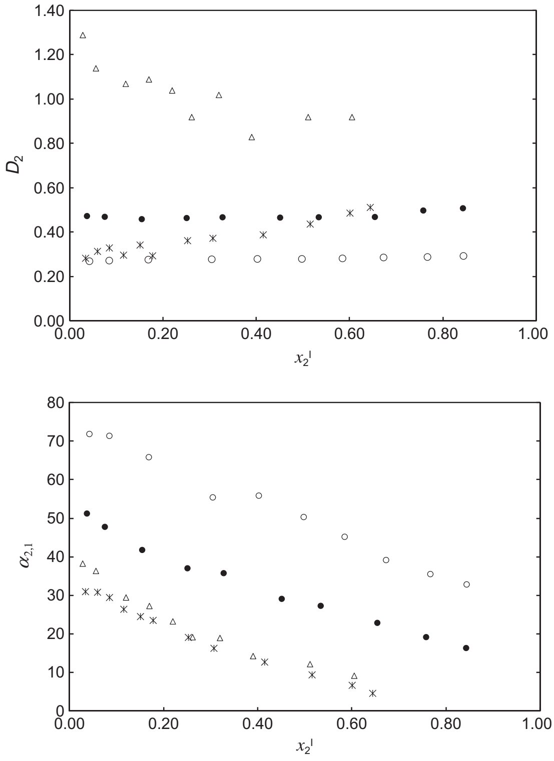


Fig. 5. Toluene distribution ratios (D_2) and toluene/*n*-heptane selectivities ($\alpha_{2,1}$) at $T = 313.2$ K for the systems: ● *n*-heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; ○ *n*-heptane (1) + toluene (2) + [emim][DCA] (3) from Ref. [24]; Δ, *n*-heptane (1) + toluene (2) + [4empy][Tf_2N] (3) from Ref. [21]; ⁎, *n*-heptane (1) + toluene (2) + sulfolane (3) from Ref. [38].

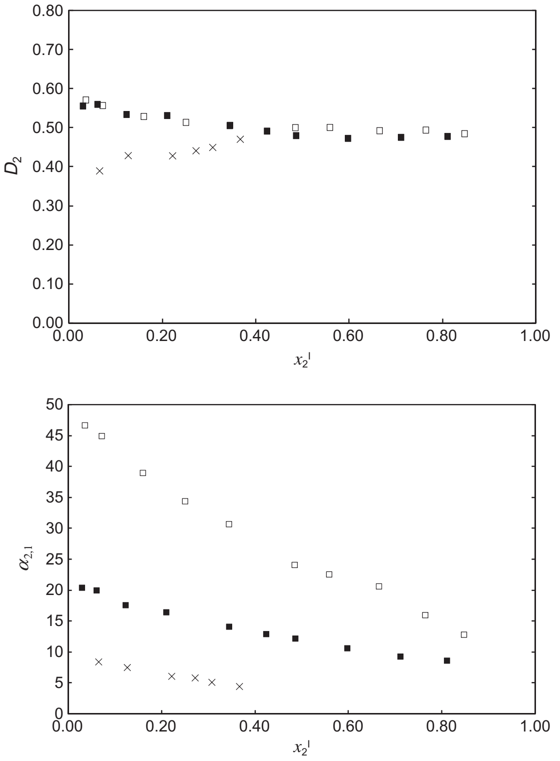


Fig. 6. Toluene distribution ratios (D_2) and toluene/alkane selectivities ($\alpha_{2,1}$) at $T = 313.2$ K for the systems: □ 2,3-dimethylpentane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; ■ cyclohexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; × Cyclohexane (1) + toluene (2) + sulfolane (3) at $T = 303.2$ K from Ref. [39].

vent were higher than the sulfolane values in the whole range of compositions, and their toluene/cyclohexane selectivities were over two times higher than those of sulfolane. Hence, this mixed IL solvent has shown adequate extractive properties to be considered as an alternative to sulfolane in the liquid–liquid extraction of toluene from alkanes.

As seen in Fig. 6, experimental values of toluene distribution ratios in the extraction of toluene from 2,3-dimethylpentane and cyclohexane were very similar. Therefore, the change of 2,3-dimethylpentane by cyclohexane hardly affects the toluene solubility in the IL-based solvent. However, toluene/2,3-dimethylpentane selectivities were considerably higher than the values of toluene/cyclohexane selectivities as a result of the higher solubility of cyclohexane in the {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} IL mixture.

4. Conclusions

In this work, we have studied the potential use of the {[4empy][Tf_2N] + [emim][DCA]} mixed IL solvent in the liquid–liquid extraction of toluene from a straight-chain alkane (*n*-heptane), a branched-chain alkane (2,3-dimethylpentane), and a cycloalkane (cyclohexane) at 313.2 K. Toluene distribution ratios and toluene/alkane selectivities for binary IL mixtures with different compositions have been compared to those of sulfolane.

Toluene distribution ratios and toluene/alkane selectivities of {[4empy][Tf_2N] + [emim][DCA]} mixtures have been intermediate between those corresponding to the pure. These extractive properties have been adequately predicted by the Yalkowsky and Roseman model from the LLE data of pure ILs. In addition, densities and viscosities of the mixed IL solvents have also been between the physical properties of [4empy][Tf_2N] and [emim][DCA] ILs. The group contribution method proposed by Ye and Shreeve has accurately predicted the densities of the binary IL mixtures, whereas a linear mixing rule has been successfully employed to estimate dynamic viscosities of the mixed IL solvents from the viscosities of the pure ILs.

From the LLE data of the screening with different composition of the mixed IL solvent and the study on the physical properties of the mixtures, we have selected a {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} IL mixture to obtain a solvent with good extractive properties and adequate physical properties to be applied at industrial scale. The reliability of the LLE data for the pseudoternary systems (*n*-heptane, 2,3-dimethylpentane, or cyclohexane) (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$ and 313.2 K has been checked using the Othmer–Tobias correlation. The NRTL model was used to fit the LLE data.

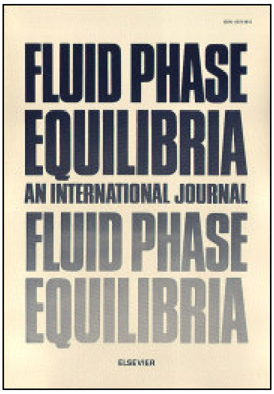
The {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} mixed IL solvent has shown toluene distribution ratios and selectivities higher than those of sulfolane in the liquid–liquid extraction of toluene from *n*-heptane, 2,3-dimethylpentane, and cyclohexane. The branching of the hydrocarbon chain has caused a slight increase in the solubility of 2,3-dimethylpentane in the mixed ILs with respect to that of *n*-heptane. Finally, the cyclohexane has shown a higher solubility in the IL-based solvent than that of *n*-heptane and 2,3-dimethylpentane, and because of this, the toluene/cyclohexane selectivities have been considerably lower. In future studies, separations of different pairs of aromatic and aliphatic hydrocarbons employing the {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} IL mixture should be studied to confirm the applicability of the IL-based solvent at industrial scale.

Acknowledgments

The authors are grateful to the Ministerio de Economía y Competitividad (MINECO) of Spain and the Comunidad Autónoma de Madrid for financial support of Projects CTQ2011–23533 and S2009/PPQ–1545, respectively. Marcos Larriba thanks Ministerio de Educación, Cultura y Deporte for awarding him an FPU Grant (Reference AP–2010–0318), and Pablo Navarro also thanks MINECO for awarding him an FPI grant (Reference BES–2012–052312).

References

[1] M. Matsumoto, K. Mochiduki, K. Fukunishi, K. Kondo, Extraction of organic acids using imidazolium-based ionic liquids and their toxicity to *Lactobacillus rhamnosus*, Sep. Purif. Technol. 40 (2004) 97–101.
[2] A.B. Pereiro, A. Rodríguez, Azeotrope-breaking using [BMIM][$MeSO_4$] ionic liquid in an extraction column, Sep. Purif. Technol. 62 (2008) 733–738.
[3] L.I.N. Tomé, V.R. Catambas, A.R.R. Teles, M.G. Freire, I.M. Marrucho, J.A.P. Coutinho, Tryptophan extraction using hydrophobic ionic liquids, Sep. Purif. Technol. 72 (2010) 167–173.
[4] A.F.M. Claudio, M.G. Freire, C.S.R. Freire, A.J.D. Silvestre, J.A.P. Coutinho, Extraction of vanillin using ionic-liquid-based aqueous two-phase systems, Sep. Purif. Technol. 75 (2010) 39–47.
[5] F.S. Oliveira, J.M.M. Araujo, R. Ferreira, L.P.N. Rebelo, I.M. Marrucho, Extraction of L-lactic, L-malic, and succinic acids using phosphonium-based ionic liquids, Sep. Purif. Technol. 85 (2012) 137–146.
[6] E. Alvarez-Guerra, A. Irabien, Extraction of lactoferrin with hydrophobic ionic liquids, Sep. Purif. Technol. 98 (2012) 432–440.
[7] M. Zawadzki, L. Niedzicki, W. Wieczorek, U. Domanska, Estimation of extraction properties of new imidazolide anion based ionic liquids on the basis of activity coefficient at infinite dilution measurements, Sep. Purif. Technol. 118 (2013) 242–254.
[8] S.T. Anjan, Ionic liquid for aromatic extraction: are they ready?, Chem Eng. Prog. 102 (2006) 30–39.
[9] G.W. Meindersma, A.R. Hansmeier, A.B. de Haan, Ionic liquids for aromatics extraction. Present status and future outlook, Ind. Eng. Chem. Res. 49 (2010) 7530–7540.
[10] F. Farshad, M. Iravaninia, N. Kasiri, T. Mohammadi, J. Ivakpour, Separation of toluene/*n*-heptane mixtures experimental, modeling and optimization, Chem. Eng. J. 173 (2011) 11–18.
[11] K. Weissermel, H.J. Arpe, Industrial Organic Chemistry, fourth ed., Wiley–VCH, 2003.
[12] G.W. Meindersma, A.J.G. Podt, A.B. de Haan, Selection of ionic liquids for the extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures, Fuel Process. Technol. 87 (2005) 59–70.
[13] V.R. Ferro, E. Ruiz, J. de Riva, J. Palomar, Introducing process simulation in ionic liquids design/selection for separation processes based on operational and economic criteria through the example their regeneration, Sep. Purif. Technol. 97 (2012) 195–204.
[14] G.W. Meindersma, A.B de Haan, Conceptual process design for aromatic/aliphatic separation with ionic liquids, Chem. Eng. Res. Des. 86 (2008) 745–752.
[15] G.W. Meindersma, A.B. de Haan, Cyano-containing ionic liquids for the extraction of aromatic hydrocarbons from an aromatic/aliphatic mixture, Sci. China Chem. 55 (2012) 1488–1499.
[16] F. Onink, C. Drumm, G.W. Meindersma, H.J. Bart, A.B. de Haan, Hydrodynamic behavior analysis of a rotating disc contactor for aromatics extraction with 4-methyl-butyl-pyridinium·BF4 by CFD, Chem. Eng. J. 160 (2010) 511–521.
[17] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, Liquid–liquid extraction of toluene from *n*-heptane using binary mixtures of N-butylpyridium tetrafluoroborate and N-butylpyridinium bis(trifluoromethylsulfonyl)imide ionic liquids, Chem. Eng. J. 180 (2012) 210–215.
[18] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, Separation of toluene from *n*-heptane by liquid–liquid extraction using binary mixtures of [bpy][BF_4] and [4bmpy][Tf_2N] ionic liquids as solvent, J. Chem. Thermodyn. 53 (2012) 119–124.
[19] M. Larriba, S. García, P. Navarro, J. García, F. Rodríguez, Physical properties of *N*–butylpyridinium tetrafluoroborate and *N*–butylpyridinium bis(trifluoromethylsulfonyl)imide binary ionic liquid mixtures, J. Chem. Eng. Data 57 (2012) 1318–1325.
[20] M. Larriba, S. García, P. Navarro, J. García, F. Rodríguez, Physical characterization of an aromatic extraction solvent formed by [bpy][BF_4] and [4bmpy][Tf_2N] mixed ionic liquids, J. Chem. Eng. Data 58 (2013) 1496–1504.
[21] J. García, S. García, J.S. Torrecilla, F. Rodríguez, Solvent extraction of toluene from heptane with the ionic liquids *N*-ethylpyridinium bis(trifluoromethylsulfonyl)imide and *z*-methyl-*N*-ethylpyridinium bis(trifluoromethylsulfonyl)imide ($z = 2$, 3 or 4) at $T = 313.2$ K, J. Chem. Eng. Data 55 (2010) 4937–4942.
[22] F.S. Oliveira, M.G. Freire, P.J. Carvalho, J.A.P. Coutinho, J.N. Canongia Lopes, L.P.N. Rebelo, I.M. Marrucho, Structural and positional isomerism influence in the physical properties of pyridinium NTf_2-based ionic liquids: pure and water-saturated mixtures, J. Chem. Eng. Data 55 (2010) 4514–4520.
[23] J.M. Crosthwaite, M. Muldoon, J.K. Dixon, J.L. Anderson, J.F. Brennecke, Phase transition and decomposition temperatures, heat capacities and viscosities of pyridinium ionic liquids, J Chem. Thermodyn. 37 (2005) 559–568.
[24] M. Larriba, P. Navarro, J. García, F. Rodríguez, Liquid–liquid extraction of toluene from heptane using [emim][DCA], [bmim][DCA], and [emim][TCM] ionic liquids, Ind. Eng. Chem. Res. 52 (2013) 2714–2720.
[25] P. Navarro, M. Larriba, E. Rojo, J. García, F. Rodríguez, Thermal properties of cyano-based ionic liquids, J. Chem. Eng. Data 58 (2013) 2187–2193.
[26] M. Larriba, S. García, J. García, J.S. Torrecilla, F. Rodríguez, Thermophysical properties of 1-ethyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate and 1-ethyl-3-methylimidazolium ethylsulfate ionic liquids as a function of temperature, J. Chem. Eng. Data 56 (2011) 3589–3597.
[27] P. Navarro, M. Larriba, S. García, J. García, F. Rodríguez, Physical properties of binary and ternary mixtures of 2-propanol, water, and 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid, J. Chem. Eng. Data 57 (2012) 1165–1173.
[28] S.H. Yalkowsky, T.J. Roseman, Chapter 3: Solubilization of drugs by cosolvents, in: Techniques of Solubilization of Drugs, Dekker, New York, 1981.
[29] G.W. Meindersma, B.T.J. Simons, A.B. de Haan, Physical properties of 3-methyl-N-butylpyridinium tetracyanoborate and 1-butyl-1-methylpyrrolidinium tetracyanoborate and ternary LLE data of [3-mebupy]B$(CN)_4$ with an aromatic and an aliphatic hydrocarbon at $T = 303.2$ K and 328.2 K and $p = 0.1$ MPa, J. Chem. Thermodyn. 43 (2011) 1628–1640.
[30] C. Ye, J.M. Shreeve, Rapid and accurate estimation of densities of room-temperature ionic liquids and salts, J. Phys. Chem. A 111 (2007) 1456–1461.
[31] R.L. Gardas, J.A.P. Coutinho, Extension of the Ye and Shreeve group contribution method for density estimation of ionic liquids in a wide range of temperatures and pressures, Fluid Phase Equilib. 263 (2008) 26–32.
[32] D.F. Othmer, P.E. Tobias, Toluene and acetaldehyde systems, tie line correlation, partial pressures of ternary liquid systems and the prediction of tie lines, Ind. Eng. Chem. 34 (1942) 693–696.
[33] H. Renon, J.M. Prausnitz, Local compositions in thermodynamic excess functions for liquid mixtures, AIChE J. 14 (1968) 135–144.
[34] L.D. Simoni, Y. Lin, J.F. Brennecke, M.A. Stadtherr, Modeling liquid–liquid equilibrium of ionic liquid systems with NRTL, electrolyte–NRTL, and UNIQUAC, Ind. Eng. Chem. Res. 47 (2008) 256–272.
[35] A. Marciniak, M. Królikowski, Ternary (liquid + liquid) equilibria of {trifluorotris(perfluoroethyl)phosphate based ionic liquids + thiophene + heptane}, J. Chem. Thermodyn. 49 (2012) 154–158.
[36] J.P. Gutiérrez, G.W. Meindersma, A.B. de Haan, COSMO-RS-based ionic-liquid selection for extractive distillation processes, Ind. Eng. Chem. Res. 51 (2012) 11518–11529.
[37] M. Królikowski, K. Walczak, U. Domanska, Solvent extraction of aromatic sulfur compounds from *n*-heptane using the 1-ethyl-methylimidazolium tricyanomethanide ionic liquid, J. Chem. Thermodyn. 65 (2013) 168–173.
[38] G.W. Meindersma, A.J.G. Podt, A.B. de Haan, Ternary liquid–liquid equilibria for mixtures of toluene + *n*-heptane + an ionic liquid, Fluid Phase Equilib. 247 (2006) 158–168.
[39] I. Ashour, Liquid–liquid equilibria of ternary and six-component systems including cyclohexane, benzene, toluene, ethylbenzene, cumene and sulfolane at 303.15 K, J. Chem. Eng. Data 51 (2006) 1717–1722.
[40] S. Corderí, E.J. González, N. Calvar, A. Domínguez, Application of [HMim][NTf_2], [HMim][TfO] and [BMim][TfO] ionic liquids on the extraction of toluene from alkanes: Effect of the anion and the alkyl chain length of the cation on the LLE, J Chem. Thermodyn. 53 (2012) 60–66.



Fluid Phase Equilibria

Factor de impacto (2013): 2,24

Publicación 4:

Liquid–liquid Extraction of Toluene from *n*-Heptane by {[emim][TCM] + [emim][DCA]} Binary Ionic Liquid Mixtures

Marcos Larriba, Pablo Navarro, Julián García, Francisco Rodríguez

Fluid Phase Equilibria, 2014, 364, 48-54.

Fluid Phase Equilibria 364 (2014) 48–54

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Liquid–liquid extraction of toluene from *n*-heptane by {[emim][TCM] + [emim][DCA]} binary ionic liquid mixtures

Marcos Larriba, Pablo Navarro, Julián García*, Francisco Rodríguez

Department of Chemical Engineering, Complutense University of Madrid, E-28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 30 October 2013
Received in revised form 9 December 2013
Accepted 11 December 2013
Available online 22 December 2013

Keywords:
Toluene/*n*-heptane separation
Liquid–liquid extraction
Ionic liquids
Mixed solvents

ABSTRACT

Ionic liquids (ILs) have been widely researched to replace organic solvents in the liquid–liquid extraction of aromatics from their mixtures with aliphatic hydrocarbons. However, the ILs studied so far have exhibited high dynamic viscosities and most of them have not shown better extractive properties than those of conventional solvents. Recently, the 1-ethyl-3-methylimidazolium tricyanomethanide ([emim][TCM]) and the 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) ILs have been proposed as aromatic extraction solvents. Both ILs have shown high toluene distribution ratios and toluene/*n*-heptane selectivities, dynamic viscosities comparable to the sulfolane value, and adequate thermal stabilities. In this paper, we have mixed [emim][TCM] and [emim][DCA] ILs to obtain an IL-based solvent with intermediate extractive and physical properties between the values of pure ILs. The liquid–liquid equilibrium (LLE) of the *n*-heptane + toluene + {[emim][TCM] + [emim][DCA]} pseudoternary system at 313.2 K and atmospheric pressure has been measured. LLE data have been validated using the Othmer–Tobias correlation and fitted to the NRTL model. Densities and viscosities of the mixed ILs have also been determined as a function of temperature, and the reliability of several predictive models of these physical properties has been studied. The {[emim][TCM] + [emim][DCA]} IL mixture with [emim][TCM] mole fraction of 0.8 has shown suitable physical properties and extractive properties higher than the sulfolane values. Therefore, this IL-based solvent could be considered as a potential substitute of conventional solvents used in the extraction of aromatics.

1. Introduction

The main sources of benzene, toluene, ethylbenzene, and xylenes (BTEX) are pyrolysis gasoline, reformer gasoline, and coke oven benzole [1]. At industrial scale, a liquid–liquid extraction unit is employed to obtain streams with a high content of BTEX from the previously cited sources; being the Shell-UOP Sulfolane the most frequently used process. However, this process has several drawbacks due to high operating costs of solvent regeneration and recovery of dissolved sulfolane in raffinate phase [2]. Both disadvantages could be solved using ILs as solvents, due to their nonvolatile nature and the negligible solubility of ILs in hydrocarbons [3].

In recent years, the performance of a large number of ILs as aromatic extraction solvents has been studied by measuring the LLE of ternary systems formed by an aromatic hydrocarbon, an aliphatic hydrocarbon, and an IL [4–13]. Most of the ILs have not shown simultaneously higher aromatic distribution ratios and aromatic/aliphatic selectivities than those of sulfolane [11]. In addition, the main difference between ILs and the sulfolane was their considerably higher viscosity [14].

In our recent papers, we have proposed the use of binary ILs mixtures as extraction solvents. We obtained mixed ILs with intermediate extractive and physical properties between the values of pure ILs [15–19]. Therefore, the ILs selected to form a mixed solvent must have extractive properties close to those of sulfolane and moderate dynamic viscosities.

The aim of this work was to study the liquid–liquid extraction of toluene from *n*-heptane using {[emim][TCM] + [emim][DCA]} mixed ILs at 313.2 K. Both ILs have showed toluene/*n*-heptane selectivities considerably higher than the sulfolane values, and the toluene distribution ratio using [emim][TCM] was also slightly higher than that of sulfolane [20]. Moreover, the dynamic viscosities of the [emim][TCM] and [emim][DCA] ILs were close to that of sulfolane and both ILs exhibited high thermal stabilities [20,21].

In order to select the most appropriate composition in the {[emim][TCM] + [emim][DCA]} mixed solvent, LLE screening experiments were performed using IL mixtures over the whole range of composition. For the same purpose, densities and viscosities of the IL mixtures were also measured at the temperature range of 293.15–353.15 K. Several predictive models were used to

---

* Corresponding author. Tel.: +34 91 394 51 19; fax: +34 91 394 42 43.
E-mail address: jgarcia@quim.ucm.es (J. García).

0378-3812/$ – see front matter © 2014 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.fluid.2013.12.008

Table 1
Suppliers and purities of chemicals.

Chemical	Supplier	Mass fraction purity	Analysis method
[emim][TCM][a]	Iolitec GmbH	0.98	NMR[c] and IC[d]
[emim][DCA][b]	Iolitec GmbH	0.98	NMR[c] and IC[d]
Toluene	Sigma–Aldrich	0.995	GC[e]
n-Heptane	Sigma–Aldrich	0.997	GC[e]

[a] [emim][TCM] = 1-ethyl-3-methylimidazolium tricyanomethanide.
[b] [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide.
[c] Nuclear magnetic resonance.
[d] Ion chromatography.
[e] Gas chromatography.

estimate extractive and physical properties of mixed ILs from the data of the pure ILs forming the mixture.

2. Materials and methods

2.1. Materials

[emim][TCM] and [emim][DCA] ILs were supplied by Iolitec GmbH with a purity higher than 0.98 in mass fraction. Water mass fractions in ILs were less than 2×10^{-3}, whereas halides mass fractions were less than 2×10^{-2}. *n*-Heptane and toluene over molecular sieves were purchased from Sigma-Aldrich. In Table 1, specifications of the chemicals used in this study are listed. Chemicals were employed as received without further purification. They were placed in a desiccator during the experimental period in tightly closed bottles, and the ILs were also handled in a glove box filled with dry nitrogen to avoid water hydration.

2.2. Liquid–liquid extraction. Experimental procedure and analysis

LLE experiments were gravimetrically prepared in 8 mL closed vials using a Mettler Toledo XS 205 balance with a precision of $\pm 1 \times 10^{-5}$ g. Filled vials were placed in a Labnet Vortemp 1550 shaking incubator at 313.2 ± 0.1 K and 800 rpm for 5 h to reach the LLE. After the mixing period, vials were located in a Labnet Accublock dry bath at 313.2 ± 0.1 K for 12 h to ensure a complete phase separation.

To study the influence of the composition in the mixed IL solvent on extractive properties, LLE screening experiments were made using {[emim][TCM] + [emim][DCA]} IL mixtures over the whole range of compositions as solvents. 2 mL of a hydrocarbon mixture formed by *n*-heptane and toluene with 10% of toluene in mass basis was added to the vials along with the same volume of mixed ILs. Studying the extractive properties of the mixed solvents in the screening and their physical properties the most appropriate composition of the IL mixture was selected. Subsequently, LLE data of the *n*-heptane (1) + toluene (2) + {[emim][TCM] (3) + [emim][DCA] (4)} pseudoternary system with a [emim][TCM] mole fraction of 0.8 in the mixed solvent at 313.2 K and atmospheric pressure were determined.

Compositions of the hydrocarbon-rich (raffinate) phases were measured using an Agilent 7890A gas chromatograph (GC) equipped with a flame ionization detector (FID) and a liquid autosampler Agilent 7693. Samples were taken in triplicate from the hydrocarbon-rich phases, being the average values compositions gathered in this work. A more detailed description of the method can be found elsewhere [20]. The absence of IL in the hydrocarbon-rich phases was checked using a Bruker Avance 500 MHz NMR spectrometer. Samples from raffinate phases were analyzed and signals corresponding to ILs were not found in the ^{1}H NMR spectra. This negligible solubility in the hydrocarbons is an important advantage of ILs compared with sulfolane. In the Shell-UOP Sulfolane process, a raffinate wash column is used to recover the sulfolane dissolved in the hydrocarbons [1] and this step would not be required using the IL-based solvents presented in this paper.

Extract (IL-rich) phases were analyzed using a multiple headspace extraction (MHE) method employing an Agilent 7890A GC with a Headspace Sampler Agilent 7697A. Triplicate samples were analyzed and the average compositions are shown here. Approximately 100 μL of IL-rich phases were added to 20 mL closed vials. Vials were shaken at 100 rpm and 393 K in the oven of the HS Sampler for 1 h to promote volatilization of the dissolved hydrocarbons in ILs. Five extractions from the vapor phase of the same vial were performed, calculating the hydrocarbon amounts in samples as the sum of peak areas in consecutive chromatograms. Correlation coefficients higher than 0.998 for the semi-logarithmic relationship between peak areas and the number of extraction were obtained, ensuring MHE successful measurements. Because of its nonvolatile nature, the IL amount was estimated as the difference between the weight of the initial sample in the vial and the mass of hydrocarbons measured by MHE. A detailed description of the MHE method can be found elsewhere [20].

2.3. Physical characterization of the IL-based solvents

Densities and dynamic viscosities of {[emim][TCM] + [emim][DCA]} binary IL mixtures were measured at temperatures between 293.15 and 353.15 K. Densities were determined employing an Anton Paar DMA-5000 oscillating U-tube, whereas dynamic viscosities were measured with an Anton Paar Automated Micro Viscometer (AMVn) based on the falling ball principle. The reliability of both methods was checked in our previous works by comparisons between experimental densities and dynamic viscosities with literature data for several pure ILs [18,19,22,23].

3. Results and discussion

3.1. Screening LLE experiments with {[emim][TCM] + [emim][DCA]} IL mixtures as solvents

Firstly, the liquid–liquid extraction of toluene from *n*-heptane/toluene mixtures with a 10% of toluene in mass basis using pure [emim][TCM] and [emim][DCA] ILs and their binary IL mixtures was studied. This screening was performed to select the most appropriate composition in the IL mixture. Experimental LLE data as a function of [emim][TCM] mole fraction (ϕ_3) in the mixed IL solvent are shown in Table 2 together with the estimated uncertainties of the compositions.

To made a comparative analysis on the performance of the IL-based solvents, *n*-heptane and toluene distribution ratios (D_i) and toluene/*n*-heptane selectivities ($\alpha_{2,1}$) were calculated from the LLE compositions according to Eqs. (1)–(3):

$$D_1 = \frac{x_1^{II}}{x_1^{I}} \quad (1)$$

$$D_2 = \frac{x_2^{II}}{x_2^{I}} \quad (2)$$

$$\alpha_{2,1} = \frac{x_2^{II} x_1^{I}}{x_2^{I} x_1^{II}} = \frac{D_2}{D_1} \quad (3)$$

where x denotes the hydrocarbon mole fraction and subscripts 1 and 2 refer to *n*-heptane and toluene, respectively. The superscript I indicates the raffinate phase, whereas the superscript II indicates the extract phase. Hydrocarbon distribution ratios and toluene/*n*-heptane selectivities of pure ILs and binary IL mixtures are presented in Table 2 along with the experimental LLE data.

Table 2
Experimental LLE data on mole fraction (x), distribution ratios (D_i), and toluene/n-heptane selectivities ($\alpha_{2,1}$) of the pseudoternary system {n-heptane (1) + toluene (2) + [emim][TCM] (3) + [emim][DCA] (4)}, as a function of [emim][TCM] mole fraction in the mixed IL solvent (ϕ_3) at 313.2 K, P = 0.1 MPa, and 10% of toluene in mass basis in hydrocarbon feeds.[a]

[emim][TCM] in solvent	Hydrocarbon-rich phase (upper layer)		IL-rich phase (lower layer)			D_1	D_2	$\alpha_{2,1}$
ϕ_3	$x_1{}^{\mathrm{I}}$	$x_2{}^{\mathrm{I}}$	$x_1{}^{\mathrm{II}}$	$x_2{}^{\mathrm{II}}$	$x_{3+4}{}^{\mathrm{II}}$			
0.00	0.9158	0.0842	0.0035	0.0230	0.9735	0.004	0.273	71.5
0.20	0.9163	0.0837	0.0042	0.0247	0.9711	0.005	0.295	64.4
0.40	0.9182	0.0818	0.0053	0.0274	0.9673	0.006	0.335	58.0
0.60	0.9219	0.0781	0.0065	0.0278	0.9657	0.007	0.356	50.5
0.80	0.9250	0.0750	0.0078	0.0295	0.9627	0.008	0.393	46.6
1.00	0.9247	0.0753	0.0094	0.0332	0.9574	0.010	0.441	43.4

[a] Standard uncertainties (u) are: $u(T)$ = 0.1 K, $u(P)$ = 1 kPa, $u(x_i{}^{\mathrm{I}})$ = 0.0007, $u(x_1{}^{\mathrm{II}})$ = 0.0010, $u(x_2{}^{\mathrm{II}})$ = 0.0019.

To study the effect of the composition in the IL mixture on D_2 and $\alpha_{2,1}$, experimental data are graphically plotted in Fig. 1 as symbols. In the same figure, values of toluene distribution ratio and toluene/n-heptane selectivity using sulfolane under the same conditions (10% of toluene in mass basis in hydrocarbon feed and 313.2 K) are shown as a solid line to be used as a benchmark [17]. As seen, D_2 increased as the [emim][TCM] mole fraction (ϕ_3) in the IL mixture increased, whereas the effect of ϕ_3 on $\alpha_{2,1}$ was the opposite. This result is consistent with the performance of the pure ILs, since the pure [emim][TCM] exhibited a higher toluene distribution ratio and a lower toluene/n-heptane selectivity than those of [emim][DCA] in the liquid–liquid extraction of toluene from n-heptane [20].

As can be observed in Fig. 1, the four binary IL mixtures showed simultaneously higher values of D_2 and $\alpha_{2,1}$ than the sulfolane values. Among the mixtures studied, a mixed IL solvent with a ϕ_3 of 0.8 could be the most suitable solvent, since this showed both extractive properties significantly higher than the sulfolane values. However, the physical properties of the IL mixtures should be considered in the selection of the composition in the mixed solvent.

The use of models to predict properties of mixed ILs is essential to reduce the number of experimental determinations due to the wide number of possible binary IL mixtures. In this work, we have study the reliability of the Yalkowsky and Roseman log-linear mixing rule in the prediction of D_2 and $\alpha_{2,1}$ of binary IL mixtures from the LLE data for the pure ILs [24]:

$$\ln x^{\mathrm{I\ or\ II}}_{\mathrm{i,predicted}} = \sum_{j=3}^{4} f_j \cdot \ln x^{\mathrm{I\ or\ II}}_{i,j} \qquad (4)$$

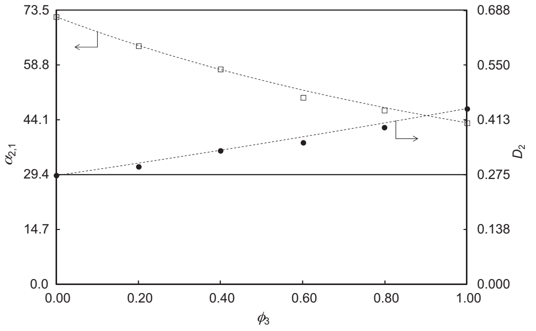


Fig. 1. Toluene distribution ratios (●) and toluene/n-heptane selectivities (□) of the n-heptane (1) + toluene (2) + {[emim][TCM] (3) + [emim][DCA] (4)} pseudoternary system at T = 313.2 K, as a function of [emim][TCM] mole fraction in the mixed IL solvent (ϕ_3). Dashed lines were calculated using Yalkowsky and Roseman model. Solid line indicates extractive properties using sulfolane at T = 313.2 K and 10% of toluene in mass basis in hydrocarbon feeds from Ref. [17].

where $x_{i,j}$ indicates the toluene or n-heptane mole fraction in LLE using a pure IL, j denotes the pure ILs, f_j is the initial volume fraction of IL in the mixed IL solvent in the absence of solutes, and $x_{\mathrm{i,predicted}}$ is the toluene or n-heptane mole fraction predicted using mixed solvents. Eq. (4) was used to predict the compositions in LLE of both extract and raffinate phases employing the different {[emim][TCM] + [emim][DCA]} mixtures.

From the compositions estimated in the mixed IL solvents by the Yalkowsky and Roseman equation, values of D_2 and $\alpha_{2,1}$ were calculated and plotted in Fig. 1 as dashed lines. As can be seen, experimental and predicted values were very similar. The average deviation between the experimental toluene distribution ratios and those predicted by Eq. (4) was 2.53%, whereas the average deviation of toluene/n-heptane selectivities was 1.43%. Hence, predictions of distribution ratios and selectivities using the Yalkowsky and Roseman log-linear mixing rule had high reliability and this equation can be used to predict extractive properties of mixed ILs from the LLE data of pure ILs.

3.2. *Physical characterization of {[emim][TCM] + [emim][DCA]} mixed IL solvents*

Dynamic viscosities and densities of {[emim][TCM] + [emim][DCA]} binary IL mixtures over the whole range of compositions were measured at temperatures between 293.15 and 353.15 K. Physical properties of the IL-based solvents are listed in Table 3 as a function of the temperature and the [emim][TCM] mole fraction. To check the reliability of the densities and viscosities gathered in this work, we have performed

Table 3
Densities (ρ) and dynamic viscosities (η) of the {[emim][TCM] (3) + [emim][DCA] (4)} mixed ILs as a function of temperature and [emim][TCM] mole fraction (ϕ_3) at P = 0.1 MPa.[a]

ϕ_3	T (K)						
	293.15	303.15	313.15	323.15	333.15	343.15	353.15
ρ/g cm^{-3}							
0.00	1.1046	1.0980	1.0914	1.0849	1.0785	1.0721	1.0658
0.20	1.0999	1.0932	1.0865	1.0799	1.0734	1.0669	1.0605
0.40	1.0958	1.0889	1.0822	1.0755	1.0688	1.0623	1.0557
0.60	1.0919	1.0850	1.0781	1.0713	1.0646	1.0579	1.0513
0.80	1.0884	1.0814	1.0745	1.0676	1.0608	1.0541	1.0474
1.00	1.0852	1.0781	1.0711	1.0641	1.0572	1.0504	1.0436
η/mPa s							
0.00	17.54	13.11	10.17	8.13	6.66	5.58	4.75
0.20	17.55	13.05	10.12	7.92	6.26	5.23	4.44
0.40	17.59	13.02	10.05	7.84	6.22	5.21	4.42
0.60	17.60	13.01	10.02	7.80	6.19	5.20	4.38
0.80	17.64	12.89	9.89	7.77	6.15	5.10	4.32
1.00	17.72	12.88	9.80	7.73	5.93	4.91	4.15

[a] Standard uncertainties u are, $u(T)$ = 0.01 K, $u(P)$ = 1 kPa, $u(\rho)$ = 0.0005 g cm^{-3}, $u(\eta)$ = 0.9%.

a comparison between our properties and literature data for the [emim][DCA] and [emim][TCM] pure ILs. The average deviations of the densities were 0.02% for the [emim][TCM] [25], and 0.05% [26], 0.23% [27], 0.32% [28], and 0.73% [29] for the densities of [emim][DCA]. The average absolute deviations between experimental and published dynamic viscosities of [emim][DCA] were 1.21% [28], 3.80% [26], and 5.16% [27]. The largest deviations were obtained for the dynamic viscosity data due to the important effect of impurities on the viscosity of ILs.

Physical properties of the IL mixtures have been compared to sulfolane values at the temperature used in the liquid–liquid extraction. Density and dynamic viscosity of the sulfolane are 1.253 g cm^{-3} and 8.1 mPa s at 313.2 K, respectively [20]. Comparing the sulfolane values with experimental densities and viscosities at the same temperature, binary IL mixtures have shown densities (1.074–1.086 g cm^{-3}) lower than that of sulfolane and viscosities (9.9–10.1 mPa s) slightly higher than the sulfolane value.

However, dynamic viscosities of the {[emim][TCM] + [emim][DCA]} IL mixtures studied in this paper were considerably lower than those of other promising IL-based solvents, such as the [3bmpy][B(CN)$_4$] (22.8 mPa s) [30], the [4bmpy][BF$_4$] (92.4 mPa s) [30,31], the {[4empy][Tf$_2$N] (0.3) + [emim][DCA] (0.7)} IL mixture (13.9 mPa s) [17], and the {[bpy][BF$_4$] (0.7) + [bpy][Tf$_2$N] (0.3)} IL mixture (53.1 mPa s) [15,18] at 313.2 K.

In order to select the optimal composition in the IL mixture to be used as extraction solvent, extractive and physical properties have been taken into account. In the initial screening, a mixed IL solvent with a ϕ_3 of 0.8 exhibited adequate values of toluene distribution ratio and toluene/*n*-heptane selectivity. As can be observed in Fig. 2, the effect of the [emim][TCM] mole fraction on the density and viscosity of the IL mixture was low, since the physical properties of both pure ILs were similar. Therefore, considering the extractive and the physical properties of the mixtures a [emim][TCM] mole fraction of 0.8 seems to be the most suitable composition in the IL mixture.

Densities and viscosities of the IL mixtures can be graphically analyzed in Fig. 2. As seen, the behavior of both physical properties has been almost ideal with intermediate values of IL mixtures between the properties of the pure ILs. In Fig. 2, properties of the mixtures estimated using predictive equations are also plotted to check the reliability of the methods. The group contribution method of Ye and Shreeve and extended by Gardas and Coutinho have been used to predict densities of the IL mixtures according to the following expression [32,33]:

$$\rho = \frac{\sum_{i=3}^{4} W_i \phi_i}{N(\sum_{i=3}^{4} V_{0,i}\phi_i)(a + bT + cP)} \tag{5}$$

where ρ denotes the estimated density of the IL mixture in kg m^{-3}, W_i is the molecular weight of the pure IL in kg mol^{-1}, N is the Avogadro constant, $V_{0,i}$ is the molecular volume of the pure IL estimated as the sum of the anion and cation volumes in m^3 molecule^{-1}, T is the temperature in K, and P is the pressure in MPa. The parameters a, b, and c published by Gardas and Coutinho were 8.005×10^{-1}, 6.652×10^{-4} K^{-1}, and -5.919×10^{-4} MPa^{-1}, respectively [33]. Volume of the [emim] cation (230 Å^3) was taken from the work of Gardas and Coutinho [33], whereas volumes of the [DCA] (86 Å^3) and [TCM] (127 Å^3) anions were calculated as the difference between the published volume of the [emim] cation and the molecular volume of [emim][DCA] and [emim][TCM] ILs calculated from experimental densities of pure ILs.

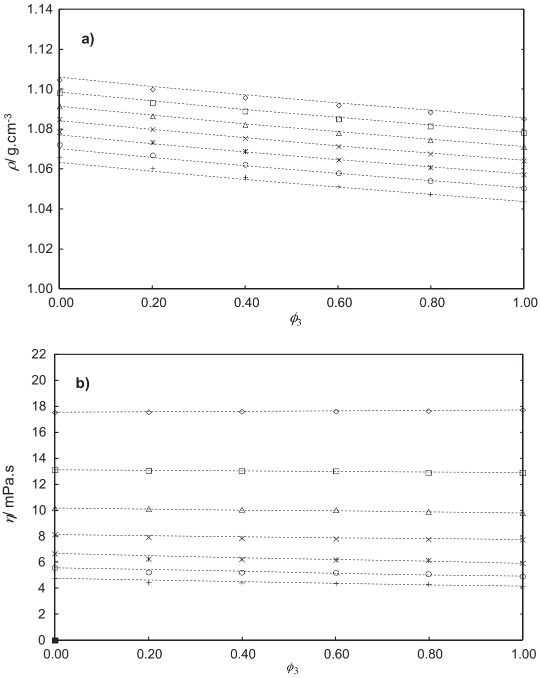


Fig. 2. Densities (a) and dynamic viscosities (b) of the {[emim][TCM] (3) + [emim][DCA] (4)} mixed IL solvent, as a function of [emim][TCM] mole fraction (ϕ_3) at several temperatures: ◊, 293.15 K; □ 303.15 K; Δ, 313.15 K; ×, 323.15 K; *, 333.15 K; ○, 343.15 K; +, 353.15 K. Dashed lines are densities estimated from the group contribution model of Ye and Shreeve and viscosities estimated from the Bingham mixing rule.

Predicted densities by the group contribution method of Ye and Shreeve are shown in Fig. 2 along with the experimental values for {[emim][TCM] + [emim][DCA]} IL mixtures. In previous works, this method has been revealed as a useful tool to estimate densities of pyridinium and imidazolium-based IL mixtures as a function of temperature and composition [17–19]. In this work, the average deviation between the experimental densities and predictions was 0.10%; therefore, the method proposed by Ye and Shreeve has also reliably estimated densities of the {[emim][TCM] + [emim][DCA]} mixtures.

In the scarce studies on viscosities of binary IL mixtures, several equations have been employed to predict dynamic viscosities of the mixtures from properties of pure ILs, being the most used the Bingham (Eq. (6)) and Grunberg–Nissan (Eq. (7)) mixing rules [18,19,34–37]:

$$\frac{1}{\eta} = \sum_{i=3}^{4} \frac{\phi_i}{\eta_i} \tag{6}$$

$$\log_{10}(\eta) = \sum_{i=3}^{4} \phi_i \log_{10}(\eta_i) \tag{7}$$

where η is the predicted viscosity of the mixed IL-based solvent, η_i indicates the viscosity of the pure IL at the same temperature and ϕ_i is the IL mole fraction in the binary IL mixture. Both mixing rules have been applied to the case of {[emim][TCM] + [emim][DCA]} mixtures. The average deviations of the predictions using the Bingham and Grunberg–Nissan mixing rules were 0.71% and 0.73%, respectively. Therefore, both equations have successfully predicted viscosities of the binary IL mixtures from data of the pure ILs. In Fig. 2, estimated viscosities by the Bingham mixing rule are plotted together with measured viscosities, since this mixing rule showed the lowest average deviation. As observed, experimental

Table 4
Experimental LLE data of the pseudoternary system *n*-heptane (1) + toluene (2) + {[emim][TCM] (3) + [emim][DCA] (4)} at $\phi_3 = 0.8$ on mole fraction (x), distribution ratios (D_i), and toluene/*n*-heptane selectivities ($\alpha_{2,1}$) at $T = 313.2$ K and $P = 0.1$ MPa.[a]

Feed (global composition)			Hydrocarbon-rich phase (upper layer)		IL-rich phase (lower layer)			D_1	D_2	$\alpha_{2,1}$
x_1	x_2	x_{3+4}	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	x_{3+4}^{II}			
0.5004	0.0000	0.4996	1.0000	0.0000	0.0070	0.0000	0.9930	0.007		
0.4882	0.0301	0.4817	0.9612	0.0388	0.0079	0.0153	0.9768	0.008	0.395	48.2
0.4764	0.0591	0.4645	0.9250	0.0750	0.0078	0.0295	0.9627	0.008	0.393	46.6
0.4370	0.1248	0.4382	0.8335	0.1665	0.0080	0.0681	0.9239	0.010	0.409	42.6
0.4095	0.1834	0.4071	0.7568	0.2432	0.0076	0.1025	0.8899	0.010	0.421	42.0
0.3545	0.2927	0.3528	0.6195	0.3805	0.0074	0.1722	0.8204	0.012	0.453	37.9
0.3155	0.3701	0.3144	0.5252	0.4748	0.0073	0.2353	0.7574	0.014	0.496	35.7
0.2819	0.4382	0.2799	0.4483	0.5517	0.0067	0.2711	0.7222	0.015	0.491	32.9
0.2354	0.5310	0.2336	0.3520	0.6480	0.0061	0.3325	0.6614	0.017	0.513	29.6
0.1778	0.6456	0.1766	0.2399	0.7601	0.0051	0.4153	0.5796	0.021	0.546	25.7
0.1228	0.7550	0.1222	0.1522	0.8478	0.0040	0.4639	0.5321	0.026	0.547	20.8
0.0000	0.8499	0.1501	0.0000	1.0000	0.0000	0.6439	0.3561		0.644	

[a] Standard uncertainties (u) are: $u(T) = 0.1$ K, $u(P) = 1$ kPa, $u(x_i) = 0.0006$, $u(x_i^{I}) = 0.0007$, $u(x_1^{II}) = 0.0010$, $u(x_2^{II}) = 0.0019$.

and predicted viscosities using Bingham mixing rule were in agreement. However, viscosities at higher temperatures than 323.15 K and at ϕ_3 lower than 0.5 were slightly lower than the predictions. This fact could be due to slight deviations from the ideal behavior at the temperatures and compositions indicated.

3.3. LLE of the n-heptane (1) + toluene (2) + {[emim][TCM] (3) + [emim][DCA] (4)} pseudoternary system at $\phi_3 = 0.8$, 313.2 K, and atmospheric pressure

3.3.1. Validation of experimental LLE results

Experimental LLE data of the *n*-heptane (1) + toluene (2) + {[emim][TCM] (3) + [emim][DCA] (4)} pseudoternary system at a [emim][TCM] mole fraction of 0.8 in the mixed solvent, atmospheric pressure, and 313.2 K are summarized in Table 4. The lie-lines are graphically shown in Fig. 3 as a ternary diagram.

The Othmer–Tobias correlation has been used to ensure the reliability of the LLE data [38]:

$$\ln\left(\frac{1-w_{(3+4)}^{II}}{w_{(3+4)}^{II}}\right) = a + b\ \ln\left(\frac{1-w_1^{I}}{w_1^{I}}\right) \tag{8}$$

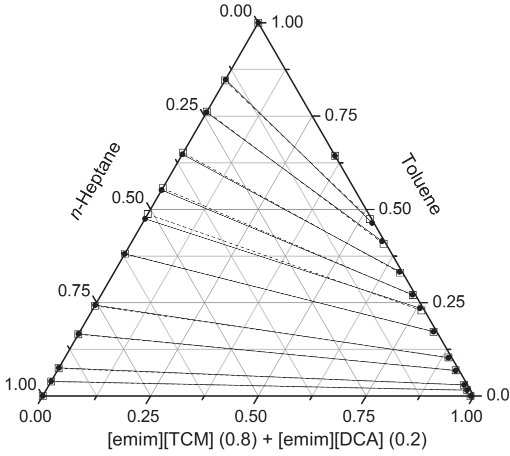


Fig. 3. LLE for the pseudoternary system *n*-heptane (1) + toluene (2) + {[emim][TCM] (3) + [emim][DCA] (4)} at $\phi_3 = 0.8$, $T = 313.2$ K and atmospheric pressure. Full points and solid lines are experimental tie-lines, and empty squares and dashed lines represent calculated LLE by the NRTL model.

Table 5
Parameters of the Othmer–Tobias correlation (a, b), regression coefficient (R^2), and standard deviation (σ) for the LLE data of the pseudoternary system *n*-heptane (1) + toluene (2) + {[emim][TCM] (3) + [emim][DCA] (4)} at $\phi_3 = 0.8$, $T = 313.2$ K, and $P = 0.1$ MPa.

a	b	R^2	σ
−1.9131	0.7739	0.9900	0.1209

where $w_{(3+4)}^{II}$ is the mass fraction of the IL mixture in the IL-rich phase, w_1^{I} is the mass fraction of *n*-heptane in the hydrocarbon-rich phase, and a and b are the fitted parameters listed in Table 5 along with the regression coefficient (R^2) and the standard deviation (σ). The value of R^2 equal to 0.99 and the low standard deviation (0.1209) confirm the degree of consistency of LLE data presented in this publication.

3.3.2. Correlation of LLE data by the NRTL model

Correlation of LLE of ternary systems formed by hydrocarbons and ILs is usually performed using the nonrandom two liquid (NRTL) model proposed by Renon and Prausnitz [39,40]. To correlate the LLE results of the pseudoternary system studied in this paper the Aspen Plus Simulator software was used. The binary interaction parameters $\Delta g_{ij}/R$ and $\Delta g_{ji}/R$ were optimized and the third nonrandomness parameter (α_{ij}) of the NRTL equation was fixed to 0.30, being the usual value of this parameter in fitting of LLE data of systems with ILs as extraction solvents [20,41–44].

Values of $\Delta g_{ij}/R$ and $\Delta g_{ji}/R$ parameters of the NRTL model for the pseudoternary system at 313.2 K and atmospheric pressure are listed in Table 6 together with the root mean square deviation (*rmsd*) of the fit calculated as follow:

$$rmsd = \left\{\frac{\sum_i\sum_l\sum_m (x_{ilm}^{exptl} - x_{ilm}^{calc})^2}{6k}\right\}^{1/2} \tag{9}$$

Table 6
Parameters of the NRTL model for the LLE data of the pseudoternary system *n*-heptane (1) + toluene (2) + {[emim][TCM] (3) + [emim][DCA] (4)} at $\phi_3 = 0.8$, $T = 313.2$ K, and $P = 0.1$ MPa.

Component	NRTL parameters			*rmsd*
i–*j*	$\Delta g_{ij}/R$ (K)	$\Delta g_{ji}/R$ (K)	α_{ij}	
1–2	−325.09	294.36	0.30	0.0041
1–(3 + 4)	−587.27	706.15	0.30	
2–(3 + 4)	4053.5	−2176.9	0.30	

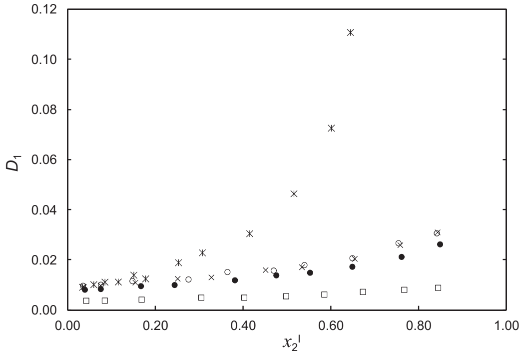


Fig. 4. *n*-Heptane distribution ratios at $T = 313.2$ K for the systems: ●, *n*-heptane (1) + toluene (2) + {[emim][TCM] (3) + [emim][DCA] (4)} at $\phi_3 = 0.8$; ○, *n*-heptane (1) + toluene (2) + [emim][TCM] (3) from Ref. [20]; □, *n*-heptane (1) + toluene (2) + [emim][DCA] (3) from Ref. [20]; ×, *n*-heptane (1) + toluene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$ from Ref. [17]; *, *n*-heptane (1) + toluene (2) + sulfolane (3) from Ref. [31].

where the subscripts i, l, and m indicate the component, phase, and tie line, respectively, *x* is mole fraction of the compound, and *k* denotes the number of tie lines measured. As seen in Fig. 3, predicted tie lines using the NRTL equation were almost coincident with the experimental LLE; thus, LLE data of the *n*-heptane + toluene + {[emim][TCM] + [emim][DCA]} pseudoternary system at 313.2 K and with a [emim][TCM] mole fraction of 0.8 in the mixed IL solvent have been adequately correlated to the NRTL model.

3.3.3. *n-Heptane and toluene distribution ratios and toluene/n-heptane selectivities*

To study the behavior of the {[emim][TCM] (0.8) + [emim][DCA] (0.2)} mixed solvent in the extraction of toluene from *n*-heptane, hydrocarbon distribution ratios (D_i) and toluene/*n*-heptane selectivities ($\alpha_{2,1}$) have been calculated according to Eqs. (1)–(3). Values of the extractive properties are listed in Table 4 together with the experimental LLE compositions.

Values of D_i and $\alpha_{2,1}$ using the {[emim][TCM] + [emim][DCA]} IL mixture with a ϕ_3 of 0.8 and those of sulfolane [31] and other promising IL-based solvents are plotted in Figs. 4–6 to perform a comparative analysis. Data using pure [emim][TCM] and [emim][DCA] ILs were selected to compare the extractive properties of the pure ILs with those of the mixed ILs [20]. The {[4empy][Tf$_2$N] (0.3) + [emim][DCA] (0.7)} IL mixture was also chosen as a benchmark, since this IL mixture has been proved to be an effective solvent in the extraction of toluene from alkanes [17].

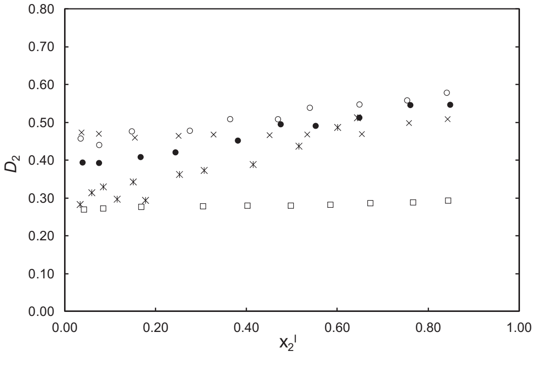


Fig. 5. Toluene distribution ratios at $T = 313.2$ K for the systems: ●, *n*-heptane (1) + toluene (2) + {[emim][TCM] (3) + [emim][DCA] (4)} at $\phi_3 = 0.8$; ○, *n*-heptane (1) + toluene (2) + [emim][TCM] (3) from Ref. [20]; □, *n*-heptane (1) + toluene (2) + [emim][DCA] (3) from Ref. [20]; ×, *n*-heptane (1) + toluene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$ from Ref. [17]; *, *n*-heptane (1) + toluene (2) + sulfolane (3) from Ref. [31].

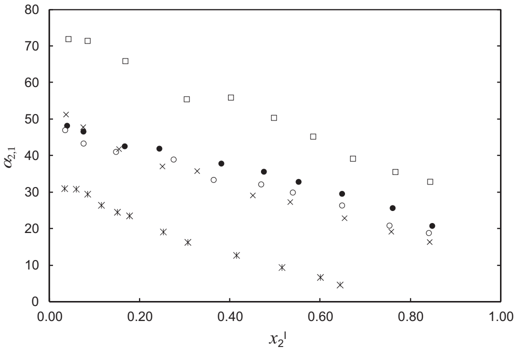


Fig. 6. Toluene/*n*-heptane selectivities at $T = 313.2$ K for the systems: ●, *n*-heptane (1) + toluene (2) + {[emim][TCM] (3) + [emim][DCA] (4)} at $\phi_3 = 0.8$; ○, *n*-heptane (1) + toluene (2) + [emim][TCM] (3) from Ref. [20]; □, *n*-heptane (1) + toluene (2) + [emim][DCA] (3) from Ref. [20]; ×, *n*-heptane (1) + toluene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$ from Ref. [17]; *, *n*-heptane (1) + toluene (2) + sulfolane (3) from Ref. [31].

As seen in Fig. 4, *n*-heptane distribution ratios using the {[emim][TCM] (0.8) + [emim][DCA] (0.2)} mixed solvent were substantially lower than those of sulfolane over the whole range of compositions, particularly at high contents of toluene in the raffinate phase. Considering the values using [emim][TCM] and [emim][DCA] pure ILs, D_1 of the mixed ILs were intermediate between those of the pure ILs, but closer to those of [emim][TCM] since this IL is the most abundant IL in the mixture. Therefore, the solubility of *n*-heptane in IL-based solvents could be finely tuned by mixing ILs in different proportions. Finally, values of D_1 using the mixed solvent studied in this work were slightly lower than the published values for the {[4empy][Tf$_2$N] (0.3) + [emim][DCA] (0.7)} IL mixture.

Experimental toluene distribution ratios for the {[emim][TCM] (0.8) + [emim][DCA] (0.2)} mixed ILs were higher than the sulfolane values, as can be observed in Fig. 5. As in the case of the *n*-heptane distribution ratios, values of D_2 using the IL mixture were between the extractive properties of the [emim][TCM] and [emim][DCA] pure ILs, confirming the intermediate behavior of the mixed solvent. Lastly, the IL mixture formed by [emim][TCM] and [emim][DCA] ILs shown D_2 higher than those of the {[4empy][Tf$_2$N] (0.3) + [emim][DCA] (0.7)} mixture at toluene mole fractions in raffinate higher than 0.5.

As can be observed in Fig. 6, toluene/*n*-heptane selectivities for the {[emim][TCM] (0.8) + [emim][DCA] (0.2)} mixed ILs were almost double than the sulfolane values. Hence, toluene extracted by the IL mixture had a considerably higher purity than that using sulfolane. It could imply lower number of stages in the extraction unit at industrial scale [14]. In addition, the maximum selectivity using the IL mixture (48.2) was higher than those of other promising ILs: [emim][Tf$_2$N] (24.2) [45], [empy][Tf$_2$N] (13.1) [45], and [hmim][Tf$_2$N] (12.5) [46]. As expected, experimental $\alpha_{2,1}$ of the mixed ILs were close to the selectivities using [emim][TCM] and were intermediate between the literature values of the pure ILs forming the IL mixture. To conclude, toluene/*n*-heptane selectivities of the IL mixture studied in this work were slightly higher than those of the {[4empy][Tf$_2$N] (0.3) + [emim][DCA] (0.7)} IL mixture at mole fractions of toluene in raffinate phase higher than 0.2 and very similar at lower toluene contents.

4. Conclusions

The aim of this work has been to study the performance of {[emim][TCM] + [emim][DCA]} IL mixtures as toluene extraction solvent from toluene/*n*-heptane mixtures. First, screening liquid–liquid extraction experiments have been carried out using binary IL mixtures over the whole range of composition. To select the most appropriate composition in the mixed solvent, extractive properties were calculated from LLE data, and densities and dynamic viscosities of the IL mixtures were measured as a function of temperature. Mixed ILs have shown higher toluene distribution ratios and toluene/*n*-heptane selectivities than the sulfolane values. Their dynamic viscosities have been slightly higher than that of sulfolane and their densities have been somewhat lower than the density of sulfolane. A {[emim][TCM] + [emim][DCA]} IL mixture with a [emim][TCM] mole fraction of 0.8 in the mixed solvent has been selected to obtain a IL-based solvent with adequate extractive and physical properties.

The reliability of several predictive models of properties of IL mixtures has been checked. Toluene distribution ratios and toluene/*n*-heptane selectivities of the mixed solvents have been adequately predicted by the Yalkowsky and Roseman model. The Ye and Shreeve group contribution method has been used to estimate the densities of the IL mixtures, and the Bingham and Grunberg–Nissan mixing rules have successfully predicted dynamic viscosities of mixed ILs.

LLE data of the *n*-heptane + toluene + {[emim][TCM] (0.8) + [emim][DCA] (0.2)} pseudoternary system have been obtained at 313.2 K and atmospheric pressure. The degree of consistency of the LLE results has been checked using the Othmer–Tobias correlation and the NRTL model has been employed to correlate the LLE data.

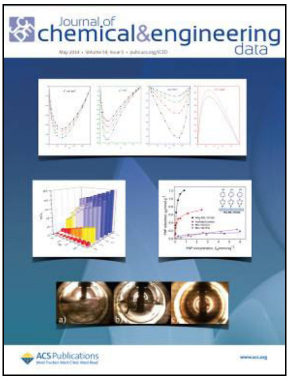
Extractive properties of the {[emim][TCM] (0.8) + [emim][DCA] (0.2)} mixed solvent have been substantially better than those of sulfolane. Hydrocarbons distribution ratios and toluene/*n*-heptane selectivities using the IL mixture have been intermediate between those of the pure ILs forming the mixture. In addition, the mixed solvent has shown higher toluene distribution ratios and toluene/*n*-heptane selectivities than those of the promising {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} IL-based solvent at high contents of toluene in hydrocarbon feeds. Considering their extractive and physical properties, the {[emim][TCM] + [emim][DCA]} IL mixture with a [emim][TCM] mole fraction of 0.8 in the mixed solvent could be considered as an alternative solvent in the liquid–liquid extraction of aromatics from their mixtures with aliphatic hydrocarbons.

Acknowledgments

The authors are grateful to the Ministerio de Economía y Competitividad (MINECO) of Spain and the Comunidad Autónoma de Madrid for financial support of Projects CTQ2011–23533 and S2009/PPQ–1545, respectively. Marcos Larriba thanks Ministerio de Educación, Cultura y Deporte for awarding him an FPU grant (Reference AP-2010-0318), and Pablo Navarro thanks MINECO for awarding him an FPI grant (Reference BES-2012-052312). The authors also thank Laura Aguilar for her contribution in this work.

References

[1] H.G. Franck, J.W. Staldelhofer, Industrial Aromatic Chemistry, Springer-Verlag, New York, 1988.
[2] G.W. Meindersma, A.J.G. Podt, A.B. de Haan, Fuel Process. Technol. 87 (2005) 59–70.
[3] S.T. Anjan, Chem. Eng. Prog. 102 (2006) 30–39.
[4] U. Domanska, A. Pobudkowska, M. Królikowski, Fluid Phase Equilib. 259 (2007) 173–179.
[5] R.M. Maduro, M. Aznar, Fluid Phase Equilib. 265 (2008) 129–138.
[6] J. García, A. Fernández, J.S. Torrecilla, M. Oliet, F. Rodríguez, Fluid Phase Equilib. 282 (2009) 117–120.
[7] E.J. González, N. Calvar, B. González, A. Domínguez, Fluid Phase Equilib. 291 (2010) 59–65.
[8] E.J. González, B. González, N. Calvar, A. Domínguez, Fluid Phase Equilib. 295 (2010) 249–254.
[9] J. García, S. García, J.S. Torrecilla, F. Rodríguez, Fluid Phase Equilib. 301 (2010) 62–66.
[10] A. Arce, M.J. Earle, H. Rodríguez, K.R. Seddon, A. Soto, Fluid Phase Equilib. 294 (2010) 180–186.
[11] G.W. Meindersma, A.R. Hansmeier, A.B. de Haan, Ind. Eng. Chem. Res. 49 (2010) 7530–7540.
[12] E.J. González, N. Calvar, E. Gómez, A. Domínguez, Fluid Phase Equilib. 303 (2011) 174–179.
[13] M.A. Kareem, F.S. Mjalli, M.A. Hashim, I.A. AlNashef, Fluid Phase Equilib. 314 (2012) 52–59.
[14] G.W. Meindersma, A.B. de Haan, Sci. China Chem. 55 (2012) 1488–1499.
[15] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, Chem. Eng. J. 180 (2012) 210–215.
[16] S. García, J. García, M. Larriba, A. Casas, F. Rodríguez, Fluid Phase Equilib. 337 (2013) 47–52.
[17] M. Larriba, P. Navarro, J. García, F. Rodríguez, Sep. Purif. Technol. 120 (2013) 392–401.
[18] M. Larriba, S. García, P. Navarro, J. García, F. Rodríguez, J. Chem. Eng. Data 57 (2012) 1318–1325.
[19] M. Larriba, S. García, P. Navarro, J. García, F. Rodríguez, J. Chem. Eng. Data 58 (2013) 1496–1504.
[20] M. Larriba, P. Navarro, J. García, F. Rodríguez, Ind. Eng. Chem. Res. 52 (2013) 2714–2720.
[21] P. Navarro, M. Larriba, E. Rojo, J. García, F. Rodríguez, J. Chem. Eng. Data 58 (2013) 2187–2193.
[22] M. Larriba, S. García, J. García, J.S. Torrecilla, F. Rodríguez, J. Chem. Eng. Data 56 (2011) 3589–3597.
[23] P. Navarro, M. Larriba, S. García, J. García, F. Rodríguez, J. Chem. Eng. Data 57 (2012) 1165–1173.
[24] S.H. Yalkowsky, T.J. Roseman, Chapter 3: Solubilization of drugs by cosolvents, in: Techniques of Solubilization of Drugs, Dekker, New York, 1981.
[25] A.P. Froba, M.H. Rausch, K. Krzeminski, D. Assenbaum, P. Wasserscheid, A. Leipertz, Int. J. Thermophys. 31 (2010) 2059–2077.
[26] C. Schreiner, S. Zugmann, R. Hartl, H.J. Gores, J. Chem. Eng. Data 55 (2010) 1784–1788.
[27] M.G. Freire, A.R.R. Teles, M.A.A. Rocha, B. Schröder, C.M.S.S. Neves, P.J. Carvalho, D.V. Evtuguin, L.M.N.B.F. Santos, J.A.P. Coutinho, J. Chem. Eng. Data 56 (2011) 4813–4822.
[28] E. Quijada-Maldonado, S. van der Boogaart, J.H. Lijbers, G.W. Meindersma, J. Chem. Thermodyn. 51 (2012) 51–58.
[29] C.L. Wong, A.N. Soriano, M.H. Li, Fluid Phase Equilib. 271 (2008) 43–52.
[30] G.W. Meindersma, B.T.J. Simons, A.B. de Haan, J. Chem. Thermodyn. 43 (2011) 1628–1640.
[31] G.W. Meindersma, A.J.G. Podt, A.B. de Haan, Fluid Phase Equilib. 247 (2006) 158–168.
[32] C. Ye, J.M. Shreeve, J. Phys. Chem. A 111 (2007) 1456–1461.
[33] R.L. Gardas, J.A.P. Coutinho, Fluid Phase Equilib. 263 (2008) 26–32.
[34] L. Grunberg, A.H. Nissan, Nature 164 (1949) 799–800.
[35] E.C. Bingham, Fluidity and Plasticity, McGraw-Hill, New York, 1922.
[36] P. Navia, J. Troncoso, L. Romaní, J. Solution Chem. 37 (2008) 677–688.
[37] A. Stoppa, R. Buchner, G. Hefter, J. Mol. Liq. 153 (2010) 46–51.
[38] D.F. Othmer, P.E. Tobias, Ind. Eng. Chem. 34 (1942) 693–696.
[39] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135–144.
[40] L.D. Simoni, Y. Lin, J.F. Brennecke, M.A. Stadtherr, Ind. Eng. Chem. Res. 47 (2008) 256–272.
[41] A. Marciniak, M. Królikowski, J. Chem. Thermodyn. 49 (2012) 154–158.
[42] J.P. Gutiérrez, G.W. Meindersma, A.B. de Haan, Ind. Eng. Chem. Res. 51 (2012) 11518–11529.
[43] M. Królikowski, K. Walczak, U. Domanska, J. Chem. Thermodyn. 65 (2013) 168–173.
[44] A.L. Revelli, F. Mutelet, J.N. Jaubert, J. Phys. Chem. B 114 (2010) 4600–4608.
[45] S. Corderi, N. Calvar, E. Gómez, A. Domínguez, Fluid Phase Equilib. 315 (2012) 46–52.
[46] S. Corderi, E.J. González, N. Calvar, A. Domínguez, J. Chem. Thermodyn. 52 (2012) 60–66.



Journal of Chemical & Engineering Data

Factor de impacto (2013): 2,05

Publicación 5:

Liquid−Liquid Extraction of Toluene from *n*-Alkanes using {[4empy][Tf$_2$N] + [emim][DCA]} Ionic Liquid Mixtures

Marcos Larriba, Pablo Navarro, Julián García, Francisco Rodríguez

Journal of Chemical & Engineering Data, 2014, 59, 1692-1699.

Journal of chemical & engineering data

Article

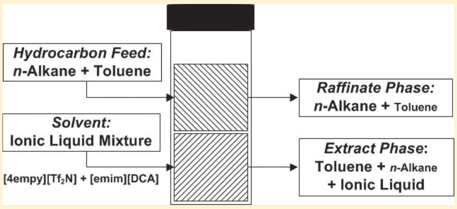
pubs.acs.org/jced

Liquid−Liquid Extraction of Toluene from *n*-Alkanes using {[4empy][Tf_2N] + [emim][DCA]} Ionic Liquid Mixtures

Marcos Larriba, Pablo Navarro, Julián García,* and Francisco Rodríguez

Department of Chemical Engineering, Complutense University of Madrid, E−28040 Madrid, Spain

ABSTRACT: Ionic liquids (ILs) as replacements of organic solvents currently used in the liquid−liquid extraction of aromatics could simplify extraction units as a result of their nonvolatile nature, reducing operating costs, and process steps. In this paper, we have studied the liquid−liquid extraction of toluene from *n*-hexane, *n*-octane, and *n*-nonane using binary mixtures of 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf_2N]) and 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) ILs at 313.2 K. Toluene distribution ratios and toluene/*n*-alkane selectivities employing the IL mixtures have been intermediate between those of pure ILs. The {[4empy][Tf_2N] + [emim][DCA]} IL mixture with a [4empy][Tf_2N] mole fraction of 0.3 has exhibited higher extractive properties than the sulfolane values. Toluene distribution ratios and toluene/*n*-alkane selectivities of the mixed ILs have been accurately predicted by the Yalkowsky and Roseman log−linear mixing rule. Liquid−liquid equilibria (LLE) data have been correlated to the NRTL model.



INTRODUCTION

The liquid−liquid extraction of aromatic hydrocarbons from their mixtures with aliphatic hydrocarbons is currently performed at industrial scale using organic solvents. The most traditional method was the Udex process developed by UOP and Dow Chemical that used diethylene glycol as solvent.[1] At present, the Sulfolane Shell UOP is the most employed industrial process in aromatic extraction. However, the sulfolane process has several drawbacks, such as the difficult regeneration of the solvent as a consequence of its high boiling point and the neccessity of recovering the sulfolane dissolved in the raffinate phase.[2]

ILs could be potential replacements of sulfolane. Their negligible solubilities in hydrocarbons could make unnecessary a raffinate wash column to remove dissolved ILs. In addition, solvent recovery from the extract stream could be easily achieved by a flash distillation at moderate temperatures due to the IL nonvolatile character.[3] Thus, an aromatic extraction unit using an IL-based solvent would have lower both energy consumption and process steps than those employing sulfolane. For this reason, pure ILs have been widely studied as aromatic extraction solvents in recent years.[4] Nevertheless, only a few number of ILs have simultaneously shown higher aromatic distribution ratios and aromatic/aliphatic selectivities than the sulfolane values. Moreover, their high viscosities could also limit their applications.[5] Mixing ILs has been recently proposed as a useful tool to tune physical and extractive properties of IL-based solvents. In this way, several binary IL mixtures have shown better extractive properties than those of sulfolane.[6−9]

In our recent work, we have suggested the use of the {[4empy][Tf_2N] + [emim][DCA]} binary IL mixtures as solvents in the extraction of aromatics.[8] These ILs were chosen because the pure [4empy][Tf_2N] IL showed higher aromatic distribution ratios than those of sulfolane.[10] On the other hand, the pure [emim][DCA] IL showed substantially higher toluene/*n*-heptane selectivities than the sulfolane values, low viscosity, and good thermal stability.[11] The {[4empy][Tf_2N] + [emim][DCA]} IL mixture with a [4empy][Tf_2N] mole fraction of 0.3 exhibited higher toluene/aliphatic selectivities and toluene distribution ratios than those of sulfolane in the liquid−liquid extraction of toluene from *n*-heptane, 2,3-dimethylpentane, and cyclohexane. In addition, this IL mixture had densities and dynamic viscosities comparable to the sulfolane values.[8]

In this paper, we have studied the performance of {[4empy][Tf_2N] + [emim][DCA]} IL mixtures in the liquid−liquid extraction of toluene from *n*-hexane, *n*-octane, and *n*-nonane, in order to evaluate the effect of increasing the *n*-alkane chain length on extractive properties. An initial screening was made using sulfolane and binary IL mixtures over the whole range of composition as toluene extraction solvents to choose the most suitable composition in the mixed solvent. Then, the LLE of the pseudoternary systems (*n*-hexane, *n*-octane, and *n*-nonane) + toluene + {[4empy][Tf_2N] + [emim][DCA]} at 313.2 K and atmospheric pressure were determined using the mixed IL solvent with the most adequate composition.

EXPERIMENTAL SECTION

Chemicals. [4empy][Tf_2N] and [emim][DCA] ILs were supplied by Iolitec GmbH with a purity higher than 0.99 and

Received: February 11, 2014
Accepted: April 23, 2014
Published: April 30, 2014

dx.doi.org/10.1021/je5001439 | J. Chem. Eng. Data 2014, 59, 1692−1699

0.98 in mass fraction, respectively. Halides mass fractions in ILs were less than $2\cdot10^{-2}$ and water mass fractions less than $2\cdot10^{-3}$. Toluene, *n*-hexane, *n*-octane, *n*-nonane, and sulfolane were purchased from Sigma-Aldrich. In Table 1, purities of the chemicals used in this paper are shown. All chemicals were used as received without further purification. ILs were stored in a desiccator in their tightly closed bottles, and the handling of them was performed in a glovebox under a dry nitrogen atmosphere to avoid water absorption.

Table 1. Suppliers and Purities of Chemicals

chemical	supplier	mass fraction purity	analysis method
[4empy][Tf_2N][a]	Iolitec GmbH	0.99	NMR[c] and IC[d]
[emim][DCA][b]	Iolitec GmbH	0.98	NMR[c] and IC[d]
toluene	Sigma−Aldrich	0.995	GC[e]
n-hexane	Sigma−Aldrich	0.99	GC[e]
n-octane	Sigma−Aldrich	0.99	GC[e]
n-nonane	Sigma−Aldrich	0.99	GC[e]
sulfolane	Sigma−Aldrich	0.99	GC[e]

[a] [4empy][Tf_2N] = 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide. [b] [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide. [c] Nuclear magnetic resonance. [d] Ion chromatography. [e] Gas chromatography.

Liquid−Liquid Extraction. Experimental Procedure and Analysis. Experiments of liquid−liquid extraction were made in 8 mL vials. Hydrocarbons and ILs were gravimetrically added to vials employing a Mettler Toledo XS 205 balance with a precision of $\pm\ 1\cdot10^{-5}$ g. The LLE was achieved using a Labnet Vortemp 1550 shaking incubator at (313.2 ± 0.1) K and 800 rpm for 5 h. Then, vials were located in a Labnet Accublock dry bath at (313.2 ± 0.1) K for 12 h to ensure the complete separation of raffinate and extract phases.

First, an initial screening was performed to select the most adequate composition in the {[4empy][Tf_2N] + [emim][DCA]} mixed solvent. For this purpose, 2 mL of hydrocarbon mixtures of (*n*-hexane, *n*-octane, or *n*-nonane) and toluene with 10% of toluene in mass basis were added to vials together with the same volume of pure [4empy][Tf_2N] and [emim][DCA] ILs and {[4empy][Tf_2N] + [emim][DCA]} binary IL mixtures with [4empy][Tf_2N] mole fraction in the mixed solvent of 0.2, 0.4, 0.6, and 0.8. LLE experiments using sulfolane as solvent were made under the same conditions to compare the extractive properties of the solvents. Afterward, the LLE of the pseudoternary systems (*n*-hexane, *n*-octane, or *n*-nonane) (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at 313.2 K and atmospheric pressure were studied using the IL mixed solvent with the selected composition in the screening.

Samples from hydrocarbon and sulfolane-rich phases were analyzed in an Agilent 7890A gas chromatograph (GC) provided with an Agilent 7693 liquid autosampler and a flame ionization detector (FID). Samples were taken in triplicate and the average compositions are the results shown in this paper. A more detailed description of the method can be found in our previous publication.[11] Raffinate phases were also analyzed using a Bruker Avance 500 MHz NMR spectrometer to check the absence of ILs. Signals corresponding to ILs were not found in ^1H NMR spectra; hence, the solubility of ILs in hydrocarbon-rich phases was assumed to be negligible. As explained in the Introduction, the negligible solubility of ILs in

Table 2. Experimental LLE Data on Mole Fraction (x), Distribution Ratios (D_i), and Toluene/*n*-Alkane Selectivities ($\alpha_{2,1}$) of the Pseudoternary Systems as a Function of [4empy][Tf_2N] Mole Fraction in the Mixed IL Solvent (ϕ_3) at T = 313.2 K, P = 0.1 MPa, and 10% of Toluene in Mass Basis in Hydrocarbon Feeds[a]

[4empy][Tf_2N] in solvent	hydrocarbon-rich phase (raffinate)		IL-rich phase (extract)					
ϕ_3	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	x_{3+4}^{II}	D_1	D_2	$\alpha_{2,1}$
			n-hexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}					
0.00	0.9209	0.0791	0.0037	0.0214	0.9749	0.004	0.270	66.6
0.20	0.9306	0.0694	0.0085	0.0311	0.9604	0.009	0.448	49.0
0.40	0.9342	0.0658	0.0142	0.0398	0.9460	0.015	0.606	40.0
0.60	0.9380	0.0620	0.0208	0.0476	0.9316	0.022	0.768	34.6
0.80	0.9410	0.0590	0.0274	0.0552	0.9174	0.029	0.936	32.1
1.00	0.9400	0.0600	0.0352	0.0623	0.9025	0.037	1.038	27.7
			n-octane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}					
0.00	0.9047	0.0953	0.0022	0.0226	0.9752	0.003	0.237	96.1
0.20	0.9137	0.0863	0.0051	0.0332	0.9617	0.006	0.385	69.2
0.40	0.9184	0.0816	0.0085	0.0411	0.9504	0.009	0.504	54.7
0.60	0.9221	0.0779	0.0132	0.0500	0.9368	0.014	0.641	44.8
0.80	0.9235	0.0765	0.0184	0.0585	0.9231	0.020	0.764	38.4
1.00	0.9257	0.0743	0.0245	0.0644	0.9111	0.026	0.867	32.8
			n-nonane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}					
0.00	0.9021	0.0979	0.0013	0.0259	0.9728	0.001	0.265	184.9
0.20	0.9085	0.0915	0.0025	0.0359	0.9616	0.003	0.393	142.7
0.40	0.9112	0.0888	0.0043	0.0457	0.9500	0.005	0.515	109.0
0.60	0.9175	0.0825	0.0072	0.0550	0.9378	0.008	0.666	84.9
0.80	0.9202	0.0798	0.0098	0.0624	0.9278	0.011	0.782	73.5
1.00	0.9233	0.0767	0.0139	0.0681	0.9180	0.015	0.887	59.0

[a] Standard uncertainties (u) are $u(T)$ = 0.1 K, $u(P)$ = 1 kPa, $u(x_i^{I})$ = 0.0008, $u(x_1^{II})$ = 0.0009, and $u(x_2^{II})$ = 0.0021.

Table 3. Experimental LLE Data on Mole Fraction (x), Distribution Ratios (D_i), and Toluene/n-Alkane Selectivities ($\alpha_{2,1}$) of n-Alkane (1) + Toluene (2) + Sulfolane (3) Ternary Systems at T = 313.2 K, P = 0.1 MPa, and 10% of Toluene in Mass Basis in Hydrocarbon Feeds[a]

hydrocarbon-rich phase (raffinate)			sulfolane-rich phase (extract)					
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}	D_1	D_2	$\alpha_{2,1}$
			n-hexane (1) + toluene (2) + sulfolane (3)					
0.9334	0.0630	0.0036	0.0113	0.0247	0.9640	0.012	0.392	32.4
			n-octane (1) + toluene (2) + sulfolane (3)					
0.9182	0.0773	0.0045	0.0076	0.0272	0.9652	0.008	0.352	42.5
			n-nonane (1) + toluene (2) + sulfolane (3)					
0.9157	0.0800	0.0043	0.0056	0.0278	0.9666	0.006	0.347	56.8

[a] Standard uncertainties (u) are $u(T)$ = 0.1 K, $u(P)$ = 1 kPa, $u(x_i^{\mathrm{I}})$ = 0.0008, and $u(x_i^{\mathrm{II}})$ = 0.0012.

hydrocarbons would be an advantage with respect to the sulfolane Shell-UOP process.

An Agilent 7890A GC provided with a Headspace (HS) Sampler Agilent 7697A was used to determine the composition of the IL-rich (extract) phases, employing a multiple headspace extraction (MHE) method. Approximately 100 μL of the IL-rich phases were taken in triplicate and gravimetrically added to 20 mL vials. In the oven of the HS sampler, vials were shaken at 100 rpm and 413 K for 1 h to evaporate the dissolved hydrocarbons in the ILs. Amounts of *n*-alkane and toluene in samples were calculated as the sum of peak areas of five consecutive extractions from the vapor phase of the same vial following mathematical relationships published by Kolb and Ettre.[12] As a consequence of the nonvolatile nature of ILs, the IL amount in the extract phase was the difference between the weight of the IL-rich phase sample added to the vial and the mass of toluene and *n*-alkane measured by MHE. A complete description of the MHE technique employed here can be found elsewhere.[11]

RESULTS AND DISCUSSION

Screening LLE Experiments Using {[4empy][Tf$_2$N] + [emim][DCA]} Binary IL Mixtures and Sulfolane at 313.2 K. To study the influence of the [4empy][Tf$_2$N] mole fraction in the mixed solvent (ϕ_3) on the liquid−liquid extraction of toluene from *n*-alkanes, we have performed LLE experiments employing IL mixtures as solvents over the whole range of compositions. Hydrocarbon feeds in the screening were composed of toluene and (*n*-hexane, *n*-octane, or *n*-nonane) binary mixtures with a 10% of toluene in mass basis. Experimental LLE data of the *n*-alkane (1) + toluene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} pseudoternary systems as a function of ϕ_3 at 313.2 K are shown in Table 2. In order to be used as benchmarks, experimental LLE data of *n*-alkane (1) + toluene (2) + sulfolane (3) systems under the same conditions are listed in Table 3.

To compare the performance of the solvents in the liquid−liquid extraction of toluene, *n*-alkane, and toluene distribution ratios (D_i) and toluene/*n*-alkane selectivities ($\alpha_{2,1}$) have been calculated from the LLE compositions using sulfolane and the IL-based solvents according to the following expressions:

$$D_1 = \frac{x_1^{\mathrm{II}}}{x_1^{\mathrm{I}}} \tag{1}$$

$$D_2 = \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}} \tag{2}$$

$$\alpha_{2,1} = \frac{x_2^{\mathrm{II}}x_1^{\mathrm{I}}}{x_2^{\mathrm{I}}x_1^{\mathrm{II}}} = \frac{D_2}{D_1} \tag{3}$$

where x is the mole fraction of the hydrocarbon and subscripts 1 and 2 indicate *n*-alkane and toluene, respectively. The superscript I refers to hydrocarbon-rich phase (raffinate) and the superscript II denotes the IL-rich or sulfolane-rich phase (extract). Toluene/*n*-alkane selectivities and hydrocarbon distribution ratios are shown in Tables 2 and 3 jointly with the experimental LLE data.

To facilitate the comparative analysis between the values of D_2 and $\alpha_{2,1}$ using the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixtures and sulfolane, the extractive properties are plotted in Figure 1. Values for the pure ILs and the IL mixtures are plotted as symbols, whereas the sulfolane values are plotted as solid lines. As can be observed, the effect of increasing the *n*-alkane chain length caused an increase in the values of toluene/*n*-alkane selectivity, whereas the values of toluene distribution ratio slightly decreased. In addition, extractive properties of the IL mixtures were intermediate between the values of D_2 and $\alpha_{2,1}$ employing the pure ILs. An increase in the [4empy][Tf$_2$N] mole fraction in the mixed solvent has increased toluene distribution ratios, whereas the effect on the toluene/*n*-alkane selectivities was the opposite. This trend can be explained by the study of the performance of the pure ILs in the liquid−liquid extraction of toluene from *n*-alkanes. The pure [4empy][Tf$_2$N] showed D_2 considerably higher and lower $\alpha_{2,1}$ than those for [emim][DCA].

As observed in Figure 1, toluene distribution ratios and toluene/*n*-alkane selectivities were simultaneously higher than the sulfolane values using {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} binary IL mixtures with ϕ_3 between 0.2 and 0.6 for the three pseudoternary systems studied. To select the optimal composition of the mixed IL solvent, their extractive and physical properties have to be considered. In our previous work, a {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture with a ϕ_3 of 0.3 showed densities and viscosities comparable to the sulfolane values, and extractive properties considerably higher than those using sulfolane in the liquid−liquid extraction of toluene from *n*-heptane, 2,3-dimethylpentane, and cyclohexane.[8] Therefore, it seems to be appropriate the selection of a [4empy][Tf$_2$N] mole fraction of 0.3 in the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture to obtain a mixed solvent with adequate physical properties and higher extractive properties than those of sulfolane in the extraction of toluene from *n*-hexane, *n*-octane, and *n*-nonane.

The Yalkowsky and Roseman log−linear mixing rule has been recently revealed as a useful tool to predict the extractive

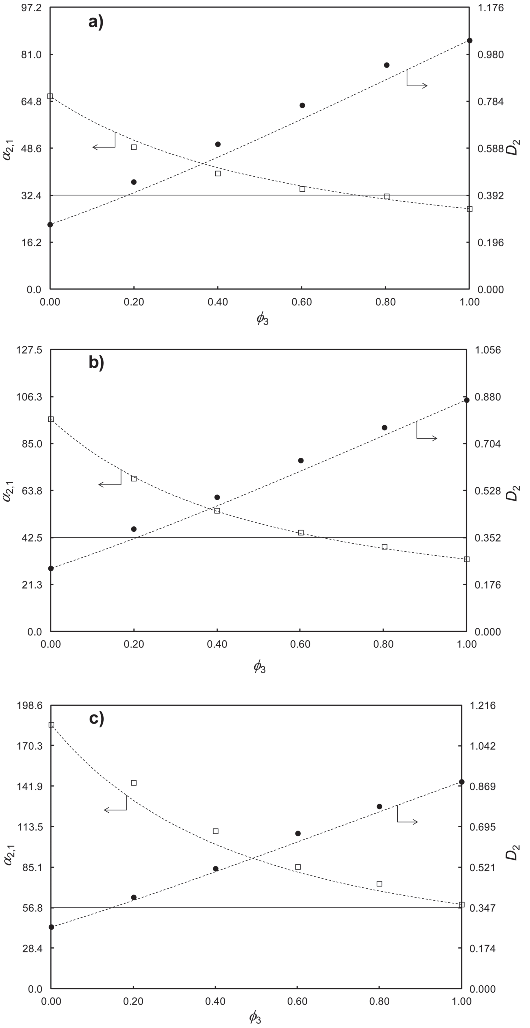


Figure 1. Toluene distribution ratios (●) and toluene/*n*-alkane selectivities (□) of the pseudoternary systems: (a) *n*-hexane (1) + toluene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)}; (b) *n*-octane (1) + toluene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)}; (c) *n*-nonane (1) + toluene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at T = 313.2 K and 10% of toluene in mass basis in hydrocarbon feeds, as a function of [4empy][Tf$_2$N] mole fraction in the mixed IL solvent (ϕ_3). Dashed lines were calculated using Yalkowsky and Roseman model and solid lines represent sulfolane values at T = 313.2 K and 10% of toluene in mass basis in hydrocarbon feeds.

properties of IL mixtures from the LLE data for the pure ILs forming the mixture:[8,13,14]

$$\ln x_{\mathrm{i,predicted}}^{\mathrm{I\ or\ II}} = \sum_{\mathrm{j}=3}^{4} f_{\mathrm{j}} \ln x_{\mathrm{i,j}}^{\mathrm{I\ or\ II}} \qquad (4)$$

where $x_{i,j}$ is the hydrocarbon mole fraction employing a pure IL as solvent, j refers to the pure ILs, f_j is the initial volume fraction of IL in the binary IL mixture in the absence of solutes, and $x_{i,\mathrm{predicted}}$ is the estimated hydrocarbon mole fraction in each

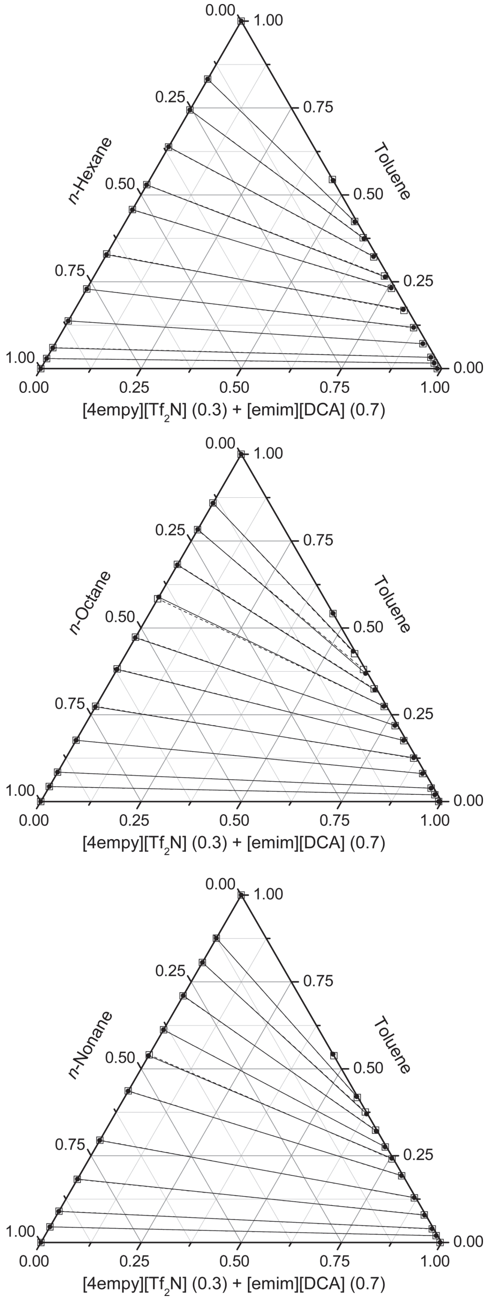


Figure 2. LLE for the pseudoternary systems *n*-alkane (1) + toluene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3, T = 313.2 K, and P = 0.1 MPa. Full points and solid lines are experimental tie lines, and empty squares and dashed lines represent calculated LLE by the NRTL model.

Table 4. Experimental LLE Data of the Pseudoternary Systems *n*-Alkane (1) + Toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3 on Mole Fraction (x), Distribution Ratios (D_i), and Toluene/*n*-Alkane Selectivities ($\alpha_{2,1}$) at T = 313.2 K and P = 0.1 MPa[a]

feed (global composition)			hydrocarbon-rich phase (raffinate)		IL-rich phase (extract)					
x_1	x_2	x_{3+4}	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	x_{3+4}^{II}	D_1	D_2	$\alpha_{2,1}$
n-hexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3										
0.5391	0.0000	0.4609	1.0000	0.0000	0.0106	0.0000	0.9894	0.011		
0.4904	0.0267	0.4829	0.9707	0.0293	0.0105	0.0158	0.9737	0.011	0.539	49.9
0.4791	0.0492	0.4717	0.9399	0.0601	0.0106	0.0324	0.9570	0.011	0.539	47.8
0.4511	0.1009	0.4480	0.8626	0.1374	0.0107	0.0715	0.9178	0.012	0.520	42.0
0.4131	0.1767	0.4102	0.7707	0.2293	0.0108	0.1183	0.8709	0.014	0.516	36.8
0.3742	0.2526	0.3732	0.6721	0.3279	0.0103	0.1701	0.8196	0.015	0.519	33.9
0.3190	0.3610	0.3200	0.5430	0.4570	0.0098	0.2321	0.7581	0.018	0.508	28.1
0.2869	0.4235	0.2896	0.4715	0.5285	0.0090	0.2642	0.7268	0.019	0.500	26.2
0.2381	0.5248	0.2371	0.3619	0.6381	0.0085	0.3228	0.6687	0.023	0.506	21.5
0.1855	0.6316	0.1829	0.2556	0.7444	0.0070	0.3741	0.6189	0.027	0.503	18.4
0.1300	0.7405	0.1295	0.1669	0.8331	0.0053	0.4225	0.5722	0.032	0.507	16.0
0.0000	0.8526	0.1474	0.0000	1.0000	0.0000	0.5419	0.4581		0.542	
n-octane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}at ϕ_3 = 0.3										
0.5023	0.0000	0.4977	1.0000	0.0000	0.0070	0.0000	0.9930	0.007		
0.4835	0.0328	0.4837	0.9570	0.0430	0.0069	0.0197	0.9734	0.007	0.458	63.5
0.4643	0.0656	0.4701	0.9154	0.0846	0.0071	0.0385	0.9544	0.008	0.455	58.7
0.4305	0.1373	0.4322	0.8235	0.1765	0.0071	0.0808	0.9121	0.009	0.458	53.1
0.3924	0.2129	0.3947	0.7270	0.2730	0.0069	0.1261	0.8670	0.009	0.462	48.7
0.3493	0.3003	0.3504	0.6192	0.3808	0.0069	0.1761	0.8170	0.011	0.462	41.5
0.3117	0.3761	0.3122	0.5279	0.4721	0.0067	0.2193	0.7740	0.013	0.465	36.6
0.2604	0.4788	0.2608	0.4112	0.5888	0.0068	0.2743	0.7189	0.017	0.466	28.2
0.2161	0.5695	0.2144	0.3182	0.6818	0.0057	0.3217	0.6726	0.018	0.472	26.3
0.1601	0.6789	0.1610	0.2166	0.7834	0.0049	0.3692	0.6259	0.023	0.471	20.8
0.1138	0.7742	0.1120	0.1405	0.8595	0.0042	0.4327	0.5631	0.030	0.503	16.8
0.0000	0.8526	0.1474	0.0000	1.0000	0.0000	0.5419	0.4581		0.542	
n-nonane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}at ϕ_3 = 0.3										
0.5004	0.0000	0.4996	1.0000	0.0000	0.0037	0.0000	0.9963	0.004		
0.4842	0.0348	0.4810	0.9550	0.0450	0.0036	0.0196	0.9768	0.004	0.436	115.5
0.4652	0.0707	0.4641	0.9103	0.0897	0.0037	0.0394	0.9569	0.004	0.439	108.1
0.4295	0.1431	0.4274	0.8177	0.1823	0.0035	0.0785	0.9180	0.004	0.431	100.6
0.3858	0.2304	0.3838	0.7062	0.2938	0.0036	0.1289	0.8675	0.005	0.439	86.1
0.3267	0.3485	0.3248	0.5642	0.4358	0.0034	0.1927	0.8039	0.006	0.442	73.4
0.2814	0.4383	0.2803	0.4621	0.5379	0.0032	0.2421	0.7547	0.007	0.450	65.0
0.2484	0.5034	0.2482	0.3877	0.6123	0.0031	0.2755	0.7214	0.008	0.450	56.3
0.2005	0.5990	0.2005	0.2894	0.7106	0.0028	0.3209	0.6763	0.010	0.452	46.7
0.1492	0.7018	0.1490	0.1942	0.8058	0.0023	0.3702	0.6275	0.012	0.459	38.8
0.1029	0.7941	0.1030	0.1245	0.8755	0.0018	0.4199	0.5783	0.014	0.480	33.2
0.0000	0.8526	0.1474	0.0000	1.0000	0.0000	0.5419	0.4581		0.542	

[a] Standard uncertainties (u) are $u(T)$ = 0.1 K, $u(P)$ = 1 kPa, $u(x_i)$ = 0.0007, $u(x_i^{I})$ = 0.0008, $u(x_1^{II})$ = 0.0009, and $u(x_2^{II})$ = 0.0021.

phase using the IL mixture. Predicted toluene distribution ratios and toluene/*n*-alkane selectivities for the (*n*-hexane, *n*-octane, or *n*-nonane) + toluene + {[4empy][Tf_2N] + [emim][DCA]} pseudoternary systems using eq 4 are shown in Figure 1 as dashed lines. As seen, the predictions were in agreement with the experimental data using mixed ILs. The maximum average deviation of the predicted D_2 was 8.4% in the *n*-hexane + toluene + {[4empy][Tf_2N] + [emim][DCA]} system, whereas the maximum deviation of the predictions of $\alpha_{2,1}$ was obtained for the *n*-nonane + toluene + {[4empy][Tf_2N] + [emim][DCA]} system with a value of 7.1%. Hence, Yalkowsky and Roseman log−linear equation has successfully predicted toluene distribution ratios and toluene/*n*-alkane selectivites using IL mixtures from the LLE data of [4empy][Tf_2N] and [emim][DCA] pure ILs.

LLE Data for *n*-Alkane (1) + Toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} Pseudoternary Systems at ϕ_3 = 0.3, 313.2 K, and Atmospheric Pressure. Experimental LLE data for (*n*-hexane, *n*-octane, or *n*-nonane) (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} pseudoternary systems with a [4empy][Tf_2N] mole fraction of 0.3 in the mixed IL solvent at 313.2 K and atmospheric pressure are plotted as ternary diagrams in Figure 2 and summarized in Table 4.

Correlation of LLE Data. The nonrandom two liquid (NRTL) thermodynamic model developed by Renon and Prausnitz has been widely used in the correlation of LLE data of ternary systems formed by hydrocarbons and ILs as solvents.[15,16] In this work, we have determined the parameters of the NRTL model for the three pseudoternary systems

Table 5. Values of the NRTL Parameters Obtained from LLE Data by Regression for the *n*-Alkane (1) + Toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} Pseudoternary Systems at ϕ_3 = 0.3, *T* = 313.2 K, and *P* = 0.1 MPa

component	NRTL parameters			
i − *j*	$(\Delta g_{ij}/R)$/K	$(\Delta g_{ji}/R)$/K	α_{ij}	rmsd
n-hexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3				
1 − 2	−141.96	181.73	0.30	0.0007
1 − (3 + 4)	311.90	−168.63	0.30	
2 − (3 + 4)	4244.1	−2159.4	0.30	
n-octane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}at ϕ_3 = 0.3				
1 − 2	−48.109	8.2395	0.30	0.0024
1 − (3 + 4)	600.75	−264.31	0.30	
2 − (3 + 4)	3811.2	−1981.1	0.30	
n-nonane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}at ϕ_3 = 0.3				
1 − 2	23.247	−37.405	0.30	0.0008
1 − (3 + 4)	2196.0	−1066.1	0.30	
2 − (3 + 4)	3558.5	−1853.9	0.30	

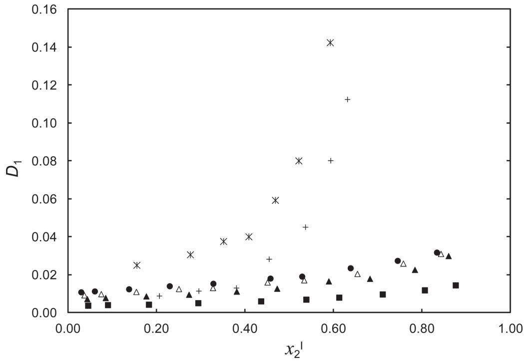


Figure 3. *n*-Alkane distribution ratios (D_1) at *T* = 313.2 K for the systems: ●, *n*-hexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3; ▲, *n*-octane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3; ■, *n*-nonane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3; Δ, *n*-heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3 (from ref 8). *, *n*-hexane (1) + toluene (2) + sulfolane (3) at 298.2 K (from ref 22). +, *n*-octane (1) + toluene (2) + sulfolane (3) at *T* = 323.2 K (from ref 23).

studied employing Aspen Plus simulator. The binary interaction parameters $\Delta g_{ij}/R$ and $\Delta g_{ji}/R$ were calculated by the software and the third nonrandomness parameter (α_{ij}) of the NRTL equation was fixed to 0.3, since α_{ij} is usually set to this value in systems formed by organic solvents and ILs.[11,17−21] In Table 5, parameters of the NRTL model are listed together with the root-mean-square deviation (rmsd) calculated as:

$$\text{rmsd} = \left\{ \frac{\sum_i \sum_l \sum_m (x_{ilm}^{\text{exptl}} - x_{ilm}^{\text{calc}})^2}{6k} \right\}^{1/2} \quad (5)$$

where the subscripts *i*, *l*, and *m* refer to the component, phase, and tie line, respectively, *x* denotes mole fraction, and *k* is the number of tie lines. As seen in Figure 2, experimental and fitted tie lines were almost coincident; therefore, the LLE data were successfully correlated using the NRTL equation.

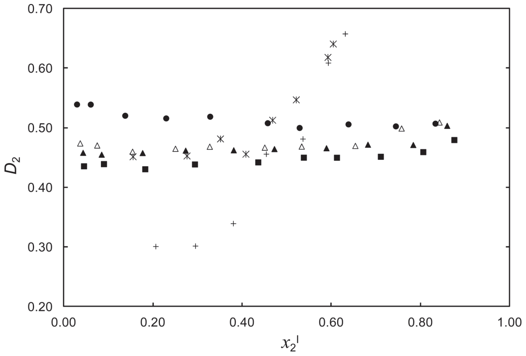


Figure 4. Toluene distribution ratios (D_2) at *T* = 313.2 K for the systems: ●, *n*-hexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3; ▲, *n*-octane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3; ■, *n*-nonane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3; Δ, *n*-heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3 (from ref 8). *, *n*-hexane (1) + toluene (2) + sulfolane (3) at 298.2 K (from ref 22). +, *n*-octane (1) + toluene (2) + sulfolane (3) at *T* = 323.2 K (from ref 23).

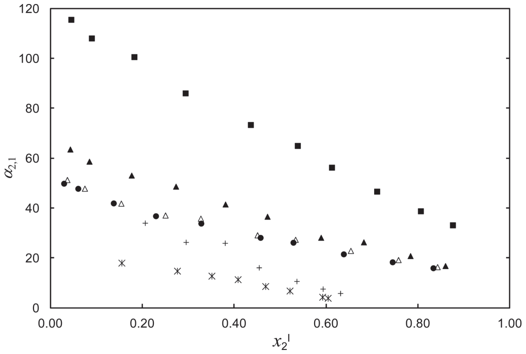


Figure 5. Toluene/*n*-alkane selectivities ($\alpha_{2,1}$) at *T* = 313.2 K for the systems: ●, *n*-hexane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3; ▲, *n*-octane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3; ■, *n*-nonane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3; Δ, *n*-heptane (1) + toluene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at ϕ_3 = 0.3 (from ref 8). *, *n*-hexane (1) + toluene (2) + sulfolane (3) at 298.2 K (from ref 22). +, *n*-octane (1) + toluene (2) + sulfolane (3) at *T* = 323.2 K (from ref 23).

Hydrocarbon Distribution Ratios and Toluene/*n*-Alkane Selectivities. To analyze the results obtained in the liquid−liquid extraction of toluene from *n*-alkanes using the {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} IL mixture, we have calculated the hydrocarbon distribution ratios and toluene/*n*-alkane selectivities according to eqs 1 to 3. Values of extractive properties are listed in Table 4 along with the experimental compositions.

n-Hexane, *n*-octane, and *n*-nonane distribution ratios employing the {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} IL mixture as solvent are plotted in Figure 3, together with the recently published values of *n*-heptane distribution ratio employing the same IL mixture in the extraction of *n*-heptane from toluene.[8] In the same figure, *n*-hexane and *n*-octane distribution ratios in the extraction of toluene from those *n*-alkanes using sulfolane are also shown to be used as benchmarks.[22,23]

As observed, *n*-alkane distribution ratios have decreased with the *n*-alkane length chain, being the *n*-hexane the alkane with the highest solubility in the IL mixture, whereas the values of *n*-heptane distribution ratios have been intermediate between those of *n*-hexane and *n*-octane.[8] This trend is in agreement with the predictions using COSMO-RS published by Ferreira et al.; it can be explained because of an increase of the *n*-alkane length chain increases the entropy of the system making difficult the packing between the ions of the IL and the *n*-alkane molecules.[24] On the other hand, *n*-hexane distribution ratios using the IL mixture have been substantially lower than the literature values using sulfolane over the whole range of composition, whereas values of *n*-octane distribution ratios have been lower than those employing sulfolane, particularly at high contents of toluene in the hydrocarbon-rich phase.

Toluene distribution ratios of the pseudoternary systems (*n*-hexane, *n*-octane, or *n*-nonane) + toluene + {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} are shown in Figure 4, along with published values employing the same IL mixture in the separation of toluene from *n*-heptane[8] and D_2 using sulfolane in the liquid−liquid extraction of toluene from *n*-hexane[22] and *n*-octane.[23]

The highest values of D_2 have been obtained in the extraction of *n*-hexane from toluene, followed by the values in the extraction of *n*-octane and *n*-nonane. Therefore, values of the toluene distribution ratio have been affected by the *n*-alkane chain length. A similar trend was observed by González et al. in the liquid−liquid extraction of toluene from *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane using [emim][$EtSO_4$].[25] Published values of toluene distribution ratios of the pseudoternary system *n*-heptane + toluene + {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)}[8] have been intermediate between the values in the extraction of toluene from *n*-hexane and *n*-octane using the same IL mixture. To conclude, D_2 values employing the IL-based solvent, at mole fractions of toluene in raffinate phase lower than 0.5 have been higher than those of sulfolane in the liquid−liquid extraction of toluene from its mixtures with *n*-hexane and *n*-octane.[22,23] Hence, the IL mixture could be an alternative solvent to sulfolane in the separation of aromatic hydrocarbons from feeds with low content of aromatics compounds.

Experimental values of toluene/*n*-alkane selectivities using the {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} IL mixture and literature values with sulfolane[22,23] are plotted in Figure 5. As observed, the highest values of $\alpha_{2,1}$ have been obtained in the extraction of toluene from *n*-nonane using the IL-based solvent. Toluene/*n*-alkane selectivities have increased with the *n*-alkane chain length, being the values of toluene/*n*-hexane selectivities close to the literature values of toluene/*n*-heptane selectivities employing the same IL mixture.[8] The effect of *n*-alkane chain length on selectivity was previously described in the extraction of toluene from *n*-alkanes using [emim][$EtSO_4$].[25] The observed trend is in agreement with the predictions of COSMO-RS and it is due to the increase of the entropy of the system caused by increasing the *n*-alkane chain length.[24] Finally, toluene/*n*-hexane and toluene/*n*-octane selectivities with the IL mixture have been approximately twice the sulfolane values;[22,23] therefore, extracted toluene using the IL-based solvent had a considerably higher purity than that obtained with sulfolane.

■ CONCLUSIONS

In this paper, we have presented the results obtained in the liquid−liquid extraction of toluene from *n*-hexane, *n*-octane, and *n*-nonane using binary mixtures of [4empy][Tf_2N] and [emim][DCA] ILs as solvents at 313.2 K and atmospheric pressure. In an initial screening, we have studied the extraction of toluene from *n*-alkanes with sulfolane and binary IL mixtures over the whole range of composition in the mixed solvent, to select the most appropriate composition in the IL mixture. Experimental extractive properties of the mixed solvents were in agreement with the values calculated by the Yalkowsky and Roseman log−linear mixing rule from LLE data employing the pure ILs as solvents. The mixture {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} has been chosen to obtain a solvent with toluene distribution ratios and toluene/*n*-alkane selectivities simultaneously higher than those of sulfolane under the same conditions and adequate densities and viscosities to be applied at industrial scale.

The LLE of the pseudoternary systems (*n*-hexane, *n*-octane, or *n*-nonane) + toluene + {[4empy][Tf_2N] + [emim][DCA]} with a [4empy][Tf_2N] mole fraction of 0.3 in the mixed solvent were studied at 313.2 K and atmospheric pressure. The NRTL model was employed to correlate the LLE data.

An increase of the *n*-alkane chain length increased the values of toluene/*n*-alkane selectivities but it caused a decrease in *n*-alkane and toluene distribution ratios. The {[4empy][Tf_2N] (0.3) + [emim][DCA] (0.7)} IL mixture showed substantially higher extractive properties than those using sulfolane, particularly at mole fractions of toluene in raffinate phase lower than 0.5. Therefore, this IL-based solvent could be a potential solvent to extract aromatic hydrocarbons from industrial streams with low contents of aromatics.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +34 91 394 51 19. Fax: +34 91 394 42 43. E-mail: jgarcia@quim.ucm.es.

Funding

The authors are grateful to the Ministerio de Economía y Competitividad (MINECO) of Spain and the Comunidad Autónoma de Madrid for financial support of Projects CTQ2011-23533 and S2009/PPQ-1545, respectively. M.L. thanks Ministerio de Educación, Cultura y Deporte for awarding him an FPU grant (Reference AP-2010-0318) and P.N. also thanks MINECO for awarding him an FPI grant (Reference BES-2012-052312).

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Franck, H. G.; Staldelhofer, J. W. *Industrial Aromatic Chemistry*; Springer-Verlag: Berlin, 1988.

(2) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Selection of Ionic Liquids for the Extraction of Aromatic Hydrocarbons from Aromatic/aliphatic Mixtures. *Fuel Process. Technol.* **2005**, *87*, 59−70.

(3) Anjan, S. T. Ionic Liquid for Aromatic Extraction: Are They Ready? *Chem. Eng. Prog.* **2006**, *102*, 30−39.

(4) Meindersma, G. W.; Hansmeier, A. R.; de Haan, A. B. Ionic Liquids for Aromatics Extraction. Present Status and Future Outlook. *Ind. Eng. Chem. Res.* **2010**, *49*, 7530−7540.

(5) Meindersma, G. W.; de Haan, A. B. Cyano-containing Ionic Liquids for the Extraction of Aromatic Hydrocarbons from an Aromatic/aliphatic Mixture. *Sci. China Chem.* **2012**, *55*, 1488−1499.

(6) Fletcher, K. A.; Baker, S. N.; Baker, G. A.; Pandey, S. Probing Solute and Solvent Interactions within Binary Ionic Liquid Mixtures. *New J. Chem.* **2003**, *27*, 1706−1712.

(7) García, S.; Larriba, M.; García, J.; Torrecilla, J. S.; Rodríguez, F. Liquid−liquid Extraction of Toluene from Heptane Using Binary Mixtures of *N*−butylpyridinium Tetrafluoroborate and *N*−butylpyridinium Bis(trifluoromethylsulfonyl)imide Ionic Liquids. *Chem. Eng. J.* **2012**, *180*, 210−215.

(8) Larriba, M.; Navarro, P.; García, J.; Rodríguez, F. Separation of Toluene from *n*-Heptane, 2,3-Dimethylpentane, and Cyclohexane using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids as Extraction Solvents. *Sep. Purif. Technol.* **2013**, *120*, 392−401.

(9) Potdar, S.; Anantharaj, R.; Banerjee, T. Aromatic Extraction Using Mixed Ionic Liquids: Experiments and COSMO-RS Predictions. *J. Chem. Eng. Data* **2012**, *57*, 1026−1035.

(10) García, J.; García, S.; Torrecilla, J. S.; Rodríguez, F. Solvent Extraction of Toluene from Heptane with the Ionic Liquids *N*−Ethylpyridinium Bis(trifluoromethylsulfonyl)imide and *z*−Methyl−*N*−ethylpyridinium Bis(trifluoromethylsulfonyl)imide (z = 2, 3 or 4) at T = 313.2 K. *J. Chem. Eng. Data* **2010**, *55*, 4937−4942.

(11) Larriba, M.; Navarro, P.; García, J.; Rodríguez, F. Liquid-liquid Extraction of Toluene from Heptane using [emim][DCA], [bmim][DCA], and [emim][TCM] Ionic Liquids. *Ind. Eng. Chem. Res.* **2013**, *52*, 2714−2720.

(12) Kolb, B.; Ettre L. S. *Static Headspace-Gas Chromatography: Theory and Practice*; Wiley-VCH: New York, 1997.

(13) Yalkowsky, S. H.; Roseman, T. J. Solubilization of drugs by cosolvents. In *Techniques of Solubilization of Drugs*; Dekker: New York, 1981; Chapter 3.

(14) Larriba, M.; Navarro, P.; García, J.; Rodríguez, F. Liquid-liquid Extraction of Toluene from *n*-Heptane by {[emim][TCM] + [emim][DCA]} Binary Ionic Liquid Mixtures. *Fluid Phase Equilib.* **2014**, *364*, 48−54.

(15) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

(16) Simoni, L. D.; Lin, Y.; Brennecke, J. F.; Stadtherr, M. A. Modeling Liquid−Liquid Equilibrium of Ionic Liquid Systems with NRTL, Electrolyte−NRTL, and UNIQUAC. *Ind. Eng. Chem. Res.* **2008**, *47*, 256−272.

(17) Larriba, M.; Navarro, P.; García, J.; Rodríguez, F. Selective Extraction of Toluene from *n*-Heptane using [emim][SCN] and [bmim][SCN] Ionic Liquids as Solvents. *J. Chem. Thermodyn.* **2013**, DOI: 10.1016/j.jct.2013.11.005.

(18) Marciniak, A.; Krolikowski, M. Ternary (Liquid + liquid) Equilibria of {Trifluorotris(perfluoroethyl)phosphate based Ionic Liquids + Thiophene + Heptane}. *J. Chem. Thermodyn.* **2012**, *49*, 154−158.

(19) Gutiérrez, J. P.; Meindersma, G. W.; de Haan, A. B. COSMO-RS-Based Ionic-Liquid Selection for Extractive Distillation Processes. *Ind. Eng. Chem. Res.* **2012**, *51*, 11518−11529.

(20) Królikowski, M.; Walczak, K.; Domanska, U. Solvent Extraction of Aromatic Sulfur Compounds from n-Heptane using the 1-Ethylmethylimidazolium Tricyanomethanide Ionic Liquid. *J. Chem. Thermodyn.* **2013**, *65*, 168−173.

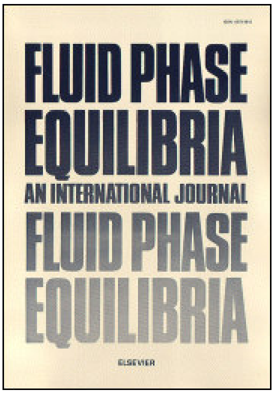
(21) Revelli, A. L.; Mutelet, F.; Jaubert, J. N. Extraction of Benzene or Thiophene from n-Heptane using Ionic Liquids. NMR and Thermodynamic Study. *J. Phys. Chem. B* **2010**, *114*, 4600−4608.

(22) Chen, J.; Duan, L. P.; Mi, J. G.; Fei, W. Y.; Li, Z. G. Liquid-liquid Equilibria of Multi-component System including *n*-Hexane, n-Octane, Benzene, Toluene, Xylene and Sulfolane at 298.15 K and Atmospheric Pressure. *Fluid Phase Equilib.* **2000**, *173*, 109−119.

(23) Lin, W. C.; Kao, N. H. Liquid-liquid Equilibria of Octane + (Benzene or Toluene or m-Xylene) + Sulfolane at 323.15, 348.15, and 373.15 K. *J. Chem. Eng. Data* **2002**, *47*, 1007−1011.

(24) Ferreira, A. R.; Freire, M. G.; Ribeiro, J. C.; Lopes, F. M.; Crespo, J. G.; Coutinho, J. A. P. Overview of the Liquid−Liquid Equilibria of Ternary Systems Composed of Ionic Liquid and Aromatic and Aliphatic Hydrocarbons, and Their Modeling by COSMO-RS. *Ind. Eng. Chem. Res.* **2012**, *51*, 3483−3507.

(25) González, E. J.; Calvar, N.; Domínguez, I.; Domínguez, A. Extraction of toluene from aliphatic compounds using an ionic liquid as solvent: Influence of the alkane on the (liquid + liquid) equilibrium. *J. Chem. Thermodyn.* **2011**, *43*, 562−568.



Fluid Phase Equilibria

Factor de impacto (2013): 2,24

Publicación 6:

Extraction of Benzene, Ethylbenzene, and Xylenes from n-Heptane using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids

Marcos Larriba, Pablo Navarro, Julián García, Francisco Rodriguez

Fluid Phase Equilibria, 2014, 380, 1-10.

Fluid Phase Equilibria 380 (2014) 1–10

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Extraction of benzene, ethylbenzene, and xylenes from *n*-heptane using binary mixtures of [4empy][Tf_2N] and [emim][DCA] ionic liquids

Marcos Larriba, Pablo Navarro, Julián García*, Francisco Rodríguez

Department of Chemical Engineering, Complutense University of Madrid, E-28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 24 April 2014
Received in revised form 15 July 2014
Accepted 24 July 2014
Available online 2 August 2014

Keywords:
Liquid–liquid equilibria
Aromatic/*n*-heptane separation
Ionic liquids
Mixed solvents

ABSTRACT

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are mainly obtained by liquid–liquid extraction from pyrolisis and reformer gasolines using sulfolane as solvent. The use of ionic liquids (ILs) as replacements of sulfolane has been extensively studied, because an industrial process of aromatic extraction using ILs could have fewer process steps and lower operating costs as a result of the exceptional properties of ILs. Nevertheless, pure ILs studied so far have not simultaneously shown physical and extractive properties comparable to those of sulfolane. In our recent work, we studied the use of 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf_2N]) and 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) binary IL mixtures as toluene extraction solvent from its mixtures with *n*-heptane, 2,3-dimethylpentane, and cyclohexane. The {[4empy][Tf_2N] + [emim][DCA]} mixture showed better extractive properties than those of sulfolane, whereas their densities and viscosities were similar to the sulfolane values. In this work, we have studied the performance of {[4empy][Tf_2N] + [emim][DCA]} IL mixtures in the liquid–liquid extraction of benzene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene from *n*-heptane at 313.2 K. To evaluate the applicability of the IL mixtures as extraction solvent of BTEX, liquid–liquid equilibria (LLE) experiments have also been performed using sulfolane under the same conditions. A {[4empy][Tf_2N] + [emim][DCA]} mixture with a [4empy][Tf_2N] mole fraction of 0.3 has been revealed as a potential replacement of sulfolane in the liquid–liquid extraction of BTEX, according to its extractive and physical properties.

1. Introduction

Pyrolisis and reformer gasolines are the most important sources for benzene, toluene, ethylbenzene, and xylenes (BTEX) [1]. Although the amount of BTEX in these streams are between 25 and 60 wt%, the production of pure aromatics by distillation is technically not feasible as a result of the similar boiling points of aromatic, paraffinic, and naphthenic hydrocarbons and the presence of azeotropic mixtures [1,2]. Because of this, the liquid–liquid extraction is employed at industrial scale to separate BTEX from pyrolisis and reformer gasolines [1,3].

The Udex process was the traditional method of liquid–liquid extraction of aromatics, using diethylene glycol and triethylene glycol as solvents at 150 °C and 9 bar [1]. This process was replaced by the Sulfolane process developed by Shell and UOP, operating at 100 °C and 2 bar. Major drawbacks of the Sulfolane process are the high energy consumption in solvent regeneration due to the high boiling point of the sulfolane and the need of a wash column to recover the sulfolane dissolved in the raffinate phase [4].

Taking into account the properties of ILs, the drawbacks of the Sulfolane process could be overcome using an IL-based solvent in aromatic extraction. As a consequence of the non-volatile nature of ILs, solvent regeneration could be achieved by stripping or simple flash distillation at mild conditions [5]. IL recovery and recycling could reduce the environmental and economic impact of the process [6]. Solvent recovery column from raffinate could not be necessary using an IL-based solvent, because of the IL negligible solubility in hydrocarbons forming the raffinate phase [7]. In addition, the extraction column using ILs could operate at temperatures close to room temperature (30–50 °C) and atmospheric pressure, reducing operating costs and energy consumption compared with those of the Sulfolane process [3,8].

An IL-based solvent would be considered as an alternative solvent to sulfolane if it showed higher aromatic distribution ratios and aromatic/aliphatic selectivities than the sulfolane values, together with suitable physical properties. However, these requirements have not been fully achieved to date by pure ILs [2,8]. For that reason, we have proposed the use of binary IL mixtures as aromatic

---

* Corresponding author. Tel.: +34 91 394 51 19; fax: +34 91 394 42 43.
E-mail address: jgarcia@quim.ucm.es (J. García).

http://dx.doi.org/10.1016/j.fluid.2014.07.034
0378-3812/

Table 1
Chemicals. Suppliers, purities, and methods of purity determination.

Chemical	Supplier	Mass fraction purity	Analysis method
$[4empy][Tf_2N]$[a]	Iolitec GmbH	0.99	NMR[c] and IC[d]
[emim][DCA][b]	Iolitec GmbH	0.98	NMR[c] and IC[d]
Benzene	Sigma–Aldrich	0.995	GC[e]
Ethylbenzene	Sigma–Aldrich	0.998	GC[e]
o-Xylene	Sigma–Aldrich	0.99	GC[e]
m-Xylene	Sigma–Aldrich	0.99	GC[e]
p-Xylene	Sigma–Aldrich	0.99	GC[e]
n-Heptane	Sigma–Aldrich	0.997	GC[e]
Sulfolane	Sigma–Aldrich	0.99	GC[e]

[a] $[4empy][Tf_2N]$ = 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide.
[b] [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide.
[c] Nuclear magnetic resonance.
[d] Ion chromatography.
[e] Gas chromatography.

extraction solvents to obtain mixed solvents with extractive and thermophysical properties intermediate between those of pure ILs forming the mixture [9–13].

In our recent work, we studied the performance of $\{[4empy][Tf_2N] + [emim][DCA]\}$ IL mixtures in the liquid–liquid extraction of toluene from *n*-heptane, 2,3-dimethylpentane, and cyclohexane at 313.2 K [11]. The pure $[4empy][Tf_2N]$ was selected because this IL had showed high values of toluene distribution ratios in the separation of toluene from *n*-heptane [14], whereas the pure [emim][DCA] had exhibited toluene/*n*-heptane selectivities substantially higher than those of sulfolane [15], low dynamic viscosities [15], and adequate thermal stability [16]. The $\{[4empy][Tf_2N] + [emim][DCA]\}$ IL mixtures showed higher extractive properties than those of sulfolane in the separation of toluene from alkanes and their densities and viscosities were similar to sulfolane values. This IL mixture also exhibited thermal stability, specific heats, and surface tensions between the values of the pure ILs [11,13]. To confirm the applicability of the IL mixture in the liquid–liquid extraction of BTEX from non-aromatic hydrocarbons, in this work we have studied the liquid–liquid extraction of benzene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene from *n*-heptane using $\{[4empy][Tf_2N] + [emim][DCA]\}$ mixtures as solvents.

2. Materials and methods

2.1. Materials

$[4empy][Tf_2N]$ and [emim][DCA] ILs were purchased from Iolitec GmbH (Germany) with a mass fraction purity higher than 0.98. Halides mass fractions in ILs were less than 2×10^{-2} and water mass fractions were lower than 2×10^{-3}. Benzene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, *n*-heptane, and sulfolane were supplied by Sigma-Aldrich (USA) with the specifications showed in Table 1. All chemicals were used as received without further purification and they were stored in a desiccator in their original tightly closed bottles. The handling of ILs was performed in a glove box under a dry nitrogen atmosphere to maintain constant their water content.

2.2. Liquid–liquid extraction. Experimental procedure and analysis of raffinate and extract phases

First, hydrocarbon feeds formed by binary mixtures of (benzene, ethylbenzene, *o*-xylene, *m*-xylene, or *p*-xylene) and *n*-heptane were gravimetrically added to 8 mL vials employing a Mettler Toledo XS 205 balance with a precision of $\pm 1 \times 10^{-5}$ g. Then, pure $[4empy][Tf_2N]$ and [emim][DCA] ILs, binary mixtures of both ILs, or sulfolane were added to the vials to be used as extraction solvents. The LLE at (313.2 ± 0.1) K was reached employing a Labnet Vortemp 1550 shaking incubator at 800 rpm for 5 h. To ensure the complete separation of the phases in LLE, vials were placed in a Labnet Accublock dry bath at (313.2 ± 0.1) K for 12 h.

A screening was initially performed to study the behavior of the $\{[4empy][Tf_2N] + [emim][DCA]\}$ IL mixtures in the liquid–liquid extraction of benzene, ethylbenzene, and xylenes from *n*-heptane. For this purpose, 2 mL of a hydrocarbon feed composed of *n*-heptane and an aromatic hydrocarbon with 10% of aromatic in mass basis was added to the vials together with the same volume of $\{[4empy][Tf_2N] + [emim][DCA]\}$ IL mixtures over the whole range of compositions. LLE experiments using pure $[4empy][Tf_2N]$ and [emim][DCA] ILs and sulfolane as solvents were also made under the same conditions, to be used as benchmarks in the selection of the most appropriate composition in the IL mixture.

Considering the extractive properties obtained in the initial screening and the physical properties of $\{[4empy][Tf_2N] + [emim][DCA]\}$ mixtures, the optimal composition in the mixed solvent was chosen. Thus, the LLE of the *n*-heptane (1) + (benzene, ethylbenzene, *o*-xylene, *m*-xylene, or *p*-xylene) (2) + $\{[4empy][Tf_2N]$ (3) + [emim][DCA] (4)$\}$ pseudoternary systems at 313.2 K and 0.1 MPa with a $[4empy][Tf_2N]$ mole fraction in the mixed solvent (ϕ_3) of 0.3 were determined.

Compositions of the raffinate and extract phases were measured by gas chromatography (GC) and headspace gas chromatography (HS–GC), respectively. An Agilent 7890A gas chromatograph with a liquid autosampler Agilent 7693 and a flame ionization detector (FID) was employed to determine compositions of triplicate samples from raffinate phases. Raffinate and extract phases in the LLE experiments using sulfolane as solvent were also analyzed by GC. A detailed description of this analytical method can be found elsewhere [12,15]. Samples from raffinate phases were also analyzed by a Bruker Avance 500 MHz NMR spectrometer to quantify the solubility of the IL-based solvents in the hydrocarbon-rich phases. The IL mole fractions in raffinate phases were assumed as negligible since signals corresponding to ILs were not obtained in the ^1H NMR spectra.

A multiple headspace extraction (MHE) technique was employed to measure the composition of the extract phases. Triplicate samples from extract phases were added to 20 mL closed vials and were analyzed by an Agilent 7890A GC with a Headspace Sampler Agilent 7697A. A more detailed description of the MHE method used can be found in our previous works [12,15].

3. Results and discussion

3.1. Screening with $\{[4empy][Tf_2N] + [emim][DCA]\}$ binary IL mixtures as aromatic extraction solvents over the whole range of composition

To select the most suitable composition in the $\{[4empy][Tf_2N] + [emim][DCA]\}$ IL mixture, we have performed an initial screening employing pure $[4empy][Tf_2N]$ and [emim][DCA] ILs and their binary mixtures in the whole range of compositions as extraction solvents at 313.2 K and 0.1 MPa. In the LLE experiments of the screening, hydrocarbon feeds formed by a 10% of aromatic hydrocarbon in mass basis (i.e. benzene, ethylbenzene, *o*-xylene, *m*-xylene, or *p*-xylene) and a 90% of *n*-heptane were used. In Table 2, experimental LLE data as a function of $[4empy][Tf_2N]$ mole fraction (ϕ_3) in the $\{[4empy][Tf_2N] + [emim][DCA]\}$ IL mixture are listed. LLE experiments using sulfolane as solvent were also made under the same conditions and the experimental LLE data are gathered in Table 3.

Table 2

LLE data on mole fraction (x) at 313.2 K, P = 0.1 MPa, and 10% of aromatic in mass basis in hydrocarbon feeds. Distribution ratios (D_i) and aromatic/n-heptane selectivities ($\alpha_{2,1}$) of the pseudoternary systems as a function of [4empy][Tf$_2$N] mole fraction in the IL mixture (ϕ_3)[a].

[4empy][Tf$_2$N] in solvent (ϕ_3)	Raffinate phase (upper layer)		Extract phase (lower layer)			D_1	D_2	$\alpha_{2,1}$
	$x_1{}^{\mathrm{I}}$	$x_2{}^{\mathrm{I}}$	$x_1{}^{\mathrm{II}}$	$x_2{}^{\mathrm{II}}$	$x_{3+4}{}^{\mathrm{II}}$			
n-Heptane (1) + benzene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)}								
0.00	0.9176	0.0824	0.0033	0.0327	0.9640	0.004	0.397	112.1
0.20	0.9270	0.0730	0.0072	0.0423	0.9505	0.008	0.579	74.6
0.40	0.9307	0.0693	0.0118	0.0510	0.9372	0.013	0.736	57.9
0.60	0.9353	0.0647	0.0175	0.0578	0.9247	0.019	0.894	47.8
0.80	0.9365	0.0635	0.0247	0.0666	0.9087	0.026	1.049	39.8
1.00	0.9352	0.0648	0.0318	0.0793	0.8889	0.034	1.223	35.9
n-Heptane (1) + ethylbenzene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)}								
0.00	0.9153	0.0847	0.0031	0.0110	0.9859	0.003	0.130	38.9
0.20	0.9190	0.0810	0.0064	0.0171	0.9765	0.007	0.211	30.3
0.40	0.9218	0.0782	0.0095	0.0209	0.9696	0.010	0.267	25.9
0.60	0.9252	0.0748	0.0157	0.0277	0.9566	0.017	0.370	21.8
0.80	0.9284	0.0716	0.0220	0.0339	0.9441	0.024	0.473	20.0
1.00	0.9276	0.0724	0.0290	0.0391	0.9319	0.031	0.540	17.2
n-Heptane (1) + o-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)}								
0.00	0.9197	0.0803	0.0033	0.0133	0.9834	0.004	0.166	45.8
0.20	0.9247	0.0753	0.0066	0.0189	0.9745	0.007	0.251	34.9
0.40	0.9270	0.0730	0.0102	0.0240	0.9658	0.011	0.329	29.8
0.60	0.9307	0.0693	0.0155	0.0297	0.9547	0.017	0.429	25.7
0.80	0.9339	0.0661	0.0233	0.0342	0.9425	0.025	0.517	20.7
1.00	0.9325	0.0675	0.0318	0.0401	0.9281	0.034	0.595	17.4
n-Heptane (1) + m-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)}								
0.00	0.9157	0.0843	0.0032	0.0128	0.9840	0.004	0.152	43.3
0.20	0.9202	0.0798	0.0064	0.0201	0.9735	0.007	0.252	36.3
0.40	0.9224	0.0776	0.0106	0.0259	0.9635	0.012	0.333	28.9
0.60	0.9270	0.0730	0.0163	0.0338	0.9499	0.018	0.463	26.3
0.80	0.9299	0.0701	0.0234	0.0403	0.9363	0.025	0.575	22.9
1.00	0.9325	0.0675	0.0299	0.0464	0.9237	0.032	0.687	21.4
n-Heptane (1) + p-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)}								
0.00	0.9172	0.0828	0.0031	0.0095	0.9874	0.003	0.115	33.9
0.20	0.9230	0.0770	0.0066	0.0159	0.9775	0.007	0.207	28.8
0.40	0.9250	0.0750	0.0114	0.0213	0.9673	0.012	0.284	23.2
0.60	0.9287	0.0713	0.0167	0.0262	0.9571	0.018	0.368	20.5
0.80	0.9311	0.0689	0.0232	0.0311	0.9457	0.025	0.451	18.1
1.00	0.9371	0.0629	0.0306	0.0338	0.9356	0.033	0.537	16.4

[a] Standard uncertainties (u) are: $u(T)$ = 0.1 K, $u(P)$ = 1 kPa, $u(x_i{}^{\mathrm{I}})$ = 0.0008, $u(x_1{}^{\mathrm{II}})$ = 0.0008, $u(x_2{}^{\mathrm{II}})$ = 0.0025.

To make a quantitative comparison of the performance of the IL-based solvents and sulfolane, n-heptane and aromatic distribution ratios (D_i) and aromatic/n-heptane selectivities ($\alpha_{2,1}$) have been calculated from the LLE data using the following equations:

$$D_1 = \frac{x_1^{\mathrm{II}}}{x_1^{\mathrm{I}}} \tag{1}$$

$$D_2 = \frac{x_2^{II}}{x_2^{I}} \tag{2}$$

$$\alpha_{2,1} = \frac{x_2^{\mathrm{II}} x_1^{\mathrm{I}}}{x_2^{\mathrm{I}} x_1^{\mathrm{II}}} = \frac{D_2}{D_1} \tag{3}$$

where x is the hydrocarbon mole fraction, subscript 1 refers to n-heptane, and subscript 2 refers to benzene, ethylbenzene, o-xylene, m-xylene, or p-xylene. The superscript I indicates the raffinate phase and the superscript II indicates the extract phase. Hydrocarbon distribution ratios and aromatic/n-heptane selectivities using pure [4empy][Tf$_2$N] and [emim][DCA] ILs and {[4empy][Tf$_2$N] + [emim][DCA]} IL mixtures are listed in Table 2 together with the LLE compositions, whereas values of D_i and $\alpha_{2,1}$ using sulfolane are shown in Table 3.

Table 3

Experimental LLE data on mole fraction (x) at 313.2 K, P = 0.1 MPa, and 10% of aromatic in mass basis in hydrocarbon feeds. Distribution ratios (D_i) and aromatic/n-heptane selectivities ($\alpha_{2,1}$) of ternary systems n-heptane (1) + aromatic hydrocarbon (2) + sulfolane (3)[a].

Raffinate phase (upper layer)			Extract phase (lower layer)			D_1	D_2	$\alpha_{2,1}$
$x_1{}^{\mathrm{I}}$	$x_2{}^{\mathrm{I}}$	$x_3{}^{\mathrm{I}}$	$x_1{}^{\mathrm{II}}$	$x_2{}^{\mathrm{II}}$	$x_3{}^{\mathrm{II}}$			
n-Heptane (1) + benzene (2) + sulfolane (3)								
0.9318	0.0643	0.0039	0.0099	0.0398	0.9503	0.011	0.619	58.4
n-Heptane (1) + ethylbenzene (2) + sulfolane (3)								
0.9246	0.0716	0.0038	0.0106	0.0179	0.9715	0.012	0.250	21.7
n-Heptane (1) + o-xylene (2) + sulfolane (3)								
0.9288	0.0675	0.0037	0.0115	0.0201	0.9684	0.012	0.299	24.2
n-Heptane (1) + m-xylene (2) + sulfolane (3)								
0.9244	0.0721	0.0035	0.0110	0.0180	0.9710	0.012	0.249	21.0
n-Heptane (1) + p-xylene (2) + sulfolane (3)								
0.9236	0.0721	0.0043	0.0095	0.0168	0.9737	0.010	0.232	22.5

[a] Standard uncertainties (u) are: $u(T)$ = 0.1 K, $u(P)$ = 1 kPa, $u(x_i{}^{\mathrm{I}})$ = 0.0008, $u(x_i{}^{\mathrm{II}})$ = 0.0012.

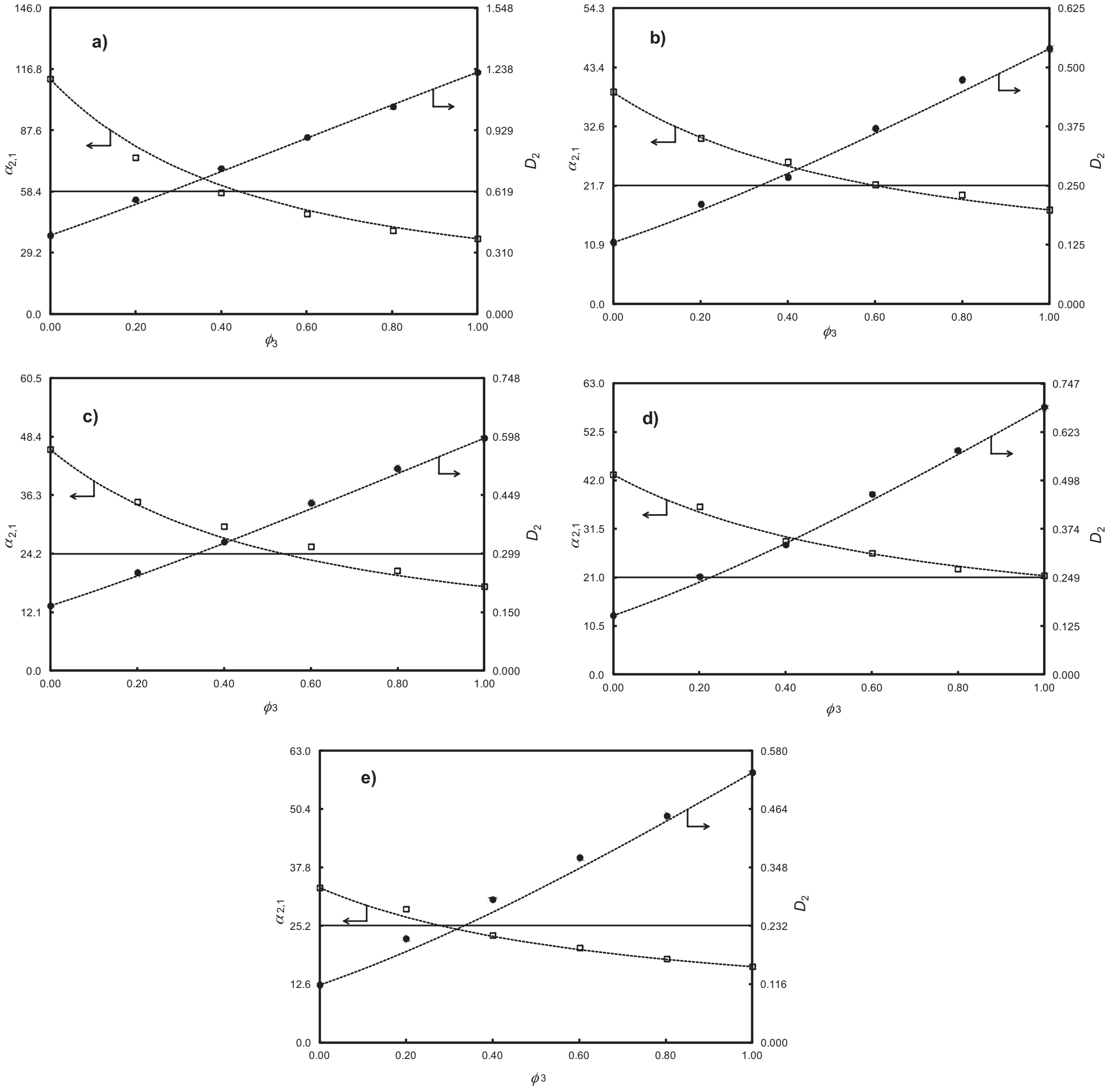


Fig. 1. Aromatic distribution ratios (●) and aromatic/*n*-heptane selectivities (□) of the pseudoternary systems: (a) *n*-heptane (1) + benzene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}; (b) *n*-heptane (1) + ethylbenzene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}; (c) *n*-heptane (1) + *o*-xylene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}; (d) *n*-heptane (1) + *m*-xylene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}; e) *n*-heptane (1) + *p*-xylene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at T = 313.2 K and 10% of aromatic in mass basis in hydrocarbon feeds, as a function of [4empy][Tf_2N] mole fraction in the IL mixture (ϕ_3). Dashed lines were calculated using Yalkowsky and Roseman log-linear mixing rule and solid lines are sulfolane values at T = 313.2 K and 10% of aromatic in mass basis in hydrocarbon feeds.

In Fig. 1, aromatic distribution ratios and aromatic/*n*-heptane selectivities of the *n*-heptane (1) + aromatic hydrocarbon (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} pseudoternary systems as a function of ϕ_3 at 313.2 K and 10 wt% of aromatic hydrocarbon in the feeds are graphically shown as symbols. In the same figure, experimental values of D_2 and $\alpha_{2,1}$ using sulfolane under the same conditions are represented as solid lines.

As observed, an increase in the [4empy][Tf_2N] mole fraction in IL mixture have caused an increase in the aromatic distribution ratios in the five pseudoternary systems, but the effect on aromatic/*n*-heptane selectivities was the opposite. This result is a consequence of the intermediate behavior of the IL mixture between those of pure ILs as aromatic extraction solvents; the pure [emim][DCA] showed higher values of aromatic/*n*-heptane selectivities whereas the pure [4empy][Tf_2N] exhibited higher aromatic distribution ratios.

High solute distribution ratios imply lower solvent to feed ratios, smaller extraction units, and lower capital investment costs, whereas aromatic/aliphatic selectivities are directly related to the purity of solute extracted [8]. Therefore, the optimal composition in the IL mixture should show values of both extractive properties higher than the sulfolane values and adequate physical properties to be considered as an alternative solvent in the aromatic extraction.

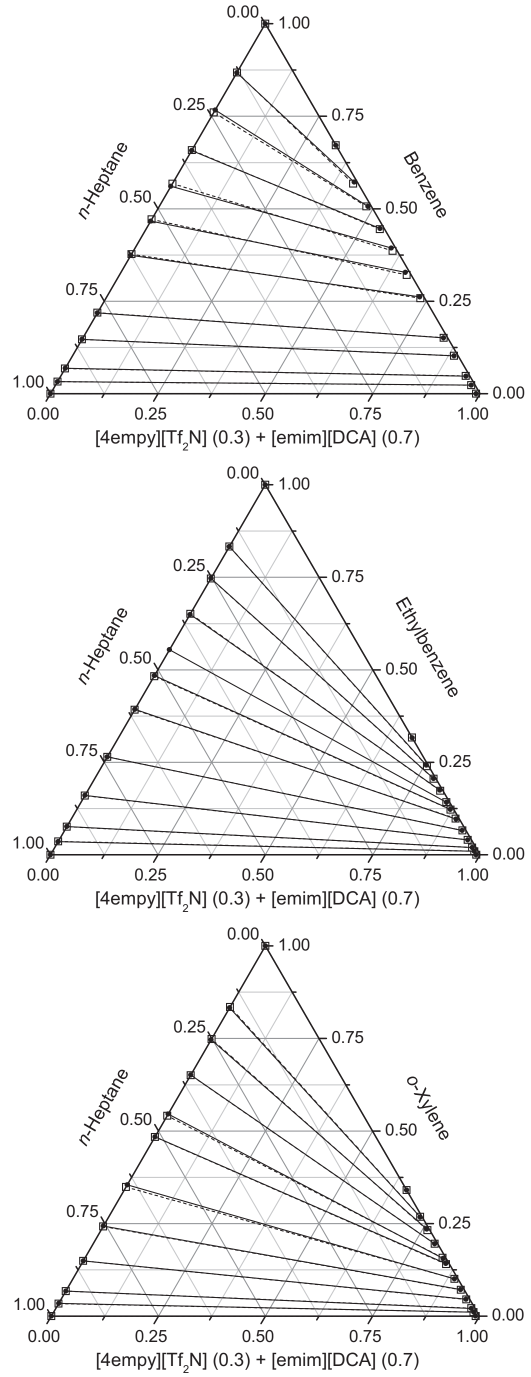


Fig. 2. LLE of the *n*-heptane (1) + aromatic hydrocarbon (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} pseudoternary systems at $\phi_3 = 0.3$, $T = 313.2$ K, and 0.1 MPa. Full points and solid lines are experimental tie lines, and empty squares and dashed lines represent calculated LLE by the NRTL model.

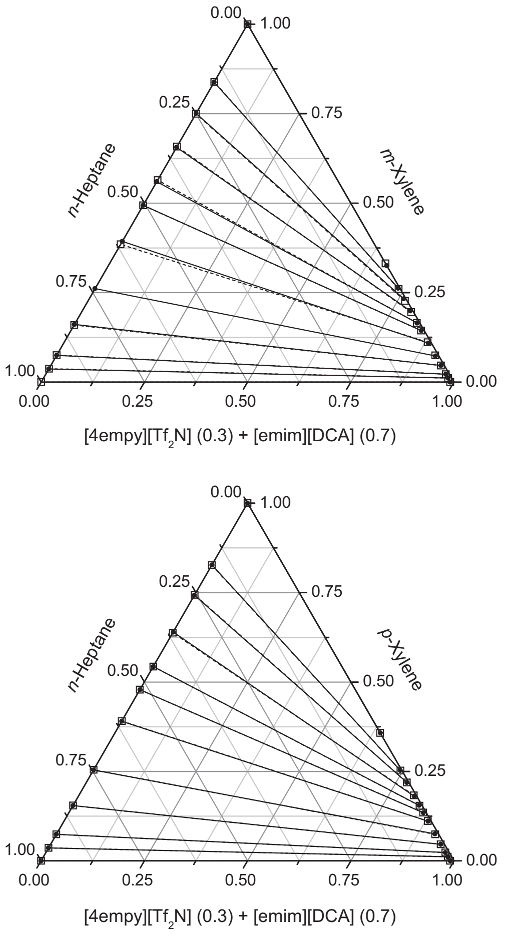


Fig. 2. (*Continued*).

As can be seen in Fig. 1, values of D_2 and $\alpha_{2,1}$ similar or higher than the sulfolane values in the five system studied can be simultaneously achieved using mixed ILs with ϕ_3 around 0.3. In our previous work, we measured densities and viscosities of {[4empy][Tf$_2$N] + [emim][DCA]} mixtures as a function of the composition [11]. The IL mixture with a [4empy][Tf$_2$N] mole fraction of 0.3 showed densities almost coincident with the sulfolane value and dynamic viscosities slightly higher than those of sulfolane. Thus, this composition in the mixed ILs ensures adequate physical properties to be applied in an industrial process of liquid–liquid extraction of aromatic hydrocarbons and extractive properties similar to the sulfolane values in the separation of BTEX from *n*-heptane.

The Yalkowsky and Roseman log-linear mixing rule has been applied to accurately estimate hydrocarbon distribution ratios and aromatic/aliphatic selectivities using IL mixtures as aromatic extraction solvent from LLE data employing the pure ILs forming the mixture [11,12,17]:

$$\ln x_{i,\text{predicted}}^{\text{I or II}} = \sum_{j=3}^{4} f_j \times \ln x_{i,j}^{\text{I or II}} \tag{4}$$

Table 4

Experimental LLE data of the pseudoternary systems *n*-heptane (1) + aromatic hydrocarbon (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$ on mole fraction (x), distribution ratios (D_i), and aromatic/*n*-heptane selectivities ($\alpha_{2,1}$) at $T = 313.2$ K and $P = 0.1$ MPa[a].

Feed (global composition)			Raffinate Phase (upper layer)		Extract Phase (lower layer)			D_1	D_2	$\alpha_{2,1}$
x_1	x_2	x_{3+4}	x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	x_{3+4}^{II}			
n-Heptane (1) + benzene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$										
0.5082	0.0000	0.4918	1.0000	0.0000	0.0090	0.0000	0.9910	0.009		
0.4858	0.0279	0.4863	0.9672	0.0328	0.0091	0.0228	0.9681	0.009	0.695	73.9
0.4658	0.0663	0.4679	0.9313	0.0687	0.0094	0.0473	0.9433	0.010	0.689	68.2
0.4287	0.1384	0.4329	0.8534	0.1466	0.0093	0.1025	0.8882	0.011	0.699	64.2
0.3962	0.2044	0.3994	0.7814	0.2186	0.0095	0.1511	0.8394	0.012	0.691	56.9
0.3293	0.3421	0.3286	0.6257	0.3743	0.0099	0.2615	0.7286	0.016	0.699	44.2
0.2877	0.4211	0.2912	0.5336	0.4664	0.0099	0.3280	0.6621	0.019	0.703	37.9
0.2512	0.5063	0.2425	0.4395	0.5605	0.0099	0.3936	0.5965	0.023	0.702	31.2
0.2057	0.5860	0.2083	0.3427	0.6573	0.0095	0.4467	0.5438	0.028	0.680	24.5
0.1552	0.6893	0.1555	0.2329	0.7671	0.0080	0.5060	0.4860	0.034	0.660	19.2
0.1028	0.7950	0.1022	0.1327	0.8673	0.0066	0.5721	0.4213	0.050	0.660	13.3
0.0000	0.8514	0.1486	0.0000	1.0000	0.0000	0.6715	0.3285		0.672	
n-Heptane (1) + ethylbenzene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$										
0.5082	0.0000	0.4918	1.0000	0.0000	0.0090	0.0000	0.9910	0.009		
0.4913	0.0233	0.4854	0.9642	0.0358	0.0087	0.0094	0.9819	0.009	0.263	29.1
0.4776	0.0503	0.4721	0.9238	0.0762	0.0084	0.0193	0.9723	0.009	0.253	27.9
0.4492	0.1070	0.4438	0.8398	0.1602	0.0085	0.0400	0.9515	0.010	0.250	24.7
0.4125	0.1803	0.4072	0.7356	0.2644	0.0085	0.0657	0.9258	0.012	0.248	21.5
0.3638	0.2776	0.3586	0.6070	0.3930	0.0078	0.0966	0.8956	0.013	0.246	19.1
0.3241	0.3524	0.3235	0.5159	0.4841	0.0078	0.1224	0.8698	0.015	0.253	16.7
0.2942	0.4139	0.2919	0.4458	0.5542	0.0071	0.1413	0.8516	0.016	0.255	16.0
0.2456	0.5093	0.2451	0.3502	0.6498	0.0063	0.1746	0.8191	0.018	0.269	14.9
0.1911	0.6195	0.1894	0.2529	0.7471	0.0054	0.2058	0.7888	0.021	0.275	12.9
0.1369	0.7274	0.1357	0.1668	0.8332	0.0041	0.2420	0.7539	0.025	0.290	11.8
0.0000	0.8526	0.1474	0.0000	1.0000	0.0000	0.3162	0.6838		0.316	
n-Heptane (1) + *o*-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$										
0.5082	0.0000	0.4918	1.0000	0.0000	0.0090	0.0000	0.9910	0.009		
0.4782	0.0241	0.4977	0.9656	0.0344	0.0080	0.0109	0.9811	0.008	0.317	38.2
0.4528	0.0474	0.4998	0.9322	0.0678	0.0084	0.0209	0.9707	0.009	0.308	34.2
0.4252	0.1048	0.4700	0.8505	0.1495	0.0084	0.0453	0.9463	0.010	0.303	30.7
0.3949	0.1715	0.4336	0.7567	0.2433	0.0082	0.0716	0.9202	0.011	0.294	27.2
0.3564	0.2517	0.3919	0.6453	0.3547	0.0079	0.1008	0.8913	0.012	0.284	23.2
0.3207	0.3574	0.3219	0.5159	0.4841	0.0076	0.1420	0.8504	0.015	0.293	19.9
0.2932	0.4143	0.2925	0.4542	0.5458	0.0072	0.1556	0.8372	0.016	0.285	18.0
0.2432	0.5148	0.2420	0.3489	0.6511	0.0068	0.1955	0.7977	0.019	0.300	15.4
0.1907	0.6184	0.1909	0.2531	0.7469	0.0056	0.2351	0.7593	0.022	0.315	14.2
0.1363	0.7280	0.1357	0.1667	0.8333	0.0044	0.2678	0.7278	0.026	0.321	12.2
0.0000	0.8505	0.1495	0.0000	1.0000	0.0000	0.3404	0.6596		0.340	
n-Heptane (1) + *m*-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$										
0.5082	0.0000	0.4918	1.0000	0.0000	0.0090	0.0000	0.9910	0.009		
0.4889	0.0246	0.4865	0.9632	0.0368	0.0084	0.0112	0.9804	0.009	0.304	34.9
0.4765	0.0499	0.4736	0.9253	0.0747	0.0083	0.0220	0.9697	0.009	0.295	32.8
0.4473	0.1077	0.4450	0.8390	0.1610	0.0084	0.0459	0.9457	0.010	0.285	28.5
0.4140	0.1772	0.4088	0.7391	0.2609	0.0082	0.0731	0.9187	0.011	0.280	25.3
0.3621	0.2761	0.3618	0.6069	0.3931	0.0075	0.1089	0.8836	0.012	0.277	22.4
0.3225	0.3611	0.3164	0.5060	0.4940	0.0072	0.1436	0.8492	0.014	0.291	20.4
0.2906	0.4218	0.2876	0.4397	0.5603	0.0067	0.1652	0.8281	0.015	0.295	19.3
0.2434	0.5172	0.2394	0.3441	0.6559	0.0062	0.1987	0.7951	0.018	0.303	16.8
0.1904	0.6220	0.1876	0.2490	0.7510	0.0054	0.2327	0.7619	0.022	0.310	14.3
0.1354	0.7301	0.1345	0.1623	0.8377	0.0039	0.2621	0.7339	0.024	0.313	13.0
0.0000	0.8503	0.1497	0.0000	1.0000	0.0000	0.3252	0.6748		0.325	
n-Heptane (1) + *p*-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$										
0.5082	0.0000	0.4918	1.0000	0.0000	0.0090	0.0000	0.9910	0.009		
0.4850	0.0244	0.4906	0.9636	0.0364	0.0096	0.0114	0.9790	0.010	0.313	31.4
0.4735	0.0499	0.4766	0.9260	0.0740	0.0095	0.0233	0.9672	0.010	0.315	30.7
0.4453	0.1052	0.4495	0.8453	0.1547	0.0090	0.0464	0.9446	0.011	0.300	28.2
0.4103	0.1749	0.4148	0.7459	0.2541	0.0087	0.0750	0.9163	0.012	0.295	25.3
0.3622	0.2763	0.3615	0.6096	0.3904	0.0076	0.1107	0.8817	0.012	0.284	22.7
0.3267	0.3497	0.3236	0.5214	0.4786	0.0072	0.1344	0.8584	0.014	0.281	20.3
0.2959	0.4073	0.2968	0.4569	0.5431	0.0069	0.1552	0.8379	0.015	0.286	18.9
0.2502	0.5021	0.2477	0.3605	0.6395	0.0061	0.1809	0.8130	0.017	0.283	16.7
0.1943	0.6124	0.1933	0.2577	0.7423	0.0048	0.2191	0.7761	0.019	0.295	15.8
0.1407	0.7230	0.1363	0.1728	0.8272	0.0038	0.2530	0.7432	0.022	0.306	13.9
0.0000	0.8505	0.1495	0.0000	1.0000	0.0000	0.3574	0.6426		0.357	

[a] Standard uncertainties (u) are: $u(T) = 0.1$ K, $u(P) = 1$ kPa, $u(x_i) = 0.0007$, $u(x_i^{\mathrm{I}}) = 0.0008$, $u(x_1^{\mathrm{II}}) = 0.0008$, $u(x_2^{\mathrm{II}}) = 0.0025$.

where $x_{i,\text{predicted}}$ is the estimated hydrocarbon mole fraction using mixed ILs, f_j denotes the initial IL volume fraction in the IL mixture in the absence of solutes, j refers to the pure ILs, and $x_{i,j}$ is the hydrocarbon mole fraction in LLE employing pure [4empy][Tf$_2$N] and [emim][DCA] ILs. Predicted values of D_2 and $\alpha_{2,1}$ using {[4empy][Tf$_2$N] + [emim][DCA]} mixtures by the Yalkowsky and Roseman mixing rule are plotted in Fig. 1 as dashed lines. As can be seen, estimated D_2 and $\alpha_{2,1}$ were very close to experimental values.

To evaluate the goodness of the predictions, average percent deviations between experimental and predicted aromatic distribution ratios and selectivities were calculated for each system. The maximum average deviation of the predictions of aromatic distribution ratios was 7.3% in the *n*-heptane + *p*-xylene + {[4empy][Tf$_2$N] + [emim][DCA]} system, whereas the maximum deviation of the estimated aromatic/*n*-heptane selectivities was obtained in the *n*-heptane + *p*-xylene + {[4empy][Tf$_2$N] + [emim][DCA]} pseudoternary system with a value of 6.1%. Thus, considering the low deviations of the predictions using the Yalkowsky and Roseman mixing rule, this equation seems to be a useful tool to predict extractive properties of IL mixtures reducing the number of experimental determinations.

3.2. LLE of the n-heptane + (benzene, ethylbenzene, o-xylene, m-xylene, or p-xylene) + {[4empy][Tf$_2$N] + [emim][DCA]} pseudoternary systems

Experimental LLE data of *n*-heptane (1) + (benzene, ethylbenzene, *o*-xylene, *m*-xylene, or *p*-xylene) (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} pseudoternary systems at $\phi_3 = 0.3$, 313.2 K, and 0.1 MPa are listed in Table 4 and plotted in Fig. 2 as ternary diagrams. First, the reliability of the LLE gathered in this work has been assessed using the Othmer–Tobias correlation [18]. This equation has been employed in a wide number of recently published papers involving the LLE of hydrocarbons and ILs to check the reliability of LLE data [19–23]:

$$\ln\left(\frac{1-w_{(3+4)}^{\mathrm{II}}}{w_{(3+4)}^{\mathrm{II}}}\right) = a + b\ \ln\left(\frac{1-w_1^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right) \tag{5}$$

where $w_{(3+4)}{}^{\mathrm{II}}$ denotes the mass fraction of the {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} mixed solvent in the extract phase, $w_1{}^{\mathrm{I}}$ indicates the *n*-heptane mass fraction in the raffinate phase, whereas *a* and *b* are the fitted parameters showed in Table 5 together with the standard deviations of the fit (σ) and the regression coefficients (R^2). The consistency of the LLE data was checked considering the values of R^2 higher than 0.98 and the low standard deviations obtained.

3.2.1. Correlation of LLE to the nonrandom two liquid (NRTL) model

The nonrandom two liquid (NRTL) model [24] has been extensively used to correlate LLE data of ternary and pseudoternary systems composed of hydrocarbons and ILs [25–29]. Aspen Plus Simulator has been employed in this work to fit the experimental LLE data of the *n*-heptane + (benzene, ethylbenzene, *o*-xylene, *m*-xylene, or *p*-xylene) + {[4empy][Tf$_2$N] + [emim][DCA]} pseudoternary systems at $\phi_3 = 0.3$, 313.2 K, and 0.1 MPa. Values of $\Delta g_{ij}/R$ and $\Delta g_{ji}/R$ binary parameters of the NRTL model are shown in Table 6. The nonrandomness parameter (α_{ij}) of the NRTL model was set as 0.30, since this is the most commonly used value of the α_{ij} parameter in fitting of data of liquid–liquid extraction of hydrocarbons using IL-based solvents [26–29]. In Table 6, the root mean square deviations (*rmsd*) of the fits calculated using the following equation are also listed:

$$rmsd = \left\{\frac{\sum_i\sum_l\sum_m\left(x_{ilm}^{\mathrm{exptl}} - x_{ilm}^{\mathrm{calc}}\right)^2}{6k}\right\}^{1/2} \tag{6}$$

where the subscripts *i*, *l*, and *m* refer to the component, phase, and tie line, respectively, *x* indicates the mole fraction of the component, and *k* is the number of experimental tie lines. As can be observed in the ternary diagrams showed in Fig. 2, experimental and calculated tie lines by the NRTL model were almost coincident. Hence, the experimental LLE data of the *n*-heptane + (benzene, ethylbenzene, *o*-xylene, *m*-xylene, or *p*-xylene) + {[4empy][Tf$_2$N] + [emim][DCA]} pseudoternary systems at 313.2 K with a [4empy][Tf$_2$N] mole fraction of 0.3 in the IL mixture have been properly fitted to the NRTL model.

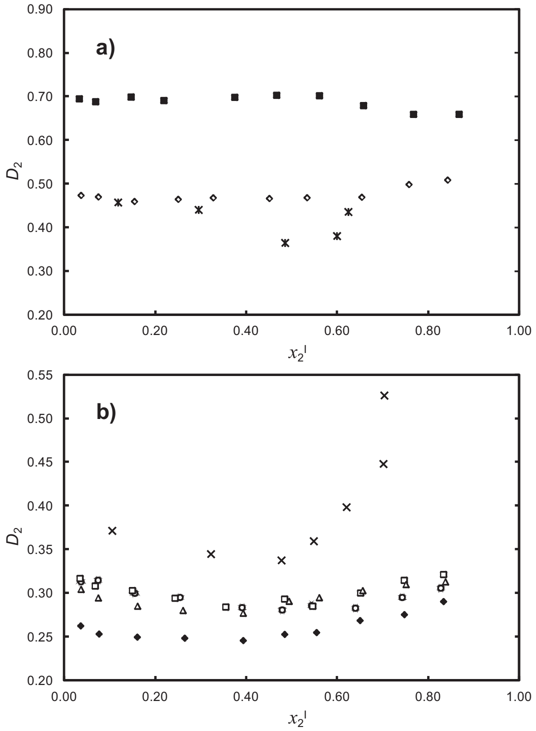


Fig. 3. Aromatic distribution ratios (D_2) at T = 313.2 K. (a) ■, *n*-heptane (1) + benzene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; ◇, *n*-heptane (1) + toluene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$ from Ref. [11]. ∗ , *n*-heptane (1) + benzene (2) + sulfolane (3) at T = 303.2 K from Ref. [30]. (b) ◆, *n*-heptane (1) + ethylbenzene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; □, *n*-heptane (1) + *o*-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; △, *n*-heptane (1) + *m*-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; ○, *n*-heptane (1) + *p*-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; ×, *n*-heptane (1) + *p*-xylene (2) + sulfolane (3) at 303.2 K from Ref. [30].

3.2.2. Aromatic distribution ratios and aromatic/n-heptane selectivities

To evaluate the results obtained using the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture with a [4empy][Tf$_2$N] mole fraction of 0.3 as extraction solvent of benzene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene from *n*-heptane at 313.2 K, hydrocarbon distribution ratios and aromatic/*n*-heptane selectivities have been calculated from the experimental LLE data using Eqs. (1)–(3). Values of D_i and $\alpha_{2,1}$ are listed in Table 4 along with the experimental compositions.

Aromatic distribution ratios (D_2) of the *n*-heptane (1) + (benzene, ethylbenzene, *o*-xylene, *m*-xylene, or *p*-xylene) (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} pseudoternary systems are also graphically shown in Fig. 3. In the same figure, literature values of benzene and *p*-xylene distribution

Table 5
Constants of the Othmer–Tobias correlation (a, b), regression coefficients (R^2), and standard deviations (σ) for the LLE Data of the pseudoternary systems n-heptane (1) + aromatic hydrocarbon (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$, $T = 313.2$ K, and $P = 0.1$ MPa.

a	b	R^2	σ
n-Heptane (1) + benzene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}at $\phi_3 = 0.3$			
−1.7049	0.7326	0.9827	0.2133
n-Heptane (1) + ethylbenzene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)}at $\phi_3 = 0.3$			
−2.8292	0.6180	0.9931	0.0527
n-Heptane (1) + o-xylene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$			
−2.6821	0.6259	0.9908	0.0748
n-Heptane (1) + m-xylene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$			
−2.7024	0.6267	0.9891	0.0863
n-Heptane (1) + p-xylene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$			
−2.7070	0.5965	0.9914	0.0603

Table 6
Values of the NRTL parameters obtained from LLE data by regression for the pseudoternary systems n-heptane (1) + aromatic hydrocarbon (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$, $T = 313.2$ K, and $P = 0.1$ MPa.

Component	NRTL parameters			*rmsd*
$i - j$	$(\Delta g_{ij}/R)$ (K)	$(\Delta g_{ji}/R)$ (K)	α_{ij}	
n-Heptane (1) + benzene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$				
1 − 2	−91.349	625.09	0.30	0.0034
1 − (3 + 4)	2132.5	−1312.3	0.30	
2 − (3 + 4)	3726.9	−2028.3	0.30	
n-Heptane (1) + ethylbenzene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$				
1 − 2	990.02	−996.98	0.30	0.0008
1 − (3 + 4)	2334.3	−1399.1	0.30	
2 − (3 + 4)	2662.8	−1270.7	0.30	
n-Heptane (1) + o-xylene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$				
1 − 2	889.64	−911.71	0.30	0.0023
1 − (3 + 4)	2795.3	−1610.7	0.30	
2 − (3 + 4)	2879.1	−1394.9	0.30	
n-Heptane (1) + m-xylene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$				
1 − 2	335.25	−390.29	0.30	0.0030
1 − (3 + 4)	1715.6	−1061.0	0.30	
2 − (3 + 4)	2920.6	−1409.3	0.30	
n-Heptane (1) + p-xylene (2) + {[4empy][Tf_2N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$				
1 − 2	763.99	−791.30	0.30	0.0008
1 − (3 + 4)	4369.1	−2215.3	0.30	
2 − (3 + 4)	2660.8	−1288.0	0.30	

ratios in the liquid–liquid extraction of benzene and p-xylene from n-heptane using sulfolane at 303.2 K are plotted [30]. In addition, published toluene distribution ratios using the {[4empy][Tf_2N] + [emim][DCA]} IL mixture at $\phi_3 = 0.3$ and 313.2 K in the liquid–liquid extraction of toluene from n-heptane are also included in Fig. 3 to quantify the effect of changing the aromatic hydrocarbon in the separation from n-heptane [11].

As observed, the highest values of D_2 were obtained in the separation of benzene from n-heptane; thus, benzene was the aromatic with a higher solubility in the {[4empy][Tf_2N] + [emim][DCA]} mixed solvent. Literature values of toluene distribution ratio using the same IL mixture were intermediate between experimental benzene and xylene distribution ratios. Significant differences were not found in the separation of xylene isomers from n-heptane, being the values of o-xylene, m-xylene, and p-xylene distribution ratios very similar. The small differences among the solubility of positional isomers can be explained by the effect of xylene molecular structure on the aromatic induced dipole moment [31]. Finally, the less soluble aromatic hydrocarbon in the IL mixture was the ethylbenzene, obtaining the lowest values of D_2 in the liquid–liquid extraction of this hydrocarbon from n-heptane.

Experimental values of aromatic distribution ratios are in agreement with the recently published work of González et al. on the solubility of benzene, toluene, ethylbenzene, and xylenes in the pure 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([3empy][Tf_2N]) IL. These authors found the following order of solubility: benzene > toluene > o-xylene > m-xylene ~ p-xylene ~ ethylbenzene [32]. In addition, predictions using COSMO-RS (Conductor-like Screening Model for Real Solvents) were also coincident with the results gathered in this paper; Ferreira et al. predicted that an increase in the aromatic alkyl chain substituted length causes a decrease in the distribution ratio because the solubility of the aromatic hydrocarbons in ILs follows the order benzene > toluene > ethylbenzene [33]. This trend can be explained by the polarizability values of the aromatic hydrocarbons, since a higher polarizability causes a higher solubility in IL-based solvents. Values of polarity-polarizability of the aromatics were published by Catalán et al.: benzene (0.667), toluene (0.665), ethylbenzene (0.650), o-xylene (0.641), m-xylene (0.616), and p-xylene (0.617) [34].

To conclude the discussion on aromatic distribution ratios a comparison with the sulfolane values have been performed. As seen in Fig. 3, values of benzene distribution ratios using the {[4empy][Tf_2N] + [emim][DCA]} IL mixture at $\phi_3 = 0.3$ have been substantially higher than those of sulfolane. On the contrary, p-xylene distribution ratios employing the IL-based solvent have been somewhat lower than the literature values of sulfolane. It is important to highlight that D_2 values using IL mixtures were almost constant with the increase of aromatic mole fraction in raffinate, whereas the p-xylene distribution ratios using sulfolane from Letcher et al. considerably increased with the p-xylene mole fraction in the raffinate phase [30].

In Fig. 4, aromatic/n-heptane selectivities of the n-heptane + (benzene, ethylbenzene, o-xylene, m-xylene, or p-xylene) + {[4empy][Tf_2N] + [emim][DCA]} pseudoternary

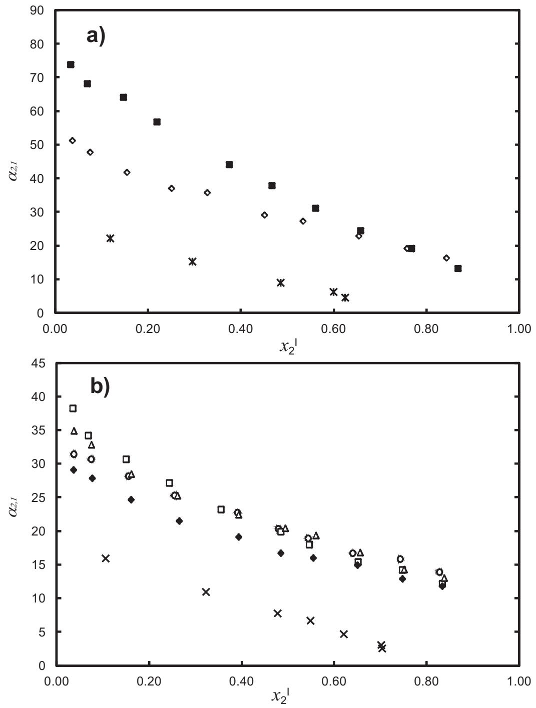


Fig. 4. Aromatic/*n*-heptane selectivities ($\alpha_{2,1}$) at $T = 313.2$ K. (a) ■, *n*-heptane (1) + benzene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; ◇, *n*-heptane (1) + toluene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$ from Ref. [11]. ∗, *n*-heptane (1) + benzene (2) + sulfolane (3) at $T = 303.2$ K from Ref. [30]. (b) ♦, *n*-heptane (1) + ethylbenzene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; □, *n*-heptane (1) + *o*-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; △, *n*-heptane (1) + *m*-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; ○, *n*-heptane (1) + *p*-xylene (2) + {[4empy][Tf$_2$N] (3) + [emim][DCA] (4)} at $\phi_3 = 0.3$; ×, *n*-heptane (1) + *p*-xylene (2) + sulfolane (3) at 303.2 K from Ref. [30].

systems at $\phi_3 = 0.3$ and 313.2 K are plotted along with benzene/*n*-heptane and *p*-xylene/*n*-heptane selectivities using sulfolane at 303.2 K [30] and published values of toluene/*n*-heptane selectivities using the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture at $\phi_3 = 0.3$ and 313.2 K [11].

As seen, the highest value of $\alpha_{2,1}$ was achieved in the separation of benzene from *n*-heptane, as a result of the higher aromatic character of this hydrocarbon. Literature values of toluene/*n*-heptane selectivities using the same mixed ILs [11] were intermediate between benzene/*n*-heptane and *o*-xylene/*n*-heptane selectivities. Experimental selectivities in the separation of the different xylene isomers were similar, being slightly higher the *o*-xylene/*n*-heptane selectivities at low contents of xylene in the hydrocarbon feeds than those in the separation of *m*-xylene and *p*-xylene from *n*-heptane. As in the case of the aromatic distribution ratios, the lowest values of selectivity were obtained in the liquid–liquid extraction of ethylbenzene from *n*-heptane.

Ferreira et al. predicted the effect of changing the aromatic hydrocarbon on the values of aromatic/aliphatic selectivities using COSMO-RS. Predictions were in agreement with the trend observed in our results, decreasing the aromatic/aliphatic selectivity with the increase in the aromatic alkyl chain substituted length [33].

Benzene/*n*-heptane selectivities using the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture with a [4empy][Tf$_2$N] mole fraction of 0.3 were almost three times higher than the published values using sulfolane [30]. Hence, benzene extracted by the IL-based solvent had purity substantially higher than that employing sulfolane. This fact would simplify subsequent purification steps, reducing investment and operating costs. In addition, *p*-xylene/*n*-heptane selectivities using the IL-based solvent were approximately double than those of sulfolane. Therefore, the {[4empy][Tf$_2$N] + [emim][DCA]} with a ϕ_3 of 0.3 could be used at industrial scale as extraction solvent to selectively separate aromatic hydrocarbons with their mixtures with aliphatics considering its extractive and physical properties.

4. Conclusions

In this work, we have studied the liquid–liquid extraction of benzene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene from *n*-heptane using binary mixtures of [4empy][Tf$_2$N] and [emim][DCA] ILs at 313.2 K and 0.1 MPa. Initially, we have studied the performance of {[4empy][Tf$_2$N] + [emim][DCA]} IL mixtures over the whole range of composition in the separation of aromatics from *n*-heptane. Aromatic distribution ratios and aromatic/*n*-heptane selectivities have been intermediate between those of the pure ILs. Extractive properties of the IL mixtures have been successfully predicted by the Yalkowsky and Roseman log-linear mixing rule from LLE data employing the pure [4empy][Tf$_2$N] and [emim][DCA] ILs. Considering the results obtained in the screening using the IL mixtures and the physical properties of the {[4empy][Tf$_2$N] + [emim][DCA]} mixture, a [4empy][Tf$_2$N] mole fraction of 0.3 was selected as the optimal composition in the IL mixture to achieve extractive and physical properties comparable to those of sulfolane.

LLE of *n*-heptane + (benzene, ethylbenzene, *o*-xylene, *m*-xylene, or *p*-xylene) + {[4empy][Tf$_2$N] + [emim][DCA]} pseudoternary systems at 313.2 K, 0.1 MPa, and $\phi_3 = 0.3$ have been measured. Aromatic distribution ratios and aromatic/*n*-heptane selectivities have been calculated from LLE data. The highest extractive properties have been achieved in the separation of benzene from *n*-heptane. Results in the separation of the three xylene isomers from *n*-heptane have been similar to each other, whereas the lowest values of distribution ratios and selectivities have been obtained in the liquid–liquid extraction of ethylbenzene.

Aromatic distribution ratios and aromatic/aliphatic selectivities using the IL mixture have been compared to literature values employing sulfolane in the liquid–liquid extraction of benzene and *p*-xylene from *n*-heptane. The IL-based solvent has shown higher extractive properties than those of sulfolane in the separation of benzene, higher *p*-xylene/*n*-heptane selectivities and slightly lower *p*-xylene distribution ratios.

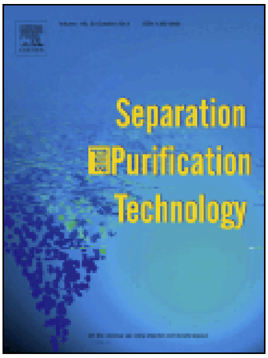
To confirm the applicability of the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture at industrial scale, the liquid–liquid extraction of different aromatic hydrocarbons (e.g. benzene, toluene, xylenes, and ethylbenzene) from multicomponent mixtures with several *n*-alkanes should be studied.

Acknowledgments

The authors are grateful to the Ministerio de Economía y Competitividad (MINECO) of Spain and the Comunidad Autónoma de Madrid for financial support of Projects CTQ2011–23533 and S2009/PPQ–1545, respectively. Marcos Larriba thanks Ministerio de Educación, Cultura y Deporte for awarding him an FPU grant (Reference AP–2010–0318), and Pablo Navarro thanks MINECO for awarding him an FPI grant (Reference BES–2012–052312).

References

[1] H.G. Franck, J.W. Staldelhofer, Industrial Aromatic Chemistry, Springer-Verlag, New York, NY, 1988.
[2] G.W. Meindersma, A.R. Hansmeier, A.B. de Haan, Ind. Eng. Chem. Res. 49 (2010) 7530–7540.
[3] G.W. Meindersma, A.B. de Haan, Chem. Eng. Res. Des. 86 (2008) 745–752.
[4] G.W. Meindersma, A.J.G. Podt, A.B. de Haan, Fuel Process. Technol. 87 (2005) 59–70.
[5] S.T. Anjan, Chem. Eng. Prog. 102 (2006) 30–39.
[6] E. Alvarez-Guerra, S.P.M. Ventura, J.A.P. Coutinho, A. Irabien, Fluid Phase Equilib. 371 (2014) 67–74.
[7] A. Arce, M.J. Earle, H. Rodríguez, K.R. Seddon, J. Phys. Chem. B 111 (2007) 4732–4736.
[8] G.W. Meindersma, A.B. de Haan, Sci. Chin. Chem. 55 (2012) 1488–1499.
[9] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, Chem. Eng. J. 180 (2012) 210–215.
[10] S. García, J. García, M. Larriba, A. Casas, F. Rodríguez, Fluid Phase Equilib. 337 (2013) 47–52.
[11] M. Larriba, P. Navarro, J. García, F. Rodríguez, Sep. Purif. Technol. 120 (2013) 392–401.
[12] M. Larriba, P. Navarro, J. García, F. Rodríguez, Fluid Phase Equilib. 364 (2014) 48–54.
[13] P. Navarro, M. Larriba, J. García, F. Rodríguez, J. Chem. Thermodyn. (2014), http://dx.doi.org/10.1016/j.jct.2014.03.023.
[14] J. García, S. García, J.S. Torrecilla, F. Rodríguez, J. Chem. Eng. Data 55 (2010) 4937–4942.
[15] M. Larriba, P. Navarro, J. García, F. Rodríguez, Ind. Eng. Chem. Res. 52 (2013) 2714–2720.
[16] P. Navarro, M. Larriba, E. Rojo, J. García, F. Rodríguez, J. Chem. Eng. Data 58 (2013) 2187–2193.
[17] S.H. Yalkowsky, T.J. Roseman, Solubilization of drugs by cosolvents, in: Techniques of Solubilization of Drugs, Dekker, New York, NY, 1981 (Chapter 3).
[18] D.F. Othmer, P.E. Tobias, Ind. Eng. Chem. 34 (1942) 693–696.
[19] E.J. González, N. Calvar, E. Gómez, A. Domínguez, Fluid Phase Equilib. 303 (2011) 174–179.
[20] M.S. Fandari, K.H.A.E. Alkhaldi, A.S. Al-Jimaz, M.H. Al-Rashed, M.S. AlTuwaim, J. Chem. Thermodyn. 54 (2012) 322–329.
[21] A. Kamanesh, M. Vossoughi, A. Shamloo, S.A. Mirkhani, J. Akbari, Fluid Phase Equilib. 332 (2012) 48–54.
[22] A. Al-Jimaz, K.H.A.E. Alkhaldi, M.H. Al-Rashed, M.S. Fandary, M.S. AlTuwaim, Fluid Phase Equilib. 354 (2013) 29–37.
[23] E. Gómez, I. Domínguez, N. Calvar, J. Palomar, A. Domínguez, Fluid Phase Equilib. 361 (2014) 83–92.
[24] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135–144.
[25] L.D. Simoni, Y. Lin, J.F. Brennecke, M.A. Stadtherr, Ind. Eng. Chem. Res. 47 (2008) 256–272.
[26] A. Marciniak, M. Królikowski, J. Chem. Thermodyn. 49 (2012) 154–158.
[27] J.P. Gutiérrez, G.W. Meindersma, A.B. de Haan, Ind. Eng. Chem. Res. 51 (2012) 11518–11529.
[28] M. Królikowski, K. Walczak, U. Domanska, J. Chem. Thermodyn. 65 (2013) 168–173.
[29] A.L. Revelli, F. Mutelet, J.N. Jaubert, J. Phys. Chem. B 114 (2010) 4600–4608.
[30] T.M. Letcher, G.G. Redhi, S.E. Radloff, J. Chem. Eng. Data 41 (1996) 634–638.
[31] A.R. Ferreira, M.G. Freire, J.C. Ribeiro, F.M. Lopes, J.G. Crespo, J.A.P. Coutinho, Ind. Eng. Chem. Res. 50 (2011) 5279–5294.
[32] E.J. González, P.F. Requejo, A. Domínguez, E.A. Macedo, Fluid Phase Equilib. 360 (2013) 416–422.
[33] A.R. Ferreira, M.G. Freire, J.C. Ribeiro, F.M. Lopes, J.G. Crespo, J.A.P. Coutinho, Ind. Eng. Chem. Res. 51 (2012) 3483–3507.
[34] J. Catalán, V. López, P. Pérez, R. Martín-Villamil, J.G. Rodríguez, Liebigs Ann. 2 (1995) 241–252.



Separation and Purification Technology

Factor de impacto (2013): 3,07

Publicación 7:

Separation of BTEX from a naphtha feed to ethylene crackers using a binary mixture of [4empy][Tf_2N] and [emim][DCA] ionic liquids

Marcos Larriba, Pablo Navarro, Emilio J. González, Julián García, Francisco Rodriguez

Separation and Purification Technology, 2015, 144, 54-62.

Separation and Purification Technology 144 (2015) 54–62

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Separation of BTEX from a naphtha feed to ethylene crackers using a binary mixture of [4empy][Tf_2N] and [emim][DCA] ionic liquids

Marcos Larriba, Pablo Navarro, Emilio J. González, Julián García *, Francisco Rodríguez

Department of Chemical Engineering, Complutense University of Madrid, E-28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 9 January 2015
Received in revised form 11 February 2015
Accepted 13 February 2015
Available online 21 February 2015

Keywords:
Liquid–liquid extraction
Aromatic separation
Ionic liquids
Naphtha
Countercurrent column simulation

ABSTRACT

The separation of BTEX from petroleum streams with aromatic contents between 20 and 65 wt.% is usually made by liquid–liquid extraction. Nevertheless, there are no technologies currently available to perform the separation of aromatics from streams with an aromatic content lower than 20 wt.%. In this work, we have studied the separation of BTEX from a naphtha feed to ethylene crackers with a total aromatic content equal to 10 wt.%. Aromatics are not converted to olefins in ethylene crackers and their presence increases operating costs and the size of furnaces. Because of this, the separation of BTEX from this stream has been studied using the binary IL mixture formed by the 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf_2N]) and the 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]), since this IL mixture previously showed adequate extractive properties in the BTEX extraction from reformer gasoline. The separation of BTEX from the naphtha has also been studied using sulfolane, the most used solvent in aromatic extraction at industrial scale. The influence of temperature and solvent to feed ratio on several extractive properties has been carried out from the experimental results employing both extraction solvents. The Kremser equation has been used to simulate the countercurrent extraction columns in the separation of BTEX from the naphtha, studying the effect of the number of equilibrium stages in the extraction yield of BTEX and in the purity of the aromatics obtained.

1. Introduction

Reformer gasoline, pyrolysis gasoline, and coke oven benzole are the main sources of benzene, toluene, ethylbenzene, and xylenes (BTEX) [1]. In these streams, where the aromatic content is between 40 and 90 wt.%, dearomatization is being performed by liquid–liquid extraction with organic solvents such as sulfolane, *N*-methylpyrrolidone, and ethylene glycols [1–3]. However, there are no technologies available to separate BTEX from streams with an aromatic content lower than 20 wt.% [4].

Aromatic content in the ethylene crackers feed is between 10 and 25 wt.%. BTEX presented in the naphtha feed to ethylene crackers are not converted to olefins and their presence increases operating costs and the size of the furnaces [4]. Therefore, the extraction of BTEX from this naphtha could reduce costs and could produce income by selling the aromatics extracted.

Ionic liquids (ILs) have been studied as potential substitutes of conventional solvents in separation processes, highlighting their application in the aromatic extraction [5–17]. In addition to their good extractive properties, the most remarkable feature of ILs is their nonvolatile nature [18]. As a result of this exceptional property, the use of ILs in the BTEX extraction could simplify the separation of the extracted aromatics from the solvent [19]. The separation between the aromatics and the ILs could be achieved by a simpler operation than the extractive stripper and the recovery distillation column used in the UOP Sulfolane Process [2,4,19,20].

Specifically, Meindersma and de Haan proposed the application of an IL in the separation of aromatics from the naphtha feed to ethylene crackers, performing the separation of toluene from *n*-heptane from a hydrocarbon mixture with a 10 wt.% of toluene [4]. However, among the pure ILs studied so far in the separation of an aromatic from an aliphatic hydrocarbon only a few ILs have shown simultaneously physical and extractive properties equal or better than those of sulfolane [21,22]. For that reason, we proposed the use of binary IL mixtures as aromatic extraction solvents obtaining IL-based solvents with extractive and physical properties between those of the pure ILs [23–25].

The mixture formed by the [4empy][Tf_2N] and the [emim][DCA] ILs has been revealed as the most promising IL mixture to be employed as aromatic extraction solvent taking into account its physical and extractive properties. Specifically, the {[4empy][Tf_2N] + [emim][DCA]} IL mixture with a mole fraction of [4empy][Tf_2N] (x_1) of 0.3 exhibited extractive properties

---

* Corresponding author. Tel.: +34 91 394 51 19; fax: +34 91 394 42 43.
E-mail address: jgarcia@quim.ucm.es (J. García).

http://dx.doi.org/10.1016/j.seppur.2015.02.021
1383-5866/

comparable to sulfolane values in the extraction of toluene from its mixtures with *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, cyclohexane, or 2,3-dimethylpentane and in the separation of benzene, ethylbenzene, or xylenes from *n*-heptane [12,25,26]. The extractive properties of the {[4empy][Tf_2N] + [emim][DCA]} IL mixture at x_1 equal to 0.3 were also comparable to the values of the most promising IL-based solvents in the separation of toluene from *n*-heptane studied so far. In addition, densities, viscosities, surface tensions, and thermal stability of the {[4empy][Tf_2N] + [emim][DCA]} mixture were similar to those of sulfolane; therefore, this IL mixture could be applied at industrial scale [12,27,28].

We checked the performance of the {[4empy][Tf_2N] + [emim][DCA]} mixture with a x_1 of 0.3 in the liquid–liquid extraction of benzene, toluene, *p*-xylene, and ethylbenzene from a reformer gasoline model. The IL-based solvent showed purities of extracted BTEX substantially greater than the sulfolane values and yields of extraction of aromatics slightly lower than those employing sulfolane [29]. To the best of our knowledge, this work and our recently published paper on the separation of BTEX from reformer gasoline are the first experimental studies on the simultaneous separation of benzene, toluene, ethylbenzene, and *p*-xylene from several aliphatics using ILs. These results are essential to perform the design of the extraction column to separate aromatics from aliphatics at industrial scale.

In this work, we have studied the separation of benzene, toluene, ethylbenzene, and *p*-xylene from a naphtha model with a total aromatic content of 10 wt.%. The composition of the naphtha model has been selected considering the typical composition of the naphtha feed to ethylene crackers. The effect of temperature on the extractive properties of the IL mixture has been analyzed performing liquid–liquid extraction experiments at 303.2 K, 313.2 K, and 323.2 K and atmospheric pressure. These conditions of temperature and pressure are the most employed values in the separation of aromatics from alkanes using ILs [21,22]. To study the influence of the solvent to feed (S/F) ratio on the BTEX separation from the naphtha model, experiments at S/F ratios between 1.0 and 5.0 have been made at each experimental temperature. To be used as a benchmark, the liquid–liquid extraction of BTEX from the naphtha has also been performed using sulfolane as extraction solvent.

2. Materials and methods

2.1. Materials

[4empy][Tf_2N] and [emim][DCA] ILs were purchased from Iolitec GmbH with a mass fraction purity greater than 0.99 and 0.98, respectively. In the [4empy][Tf_2N], the halide content was lower than 100 ppm and its water content was 42 ppm. Water and halide contents in the [emim][DCA] were 1790 ppm and lower than 2%, respectively. *n*-Hexane, *n*-heptane, *n*-octane, benzene, toluene, ethylbenzene, *p*-xylene, and sulfolane were supplied by Sigma–Aldrich (USA). The handling of ILs was performed in a glovebox filled with dry nitrogen, whereas all chemicals were stored in a desiccator to prevent water absorption and they were used as received without further purification. In Table 1, suppliers and mass fractions purities of the chemicals are gathered together with their abbreviations in this work.

Table 1
Purities of chemicals, suppliers, and abbreviations.

Chemical	Supplier	Mass fraction purity	Analysis method	Abbreviation
[4empy][Tf_2N][a]	Iolitec GmbH	0.99	NMR[c] and IC[d]	*ILs*
[emim][DCA][b]	Iolitec GmbH	0.98	NMR[c] and IC[d]	
n-Hexane	Sigma–Aldrich	0.99	GC[e]	*hexa*
n-Heptane	Sigma–Aldrich	0.997	GC[e]	*hepta*
n-Octane	Sigma–Aldrich	0.99	GC[e]	*octa*
Benzene	Sigma–Aldrich	0.995	GC[e]	*benz*
Toluene	Sigma–Aldrich	0.995	GC[e]	*tol*
Ethylbenzene	Sigma–Aldrich	0.998	GC[e]	*etbenz*
p-Xylene	Sigma–Aldrich	0.99	GC[e]	*p-xyl*
Sulfolane	Sigma–Aldrich	0.99	GC[e]	*sulf*

[a] [4empy][Tf_2N] = 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide.
[b] [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide.
[c] Nuclear Magnetic Resonance.
[d] Ion chromatography.
[e] Gas chromatography.

2.2. Naphtha model

To select the composition of the naphtha model used in this work, a typical composition of the naphtha feed to ethylene cracker obtained from literature was used as reference, having this naphtha feed a BTEX total content of 10 wt.% [4]. The content of benzene (1.8 wt.%), toluene (3.0 wt.%), and ethylbenzene (2.0 wt.%) in the naphtha model was the same that those in the typical naphtha feed. *p*-Xylene and *o*-xylene were represented in the naphtha model as *p*-xylene (3.2 wt.%) to simplify the analytical method. For the same reason, the aliphatic content in the typical naphtha feed (90 wt.%) was represented in the naphtha model by 30 wt.% of *n*-hexane, *n*-heptane, and *n*-octane. The composition of the naphtha model employed in this work is shown in Table 2. The masses of aromatic and aliphatic hydrocarbons added in the preparation of the model were gravimetrically determined using a Mettler Toledo XS 205 balance with a precision of ±1 · 10^{-5} g.

Table 2
Composition in mass fraction of the naphtha model.

Hydrocarbon	w_i
n-Hexane	0.300
n-Heptane	0.300
n-Octane	0.300
Benzene	0.018
Toluene	0.030
Ethylbenzene	0.020
p-Xylene	0.032

2.3. Liquid–liquid extraction. Experimental procedure and analysis

To analyze the performance of the {[4empy][Tf_2N] + [emim][DCA]} IL mixture with a x_1 of 0.3 as BTEX extraction solvent, liquid–liquid equilibria (LLE) experiments were made at

Table 3
Experimental LLE on mass fraction (w) in the liquid–liquid extraction of aromatics from the naphtha model at $P = 0.1$ MPa using {[4empy][Tf_2N] + [emim][DCA]} at $x_1 = 0.3$ IL mixture as solvent as a function of temperature and Solvent/Feed (S/F) ratio.[a]

T (K)	S/F	Raffinate phase							Extract phase							
		w_{hexa}	w_{hepta}	w_{octa}	w_{benz}	w_{tol}	w_{etbenz}	$w_{p\text{-}xyl}$	w_{hexa}	w_{hepta}	w_{octa}	w_{benz}	w_{tol}	w_{etbenz}	$w_{p\text{-}xyl}$	w_{ILs}
303.2	1.0	0.2990	0.3057	0.3103	0.0130	0.0253	0.0181	0.0286	0.0012	0.0011	0.0008	0.0038	0.0051	0.0022	0.0035	0.9823
	2.0	0.2999	0.3096	0.3172	0.0102	0.0212	0.0162	0.0257	0.0012	0.0012	0.0008	0.0030	0.0043	0.0020	0.0032	0.9843
	3.0	0.2960	0.3107	0.3285	0.0083	0.0182	0.0149	0.0234	0.0012	0.0011	0.0007	0.0024	0.0037	0.0018	0.0028	0.9863
	4.0	0.3002	0.3095	0.3322	0.0071	0.0162	0.0135	0.0213	0.0013	0.0012	0.0008	0.0022	0.0034	0.0017	0.0027	0.9867
	5.0	0.3035	0.3173	0.3273	0.0062	0.0144	0.0122	0.0191	0.0013	0.0012	0.0008	0.0019	0.0030	0.0016	0.0025	0.9877
313.2	1.0	0.2956	0.3062	0.3123	0.0131	0.0255	0.0183	0.0290	0.0013	0.0013	0.0009	0.0037	0.0050	0.0022	0.0034	0.9822
	2.0	0.2978	0.3096	0.3183	0.0104	0.0215	0.0164	0.0260	0.0013	0.0013	0.0009	0.0029	0.0042	0.0020	0.0031	0.9843
	3.0	0.2957	0.3118	0.3266	0.0086	0.0187	0.0150	0.0236	0.0012	0.0012	0.0008	0.0023	0.0035	0.0017	0.0027	0.9866
	4.0	0.3037	0.2987	0.3363	0.0066	0.0160	0.0150	0.0237	0.0012	0.0013	0.0009	0.0020	0.0032	0.0017	0.0026	0.9871
	5.0	0.3055	0.2981	0.3440	0.0059	0.0140	0.0126	0.0199	0.0013	0.0013	0.0009	0.0018	0.0029	0.0015	0.0024	0.9879
323.2	1.0	0.2901	0.3068	0.3160	0.0132	0.0258	0.0186	0.0295	0.0014	0.0014	0.0010	0.0035	0.0048	0.0022	0.0033	0.9824
	2.0	0.2949	0.2917	0.3332	0.0080	0.0209	0.0197	0.0316	0.0011	0.0014	0.0012	0.0025	0.0041	0.0022	0.0034	0.9841
	3.0	0.2915	0.3131	0.3286	0.0087	0.0190	0.0152	0.0239	0.0013	0.0014	0.0009	0.0022	0.0034	0.0017	0.0027	0.9864
	4.0	0.2931	0.3159	0.3310	0.0076	0.0170	0.0138	0.0216	0.0014	0.0015	0.0010	0.0020	0.0031	0.0016	0.0025	0.9869
	5.0	0.2832	0.3175	0.3445	0.0065	0.0152	0.0129	0.0202	0.0013	0.0013	0.0010	0.0017	0.0028	0.0015	0.0023	0.9881

[a] Standard uncertainties (u) are: $u(T) = 0.1$ K, $u(P) = 1$ kPa, $u(w_{hexa,raffinate}) = 0.0008$, $u(w_{hepta,raffinate}) = 0.0008$, $u(w_{octa,raffinate}) = 0.0009$, $u(w_{benz,raffinate}) = 0.0003$, $u(w_{tol,raffinate}) = 0.0004$, $u(w_{etbenz,raffinate}) = 0.0004$, $u(w_{p\text{-}xyl,raffinate}) = 0.0005$, $u(w_{hexa,extract}) = 0.0004$, $u(w_{hepta,extract}) = 0.0004$, $u(w_{octa,extract}) = 0.0003$, $u(w_{benz,extract}) = 0.0006$, $u(w_{tol,extract}) = 0.0006$, $u(w_{etbenz,extract}) = 0.0006$, $u(w_{p\text{-}xyl,extract}) = 0.0007$, $u(w_{ILs,extract}) = 0.0011$.

Table 4
Experimental LLE on mass fraction (w) in the liquid–liquid extraction of aromatics from the naphtha model at $P = 0.1$ MPa using sulfolane as solvent as a function of temperature and Solvent/Feed (S/F) ratio.[a]

T (K)	S/F	Raffinate phase								Extract phase							
		w_{hexa}	w_{hepta}	w_{octa}	w_{benz}	w_{tol}	w_{etbenz}	$w_{p\text{-}xyl}$	w_{sulf}	w_{hexa}	w_{hepta}	w_{octa}	w_{benz}	w_{tol}	w_{etbenz}	$w_{p\text{-}xyl}$	w_{sulf}
303.2	1.0	0.2990	0.3057	0.3114	0.0119	0.0236	0.0169	0.0278	0.0037	0.0034	0.0026	0.0020	0.0063	0.0080	0.0044	0.0057	0.9676
	2.0	0.3003	0.3110	0.3182	0.0090	0.0193	0.0144	0.0244	0.0034	0.0036	0.0026	0.0021	0.0047	0.0064	0.0037	0.0049	0.9720
	3.0	0.2998	0.3135	0.3259	0.0072	0.0163	0.0125	0.0217	0.0031	0.0037	0.0026	0.0020	0.0038	0.0054	0.0032	0.0043	0.9750
	4.0	0.3017	0.3171	0.3280	0.0060	0.0140	0.0110	0.0193	0.0029	0.0038	0.0026	0.0020	0.0032	0.0047	0.0028	0.0039	0.9770
	5.0	0.3009	0.3195	0.3327	0.0050	0.0122	0.0097	0.0174	0.0026	0.0034	0.0025	0.0019	0.0026	0.0040	0.0024	0.0034	0.9798
313.2	1.0	0.2947	0.3065	0.3141	0.0120	0.0239	0.0170	0.0280	0.0038	0.0038	0.0033	0.0024	0.0064	0.0082	0.0045	0.0060	0.9654
	2.0	0.2915	0.3107	0.3272	0.0092	0.0194	0.0146	0.0247	0.0027	0.0039	0.0031	0.0024	0.0048	0.0065	0.0038	0.0051	0.9704
	3.0	0.2892	0.3133	0.3363	0.0072	0.0164	0.0128	0.0222	0.0026	0.0039	0.0030	0.0023	0.0038	0.0054	0.0032	0.0045	0.9739
	4.0	0.2918	0.3157	0.3386	0.0060	0.0141	0.0111	0.0201	0.0026	0.0039	0.0031	0.0024	0.0032	0.0047	0.0029	0.0040	0.9758
	5.0	0.2951	0.3191	0.3393	0.0051	0.0121	0.0097	0.0172	0.0024	0.0038	0.0030	0.0023	0.0027	0.0040	0.0025	0.0035	0.9782
323.2	1.0	0.2930	0.3074	0.3152	0.0121	0.0238	0.0170	0.0280	0.0035	0.0038	0.0034	0.0029	0.0060	0.0081	0.0044	0.0062	0.9652
	2.0	0.2874	0.3119	0.3300	0.0090	0.0193	0.0147	0.0247	0.0030	0.0042	0.0036	0.0030	0.0046	0.0065	0.0037	0.0053	0.9691
	3.0	0.2843	0.3151	0.3397	0.0072	0.0163	0.0128	0.0220	0.0026	0.0042	0.0036	0.0029	0.0037	0.0054	0.0032	0.0046	0.9724
	4.0	0.2867	0.3183	0.3443	0.0056	0.0136	0.0111	0.0194	0.0010	0.0043	0.0037	0.0031	0.0031	0.0047	0.0029	0.0042	0.9740
	5.0	0.2917	0.3206	0.3415	0.0053	0.0125	0.0099	0.0173	0.0012	0.0042	0.0035	0.0029	0.0027	0.0041	0.0025	0.0037	0.9764

[a] Standard uncertainties (u) are: $u(T) = 0.1$ K, $u(P) = 1$ kPa, $u(w_{hexa,raffinate}) = 0.0008$, $u(w_{hepta,raffinate}) = 0.0009$, $u(w_{octa,raffinate}) = 0.0009$, $u(w_{benz,raffinate}) = 0.0005$, $u(w_{tol,raffinate}) = 0.0005$, $u(w_{etbenz,raffinate}) = 0.0004$, $u(w_{p\text{-}xyl,raffinate}) = 0.0006$, $u(w_{sulf,raffinate}) = 0.0007$, $u(w_{hexa,extract}) = 0.0005$, $u(w_{hepta,extract}) = 0.0005$, $u(w_{octa,extract}) = 0.0005$, $u(w_{benz,extract}) = 0.0007$, $u(w_{tol,extract}) = 0.0007$, $u(w_{etbenz,extract}) = 0.0006$, $u(w_{p\text{-}xyl,extract}) = 0.0007$, $u(w_{sulf,extract}) = 0.0010$.

303.2 K, 313.2 K, and 323.2 K in 8 mL vials with screw caps employing a Labnet Vortemp 1550 shaking incubator for 5 h at 800 rpm to reach the LLE. Afterward, to get the complete separation of the phases, vials were moved to a Labnet Accublock dry bath for 12 h at the same temperature of the LLE experiments controlled with a precision of ±0.1 K. To study the influence of the solvent to feed ratio, LLE experiments were performed at each temperature at S/F ratios in mass basis of 1.0, 2.0, 3.0, 4.0, and 5.0. Employing the same conditions of temperature and S/F ratio, LLE experiments using sulfolane were also made to compare the results obtained using both extraction solvents.

An Agilent 7890A gas chromatograph (GC) together with a liquid autosampler Agilent 7693 and a flame ionization detector (FID) was employed to determine the composition of the raffinate phases in the experiments employing the IL-based solvent and the compositions of both raffinate and extract phases in the liquid–liquid extraction experiments using sulfolane. A complete description of this analytical method can be found in our previous publications [12,30]. The presence of ILs in the raffinate phases was assumed as negligible since signals corresponding to ILs were not found in ^{1}H NMR spectra obtained by a Bruker Avance 500 MHz NMR spectrometer.

Compositions of extract phases in the liquid–liquid extraction employing the {[4empy][Tf_2N] + [emim][DCA]} mixture as solvent were determined in triplicate by a multiple headspace extraction (MHE) method. An Agilent 7890A GC coupled to an Agilent 7697A Headspace Sampler was used to analyze the samples from extract phases. A complete description of the MHE technique used in this paper can be found elsewhere [12,30,31]. Standard uncertainties of the compositions of raffinate and extract phases are shown in Tables 3 and 4 together with the experimental results.

3. Results and discussion

3.1. Experimental results in the liquid–liquid extraction of BTEX from the naphtha model as a function of temperature and solvent to feed ratio

Experimental compositions of raffinate and extract phases in mass basis in the separation of BTEX from the naphtha model

Table 5
Aliphatic and aromatic distribution ratios (D_i), aromatic/aliphatic selectivities ($\alpha_{arom,aliph}$), yield of extraction of aromatics and aliphatics (Yld_i), and relative purity of extracted aromatics in the extract phase (P_{arom}) using {[4empy][Tf$_2$N] + [emim][DCA]} at x_1 = 0.3 as solvent.

T (K)	S/F	D_{aliph}	D_{arom}	$\alpha_{arom,aliph}$	Yld_{aliph} (%)	Yld_{arom} (%)	P_{arom} (%)
303.2	1.0	0.003	0.172	51.3	0.4	15.3	82.7
	2.0	0.003	0.171	50.8	0.7	25.9	80.1
	3.0	0.003	0.165	50.7	1.0	32.9	77.9
	4.0	0.004	0.172	49.0	1.5	40.6	75.1
	5.0	0.004	0.175	49.8	1.9	45.8	73.1
313.2	1.0	0.004	0.167	45.3	0.4	14.6	81.0
	2.0	0.004	0.164	44.0	0.8	24.7	77.9
	3.0	0.003	0.155	45.9	1.1	31.2	76.4
	4.0	0.004	0.157	43.3	1.5	38.7	73.9
	5.0	0.004	0.163	44.7	1.9	43.0	71.1
323.2	1.0	0.004	0.158	37.6	0.4	14.0	78.2
	2.0	0.004	0.152	38.0	0.8	24.9	76.8
	3.0	0.004	0.149	38.3	1.2	30.1	73.3
	4.0	0.004	0.155	37.8	1.7	37.6	70.7
	5.0	0.004	0.151	40.0	2.0	42.0	69.9

Table 6
Aliphatic and aromatic distribution ratios (D_i), aromatic/aliphatic selectivities ($\alpha_{arom,aliph}$), yield of extraction of aromatics and aliphatics (Yld_i), and relative purity of extracted aromatics in the extract phase (P_{arom}) using sulfolane as solvent.

T (K)	S/F	D_{aliph}	D_{arom}	$\alpha_{arom,aliph}$	Yld_{aliph} (%)	Yld_{arom} (%)	P_{arom} (%)
303.2	1.0	0.009	0.304	35.0	0.9	24.5	75.4
	2.0	0.009	0.294	33.0	1.8	39.7	70.4
	3.0	0.009	0.291	32.7	2.8	50.8	66.7
	4.0	0.009	0.290	32.9	3.7	58.7	63.6
	5.0	0.008	0.280	34.3	4.4	63.4	61.5
313.2	1.0	0.010	0.309	29.5	1.1	25.0	72.3
	2.0	0.010	0.298	29.4	2.1	40.9	68.2
	3.0	0.010	0.288	29.2	3.1	51.0	64.6
	4.0	0.010	0.287	28.9	4.2	59.4	61.1
	5.0	0.010	0.289	30.2	5.1	64.4	58.2
323.2	1.0	0.011	0.306	27.7	1.1	25.2	71.0
	2.0	0.012	0.295	25.5	2.4	40.6	65.0
	3.0	0.011	0.291	25.5	3.6	51.8	61.3
	4.0	0.012	0.297	25.6	5.0	60.1	57.3
	5.0	0.011	0.286	25.7	6.0	65.4	54.8

employing the {[4empy][Tf$_2$N] + [emim][DCA]} mixture with a x_1 of 0.3 as solvent as a function of temperature and S/F ratio are listed in Table 3. Compositions of the LLE experiments employing sulfolane in the liquid–liquid extraction of BTEX from the naphtha model at 303.2 K, 313.2 K, and 323.2 K and S/F ratios from 1.0 to 5.0 are also gathered in Table 4.

3.2. Distribution ratios and aromatic/aliphatic selectivities

From the experimental compositions of raffinate and extract phases, aliphatic and aromatic distribution ratios and aromatic/aliphatic selectivities have been calculated to evaluate the performance of the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture in the liquid–liquid extraction of BTEX from the naphtha model and to compare the extractive properties of this IL-based solvent with those employing sulfolane.

Values of aliphatic distribution ratios (D_{aliph}) have been calculated as indicated in the next expression:

$$D_{aliph} = \frac{w^{II}_{hexa} + w^{II}_{hepta} + w^{II}_{octa}}{w^{I}_{hexa} + w^{I}_{hepta} + w^{I}_{octa}} \qquad (1)$$

where w_i denotes the hydrocarbon mass fraction, I indicates the raffinate phase, and II refers to the extract phase.

Experimental values of aliphatic distribution ratios employing the IL mixture are listed in Table 5, whereas the D_{aliph} employing sulfolane are shown in Table 6. As observed, aliphatic distribution ratios using the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture were approximately two times lower than the values of D_{aliph} employing sulfolane. Therefore, the solubility of the aliphatic hydrocarbons is lower in the IL-based solvent than in the sulfolane. This result would imply lower losses of aliphatics in the extract stream and a greater purity of the extracted BTEX using the IL mixture.

The influence of temperature on the values of D_{aliph} was not significant in the results of both extraction solvents. Therefore, to reduce the energy consumption in the extractor a value of 303.2 K seems to be the most appropriate temperature. At a constant value of temperature, the change in the S/F ratio hardly affected to the experimental D_{aliph} using sulfolane and the IL mixture.

From the LLE results, aromatic distribution ratios (D_{arom}) have been estimated according to the following equation:

$$D_{arom} = \frac{w^{II}_{benz} + w^{II}_{tol} + w^{II}_{etbenz} + w^{II}_{p\text{-}xyl}}{w^{I}_{benz} + w^{I}_{tol} + w^{I}_{etbenz} + w^{I}_{p\text{-}xyl}} \qquad (2)$$

Experimental values of aromatic distribution ratios for the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture are listed in Table 5, whereas the values of D_{arom} using sulfolane are presented in Table 6. To evaluate the influence of temperature and S/F ratio on D_{arom}, experimental values using both extraction solvents are graphically shown in Fig. 1. As can be observed, D_{arom} using sulfolane were considerably greater than the values employing the IL mixture over the whole range of temperatures and solvent to feed ratios. This result would cause greater extraction yields of BTEX using sulfolane than those employing the IL-based solvent at the same temperature and S/F ratio in the separation of aromatics from the naphtha model.

As observed, the effect of temperature of the values of D_{arom} was more pronounced in the results using the IL mixture, remaining almost constant the aromatic distribution ratios with the change of temperature using sulfolane. At a constant value of S/F ratio, the highest values of aromatic distribution ratios were obtained at the lowest temperature for the IL-based solvent. This trend with temperature is in agreement with the results obtained by Hansmeier et al. in the separation of toluene from *n*-heptane employing pure pyridinium and imidazolium-based ILs [32], and with the predictions made with the COSMO-RS (Conductor-like Screening Model for Real Solvents) method [33]. Ferreira et al. proposed that the decrease in D_{arom} with temperature is due to stronger molecular

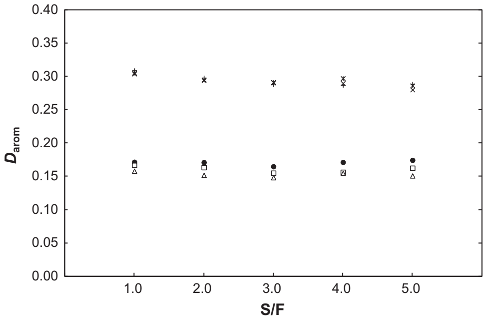


Fig. 1. Aromatic distribution ratios as a function of temperature and solvent to feed ratio using {[4empy][Tf$_2$N] + [emim][DCA]} at x_1 = 0.3 as solvent: ●, 303.2 K; □, 313.2 K; Δ, 323.2 K, and employing sulfolane: ×, 303.2 K; +, 313.2 K; and ✳, 323.2 K.

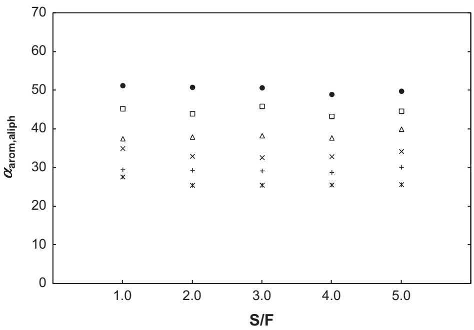


Fig. 2. Aromatic/aliphatic selectivities as a function of temperature and solvent to feed ratio using {[4empy][Tf$_2$N] + [emim][DCA]} at x_1 = 0.3 as solvent: ●, 303.2 K; □, 313.2 K; Δ, 323.2 K, and employing sulfolane: ×, 303.2 K; +, 313.2 K; and ✱, 323.2 K.

movements that reduce the π–π interactions between BTEX and the IL-based solvent [33]. Hence, to increase the amount of aromatics extracted using the IL mixture, a temperature of 303.2 K is the most appropriate. On the other hand, an increase in the value of S/F ratio hardly affected to the aromatic distribution ratios using the IL mixture and it caused a very slight decrease in the values of D_{arom} for the sulfolane.

In addition to the analysis of solute distribution ratios, aromatic/aliphatic selectivities ($\alpha_{arom,aliph}$) in the separation of BTEX from the naphtha model have been calculated following the next expression from the previously calculated values of aromatic and aliphatic distribution ratios:

$$\alpha_{arom,aliph} = \frac{D_{arom}}{D_{aliph}} \tag{3}$$

Experimental values of aromatic/aliphatic selectivities for the IL mixture are listed in Table 5, whereas the values of $\alpha_{arom,aliph}$ using sulfolane are presented in Table 6. As in the case of the aromatic distribution ratios, aromatic/aliphatic selectivities of both solvents as a function of temperature and S/F ratios have been plotted in Fig. 2 to perform a comparative analysis. As observed, selectivities employing the IL mixture were substantially greater than the sulfolane values under the same conditions of solvent to feed ratio and temperature. This result is due to the considerably smaller solubility of the aliphatic hydrocarbons in the IL-based solvent than in sulfolane. Lower values of $\alpha_{arom,aliph}$ would imply a higher purity of the BTEX extracted by the IL mixture and, therefore, it would simplify the subsequent unit of purification of solutes and regeneration of the solvent.

As can be observed in Fig. 2, the effect of temperature on the values of $\alpha_{arom,aliph}$ was similar in the results using both extraction solvents, achieving the highest values of aromatic/aliphatic selectivity at the lowest temperature (303.2 K). As in the case of D_{arom}, the same trend with temperature was previously observed in the separation of toluene from n-heptane using sulfolane [34], in the extraction of toluene from n-heptane employing pure ILs [32], and in the predictions from COSMO-RS [33]. Therefore, to increase the purity of the BTEX extracted a low value of temperature in the liquid–liquid extraction process should be selected. To conclude, the $\alpha_{arom,aliph}$ were almost constant over the whole range of S/F ratio for both extraction solvents at constant temperature. This result is due to the small influence of S/F in the values of aromatic and aliphatic distribution ratios previously discussed.

3.3. Extraction yield of aromatics and aliphatics and relative purity of extracted aromatics

In addition to the values of distribution ratios and selectivity, the extraction yields of the solutes and the purity of the extracted solutes must be considered to optimize an industrial process of liquid–liquid extraction. For that reason, extraction yield of aliphatics (Yld_{aliph}) were calculated according to the following expression:

$$\text{Yld}_{aliph}(\%) = 100\frac{m^{II}_{hexa} + m^{II}_{hepta} + m^{II}_{octa}}{m^{feed}_{hexa} + m^{feed}_{hepta} + m^{feed}_{octa}} \tag{4}$$

where m_i is the mass of each hydrocarbon in the feed or in the extract phase. To determine the amount of each hydrocarbon in the extract phase, an overall mass balance was performed in each vial considering the amounts added to the vial with the feed and the experimental compositions of raffinate and extract phases. Values of extraction yields of aliphatics using the IL mixture are listed in Table 5, whereas the values of Yld_{aliph} for the sulfolane are presented in Table 6.

As can be observed in Fig. 3, extraction yields of aliphatics employing sulfolane were several times higher than the values for the IL mixture, as a consequence of the higher solubility of the aliphatic hydrocarbons in sulfolane. To reduce the extraction yield of aliphatics employing the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture or sulfolane, a temperature of 303.2 K and a low S/F ratio seems to be the most adequate conditions.

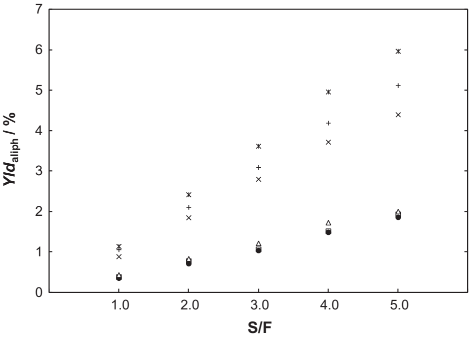


Fig. 3. Extraction yield of aliphatics as a function of temperature and solvent to feed ratio using {[4empy][Tf$_2$N] + [emim][DCA]} at x_1 = 0.3 as solvent: ●, 303.2 K; □, 313.2 K; Δ, 323.2 K, and employing sulfolane: ×, 303.2 K; +, 313.2 K; and ✱, 323.2 K.

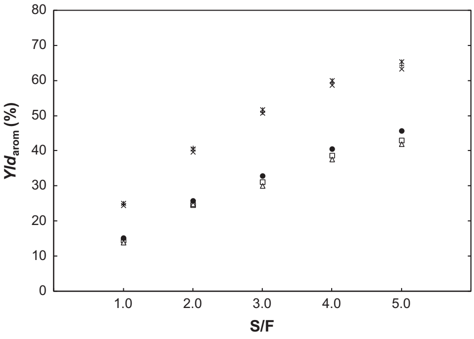


Fig. 4. Extraction yield of aromatics as a function of temperature and solvent to feed ratio using {[4empy][Tf$_2$N] + [emim][DCA]} at x_1 = 0.3 as solvent: ●, 303.2 K; □, 313.2 K; Δ, 323.2 K, and using sulfolane as solvent: ×, 303.2 K; +, 313.2 K; and ✱, 323.2 K.

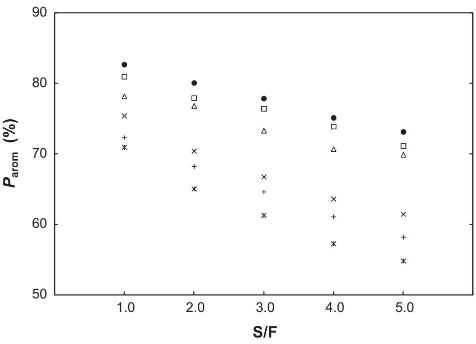


Fig. 5. Relative purity of extracted aromatics in the extract phase as a function of temperature and solvent to feed ratio using {[4empy][Tf$_2$N] + [emim][DCA]} at x_1 = 0.3 as solvent: ●, 303.2 K; □, 313.2 K; Δ, 323.2 K, and using sulfolane as solvent: ×, 303.2 K; +, 313.2 K; and ⁎, 323.2 K.

From the results obtained by overall mass balances in the vials, yields of extraction of aromatics (Yld$_{arom}$) were also calculated according to the following equation:

$$\mathrm{Yld}_{arom}(\%) = 100\frac{m^{II}_{benz} + m^{II}_{tol} + m^{II}_{etbenz} + m^{II}_{p\text{-xyl}}}{m^{feed}_{benz} + m^{feed}_{tol} + m^{feed}_{etbenz} + m^{feed}_{p\text{-xyl}}} \quad (5)$$

Experimental extraction yields of BTEX employing the {[4empy][Tf$_2$N] + [emim][DCA]} mixture are shown in Table 5, whereas the values of Yld$_{arom}$ using sulfolane are listed in Table 6. A graphical comparison between Yld$_{arom}$ for both extraction solvents are presented in Fig. 4. As seen, the extraction yields using sulfolane were greater than the values employing the IL mixture, as a result of the higher solubility of the BTEX in the conventional solvent.

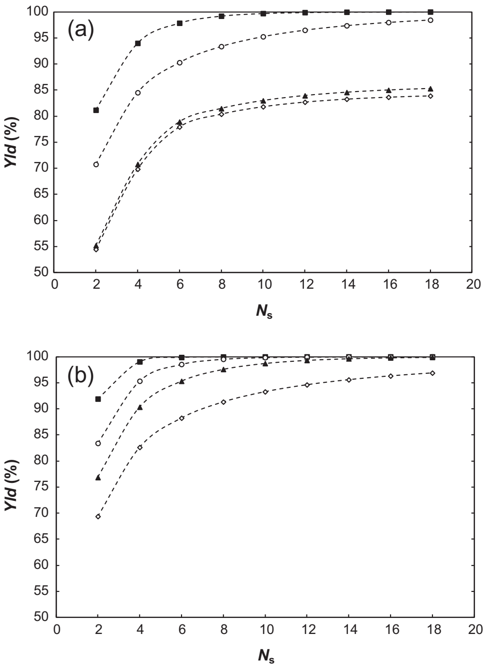


Fig. 6. Extraction yield of BTEX employing as solvents the (a) {[4empy][Tf$_2$N] + [emim][DCA]} at x_1 = 0.3 IL mixture and (b) sulfolane: ■, Benzene; ○, Toluene; ▲, Ethylbenzene; ◇, *p*-Xylene at 303.2 K and a S/F ratio equal to 5.0 as a function of the number of equilibrium stages in the extraction column. Dashed lines are to guide the eye.

The effect of changing the experimental temperature on Yld$_{arom}$ was opposite employing both extraction solvents. By contrast, the influence of the S/F ratio in the values of extraction yields of BTEX was similar for the two extraction solvents, obtaining a significant increase in Yld$_{arom}$ as the S/F ratio increases. To increase the extraction yield of BTEX using the IL mixture a temperature of 303.2 K and a S/F ratio of 5.0 should be selected.

The purity of extracted solutes will determine the difficulty and the number of required steps in the purification unit; therefore, a greater purity of the extracted BTEX would imply a more simplified unit of recovery of aromatics and it would facilitate the recycling of the IL-based solvent to the extraction column. From the experimental compositions of the extract phase, the relative purity of extracted BTX in the extract phase (P_{arom}) was calculated as follows:

$$P_{arom}(\%) = 100 \times \frac{w^{II}_{benz} + w^{II}_{tol} + w^{II}_{etbenz} + w^{II}_{p\text{-xyl}}}{\left(w^{II}_{hexa} + w^{II}_{hepta} + w^{II}_{octa}\right) + \left(w^{II}_{benz} + w^{II}_{tol} + w^{II}_{etbenz} + w^{II}_{p\text{-xyl}}\right)} \quad (6)$$

Relative purities of the extracted BTEX in the LLE experiments using the {[4empy][Tf$_2$N] + [emim][DCA]} mixture are listed in Table 5, whereas the sulfolane values are listed in Table 6. In Fig. 5, relative purities of extracted aromatics are plotted as a function of temperature and S/F ratio for both extraction solvents. As a consequence of the higher aromatic/aliphatic selectivities for the IL mixture, the values of P_{arom} of this solvent were substantially higher than those using sulfolane over the whole range of temperature and S/F ratio. As can be seen, at a constant value of S/F the highest relative purities of the extracted BTEX were obtained at the lowest temperature (303.2 K) for the two solvents. The effect of increasing the solvent to feed ratio also caused a decrease in P_{arom}, having a greater influence in the extraction employing sulfolane.

Considering the influence of temperature and the S/F ratio in the different extractive properties studied, the optimal conditions to perform the separation of BTEX from the naphtha model have been selected to increase the amount of the extracted aromatics and the relative purities of the BTEX. A temperature of 303.2 K was chosen to ensure high values of extraction yield of BTEX and relative purity of aromatics together with low extraction yield of aliphatics. On the other hand, the most appropriate solvent to feed ratio seems to be 5.0 to increase the extraction yield of aromatics with moderate relative purities of the extracted BTEX, since the effect of S/F on both properties was contrary and it is more important to obtain high values of Yld$_{arom}$ to reduce the aromatic content in the naphtha feed to cracker.

3.4. Simulation of countercurrent extraction columns using the Kremser equation

From the experimental results of the separation of BTEX from the naphtha model at 303.2 K and S/F ratio of 5.0 employing sulfolane and the IL mixture, countercurrent extraction columns were simulated using the Kremser Equation [35]. The effect of the number of equilibrium stages in the column on the extraction yield of BTEX, on the relative purity of the extracted aromatics, and on the flows and compositions of the raffinate and extract streams have been studied from the results of the simulations. The group method of Kremser to perform the simulation of an extraction column is analogous to the Kremser method employed in absorption.

The extraction factor (E) and the reciprocal of E (U) have been calculated according to the following expressions:

$$E_i = D_i \frac{V}{L} \tag{7}$$

$$U_i = \frac{1}{E_i} = \frac{L}{D_i V} \tag{8}$$

where D_i is the distribution ratio of each component in mass basis at the temperature and S/F ratio selected, L indicates the mass flow of the raffinate stream, whereas V denotes the mass flow of the extract stream. Distribution ratios of each component were calculated from the LLE results showed in Tables 3 and 4 at 303.2 K and S/F ratio of 5.0.

The simulation of an extraction column can be made by the Kremser method if extract and raffinate phases are immiscible and if the distribution ratios can be considered constant under the conditions of the simulation [36]. In all the LLE experiments of separation of BTEX from the naphtha model using the {[4empy][Tf$_2$N] + [emim][DCA]} mixture and sulfolane as solvents two immiscible phases were found. In addition, as observed in Tables 5 and 6, the distribution ratios of all hydrocarbons were nearly constant with temperature and S/F ratio using both solvents. Therefore, the two required conditions to simulate a liquid–liquid extraction column using the Kremser equation were observed in the separation of BTEX from the naphtha model. Enthalpy balances were not made in the simulation of the countercurrent extraction columns since the enthalpy changes in an adiabatic liquid–liquid extraction column can be considered as negligible [35].

To perform the simulations, first the number of the equilibrium stages (N_s) in the extraction column was set between 2 and 18. A flow of 1000 t/h of the naphtha model was selected as a basis of the calculation, being 5000 t/h the solvent flow as a consequence of the S/F ratio of 5.0 selected as the optimal. An iterative method implemented in Microsoft Excel was used to calculate the individual flows of each component in extract and raffinate streams by mass balances. A complete description of the Kremser method employed to make a simulation of extraction columns can be found elsewhere [35].

From the results of the simulations, individual extraction yields of the BTEX have been estimated as the relationship between the flow of each hydrocarbon in the extract and the feed streams. In Fig. 6, extraction yields of benzene, toluene, ethylbenzene, and *p*-xylene using the IL mixture are plotted as a function of the number of equilibrium stages. As seen, the decreasing order of extraction yields at a constant value of N_s was benzene, toluene, ethylbenzene, and *p*-xylene. This behavior is related to the order of solubility of aromatics in ILs, decreasing the solubility as the molecular weight increases [33]. An extraction yield of benzene higher than 99.9% was achieved using at least 12 equilibrium stages, whereas 16 stages were required to reach an extraction yield of toluene greater than 98.0%. At N_s equal to 18, the extraction yield of ethylbenzene and *p*-xylene were 85.3% and 83.9%, respectively. The total extraction yield of BTEX using 18 equilibrium stages using the IL mixture was 91.4%. Therefore, the {[4empy][Tf$_2$N] + [emim][DCA]} mixture could be used to perform the complete removing of benzene from the naphtha feed to ethylene cracker, to reduce almost completely the toluene content, and to made the separation of large amounts of ethylbenzene and *p*-xylene.

Extraction yields of BTEX employing sulfolane are also graphically shown in Fig. 6. As can be observed, values employing sulfolane at a constant number of equilibrium stages were higher than those employing the binary IL mixture, as a result of the greater experimental aromatic distribution ratios and extraction yields of BTEX for the sulfolane. Hence, the sulfolane could be also employed to separate BTEX from the naphtha model obtaining higher amounts of aromatics. However, the relative purity of the extracted BTEX must be also evaluated.

From the results of the simulations, values of purities of the BTEX in the extract stream have been calculated and plotted in Fig. 7. As seen, the relative purity of the aromatics extracted were substantially greater using the IL-based solvent than employing sulfolane, as a result of the higher values of aromatic/aliphatic selectivity of the IL mixture. The higher purity of the BTEX would reduce investment and operating costs because the purification of the BTEX would be simpler. As a consequence of the nonvolatile nature of the ILs, the separation between the BTEX and the ILs could be made by a flash distillation or by stripping at low temperatures, replacing this operation the extractive stripper and the distillation column currently used in the UOP Sulfolane Process [19,20].

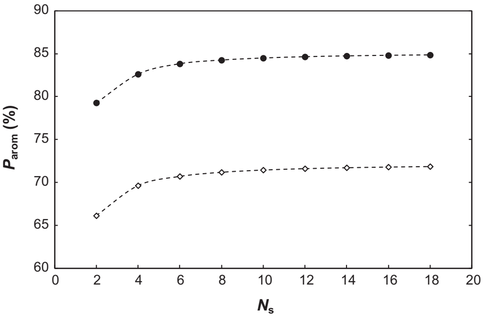


Fig. 7. Relative purities of the BTEX in the extract phase at 303.2 K and S/F equal to 5.0 as a function of the number of equilibrium stages in the extraction column. ●, employing the [4empy][Tf$_2$N] + [emim][DCA]} at x_1 = 0.3 IL mixture; ◇, using sulfolane as solvent. Dashed lines are to guide the eye.

Table 7
Results of the simulations of countercurrent extraction columns in the liquid–liquid extraction of BTEX from a naphtha model using the Kremser equation at S/F = 5.0, T = 303.2 K, and N_s = 18.

	Feed	Solvent	Raffinate phase	Extract phase
Extraction solvent: {[4empy][Tf$_2$N] + [emim][DCA]} at x_1 = 0.3				
Flow (t/h)	1000.0	5000.0	892.2	5107.8
Benzene (wt.%)	1.80	0.00	0.00	0.35
Toluene (wt.%)	3.00	0.00	0.05	0.58
Ethylbenzene (wt.%)	2.00	0.00	0.33	0.33
p-Xylene (wt.%)	3.20	0.00	0.58	0.53
Aromatics (wt.%)	10.00	0.00	0.96	1.79
n-Hexane (wt.%)	30.00	0.00	32.90	0.13
n-Heptane (wt.%)	30.00	0.00	32.95	0.12
n-Octane (wt.%)	30.00	0.00	33.19	0.07
n-Alkanes (wt.%)	90.00	0.00	99.04	0.32
Binary IL mixture (wt.%)	0.00	100.00	0.00	97.89
Extraction solvent: Sulfolane				
Flow (t/h)	1000.0	5000.0	864.5	5135.5
Benzene (wt.%)	1.80	0.00	0.00	0.35
Toluene (wt.%)	3.00	0.00	0.00	0.58
Ethylbenzene (wt.%)	2.00	0.00	0.00	0.39
p-Xylene (wt.%)	3.20	0.00	0.12	0.60
Aromatics (wt.%)	10.00	0.00	0.12	1.92
n-Hexane (wt.%)	30.00	0.00	32.64	0.35
n-Heptane (wt.%)	30.00	0.00	33.30	0.24
n-Octane (wt.%)	30.00	0.00	33.68	0.17
n-Alkanes (wt.%)	90.00	0.00	99.62	0.76
Sulfolane (wt.%)	0.00	100.00	0.26	97.32

In Table 7, flows and compositions of feed, solvent, raffinate, and extract streams obtained in the simulations of the extraction columns using sulfolane and the IL mixture are listed. These simulations were performed at 303.2 K, a solvent to feed ratio of 5.0, and employing 18 equilibrium stages to compare the results of both solvents under the same conditions. As observed, the aromatic content in the extract stream using sulfolane (1.92%) was slightly higher than that using the IL mixture (1.79%). By contrast, the aliphatic losses in the extract stream were substantially higher employing sulfolane (0.76%) than those for the IL-based solvent (0.32%). Finally, the sulfolane content in raffinate stream was 0.26% due to the solubility of the sulfolane in the hydrocarbons, being this fact an important drawback of the sulfolane with respect to IL-based solvents. Because of the negligible solubility of the ILs in the raffinate, the wash column used in the UOP Sulfolane Process to recover the sulfolane dissolved in this stream would be unnecessary in a separation process of BTEX from the naphtha model employing the {[4empy][Tf_2N] + [emim][DCA]} mixture.

4. Conclusions

In this paper, we have studied the performance of the {[4empy][Tf_2N] + [emim][DCA]} IL mixture with a [4empy][Tf_2N] mole fraction of 0.3 as extraction solvent in the separation of BTEX from a naphtha model feed to the ethylene cracker with a total aromatic content of 10 wt.%. The influence of temperature and solvent to feed ratio on the extractive properties have been analyzed from the results obtained in extraction experiments made at temperatures between 303.2 K and 323.2 K and S/F ratios from 1.0 to 5.0. Experiments under the same conditions employing sulfolane have also been performed to compare the extractive properties of both solvents.

The optimal conditions of temperature and S/F have been chosen considering the influence of these variables on aromatic distribution ratios, aromatic/aliphatic selectivities, extraction yields, and relative purities of BTEX in the extract phase. A temperature of 303.2 K has been selected to achieve high extraction yields of BTEX and high values of purity of the aromatics in the extract phase employing the IL mixture. A solvent to feed ratio of 5.0 has also been chosen as the most adequate S/F ratio to ensure high extraction yields of aromatics.

To evaluate the potential use of the {[4empy][Tf_2N] + [emim][DCA]} IL mixture in the separation of BTEX from the naphtha feed to ethylene crackers, a countercurrent extraction column has been simulated using the Kremser method. From the results of the simulations, the influence of the number of equilibrium stages in the extractor on the extraction yield of BTEX and in the relative purity of the extracted aromatics has been evaluated. The extraction yields of BTEX using the {[4empy][Tf_2N] + [emim][DCA]} IL mixture have been lower than those employing sulfolane. The IL mixture has been revealed as a useful solvent to achieve the complete separation of benzene and an almost complete recovery of toluene from the naphtha. In addition, the purity of the BTEX obtained by the IL mixture has been considerably greater than the sulfolane value. Taking into account this result and the nonvolatile character of the ILs, the unit of BTEX purification and solvent regeneration in a separation process of BTEX from the naphtha model using the IL mixture would reduce investment and operating costs with respect to the UOP Sulfolane Process.

Acknowledgments

The authors are grateful to the Ministerio de Economía y Competitividad (MINECO) of Spain and the Comunidad Autónoma de Madrid for financial support of Projects CTQ2011-23533 and S2013/MAE-2800, respectively. Marcos Larriba thanks Ministerio de Educación, Cultura y Deporte for awarding him an FPU grant (Reference AP-2010-0318), and Pablo Navarro also thanks MINECO for awarding him an FPI grant (Reference BES-2012-052312), and Emilio J. González also thanks MINECO for awarding him a Juan de la Cierva Contract (Reference JCI-2012-12005).

References

[1] H.G. Franck, J.W. Staldelhofer, Industrial Aromatic Chemistry, Springer-Verlag, New York, 1988.
[2] J. Gary, G. Handwerk, M. Kaiser, Petroleum Refining Technology and Economics, CRC Press, Boca Raton, FL, 2007.
[3] R.A. Meyers, Handbook of Petroleum Refining Processes, McGraw-Hill, New York, 2004.
[4] G.W. Meindersma, A.B. de Haan, Conceptual process design for aromatic/aliphatic separation with ionic liquids, Chem. Eng. Res. Des. 86 (2008) 745–752.
[5] M. Matsumoto, K. Mochiduki, K. Fukunishi, K. Kondo, Extraction of organic acids using imidazolium-based ionic liquids and their toxicity to *Lactobacillus rhamnosus*, Sep. Purif. Technol. 40 (2004) 97–101.
[6] A.B. Pereiro, A. Rodríguez, Azeotrope-breaking using [BMIM][$MeSO_4$] ionic liquid in an extraction column, Sep. Purif. Technol. 62 (2008) 733–738.
[7] L.I.N. Tomé, V.R. Catambas, A.R.R. Teles, M.G. Freire, I.M. Marrucho, J.A.P. Coutinho, Tryptophan extraction using hydrophobic ionic liquids, Sep. Purif. Technol. 72 (2010) 167–173.
[8] A.F.M. Claudio, M.G. Freire, C.S.R. Freire, A.J.D. Silvestre, J.A.P. Coutinho, Extraction of vanillin using ionic-liquid-based aqueous two-phase systems, Sep. Purif. Technol. 75 (2010) 39–47.
[9] F.S. Oliveira, J.M.M. Araujo, R. Ferreira, L.P.N. Rebelo, I.M. Marrucho, Extraction of L-lactic, L-malic, and succinic acids using phosphonium-based ionic liquids, Sep. Purif. Technol. 85 (2012) 137–146.
[10] E. Alvarez-Guerra, A. Irabien, Extraction of lactoferrin with hydrophobic ionic liquids, Sep. Purif. Technol. 98 (2012) 432–440.
[11] M. Zawadzki, L. Niedzicki, W. Wieczorek, U. Domanska, Estimation of extraction properties of new imidazolide anion based ionic liquids on the basis of activity coefficient at infinite dilution measurements, Sep. Purif. Technol. 118 (2013) 242–254.
[12] M. Larriba, P. Navarro, J. García, F. Rodríguez, Separation of toluene from *n*-heptane, 2,3-dimethylpentane, and cyclohexane using binary mixtures of [4empy][Tf_2N] and [emim][DCA] ionic liquids as extraction solvents, Sep. Purif. Technol. 120 (2013) 392–401.
[13] S.L. Garvey, M.L. Dietz, Ionic liquid anion effects in the extraction of metal ions by macrocyclic polyethers, Sep. Purif. Technol. 123 (2014) 145–152.
[14] Q. Hu, J. Zhao, F. Wang, F. Huo, H. Liu, Selective extraction of vanadium from chromium by pure [C_8mim][PF_6]: an anion exchange process, Sep. Purif. Technol. 131 (2014) 94–101.
[15] Y. Ji, J. Chen, J. Lv, Z. Li, L. Xing, S. Ding, Extraction of keratin with ionic liquids from poultry feather, Sep. Purif. Technol. 132 (2014) 577–583.
[16] X. Chen, S. Yuan, A.A. Abdeltawab, S.S. Al-Deyab, J. Zhang, L. Yu, G. Yu, Extractive desulfurization and denitrogenation of fuels using functional acidic ionic liquids, Sep. Purif. Technol. 133 (2014) 187–193.
[17] L. Ge, F. Xia, Y. Song, K. Yang, Z. Qin, L. Li, Solubility of luteolin in several imidazole-based ionic liquids and extraction from peanut shells using selected ionic liquid as solvent, Sep. Purif. Technol. 135 (2014) 223–228.
[18] R.D. Rogers, K.R. Seddon, Science 302 (2003) 792–793.
[19] S.T. Anjan, Ionic liquid for aromatic extraction: are they ready?, Chem Eng. Prog. 102 (2006) 30–39.
[20] P. Navarro, M. Larriba, J. García, F. Rodríguez, Vapor–liquid equilibria of n-heptane + toluene + [emim][DCA] system by headspace gas chromatography, Fluid Phase Equilib. 387 (2015) 209–216.
[21] G.W. Meindersma, A.R. Hansmeier, A.B. de Haan, Ionic liquids for aromatics extraction. Present status and future outlook, Ind. Eng. Chem. Res. 49 (2010) 7530–7540.
[22] G.W. Meindersma, A.B. de Haan, Cyano-containing ionic liquids for the extraction of aromatic hydrocarbons from an aromatic/aliphatic mixture, Sci. China Chem. 55 (2012) 1488–1499.
[23] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, Liquid–liquid extraction of toluene from *n*-heptane using binary mixtures of N-butylpyridinium tetrafluoroborate and N-butylpyridinium bis(trifluoromethylsulfonyl)imide ionic liquids, Chem. Eng. J. 180 (2012) 210–215.
[24] M. Larriba, P. Navarro, J. García, F. Rodríguez, Liquid–liquid extraction of toluene from n-heptane by [emim][TCM] + [emim][DCA] binary ionic liquid mixtures, Fluid Phase Equilib. 364 (2014) 48–54.
[25] M. Larriba, P. Navarro, J. García, F. Rodríguez, Extraction of benzene, ethylbenzene, and xylenes from n-heptaneusing binary mixtures of [4empy][Tf2N] and [emim][DCA] ionic liquids, Fluid Phase Equilib. 380 (2014) 1–10.
[26] M. Larriba, P. Navarro, J. García, F. Rodríguez, Liquid–liquid extraction of toluene from n-alkanes using [4empy][Tf2N] + [emim][DCA] ionic liquid mixtures, J. Chem. Eng. Data 59 (2014) 1692–1699.

[27] P. Navarro, M. Larriba, J. García, F. Rodríguez, Thermal stability, specific heats, and surface tensions of ([emim][DCA] + [4empy][Tf_2N]) ionic liquid mixtures, J. Chem. Thermodyn. 76 (2014) 152–160.

[28] P. Navarro, M. Larriba, E. Rojo, J. García, F. Rodríguez, Thermal properties of cyano-based ionic liquids, J. Chem. Eng. Data 58 (2013) 2187–2193.

[29] M. Larriba, P. Navarro, J. García, F. Rodríguez, Liquid–liquid extraction of BTEX from reformer gasoline using binary mixtures of [4empy][Tf_2N] and [emim][DCA] ionic liquids, Energy Fuels 28 (2014) 6666–6676.

[30] M. Larriba, P. Navarro, J. García, F. Rodríguez, Liquid–liquid extraction of toluene from heptane using [emim][DCA], [bmim][DCA], and [emim][TCM] ionic liquids, Ind. Eng. Chem. Res. 52 (2013) 2714–2720.

[31] B. Kolb, L.S. Ettre, Static Headspace-Gas Chromatography: Theory and Practice, Wiley-VCH, New York, 1997.

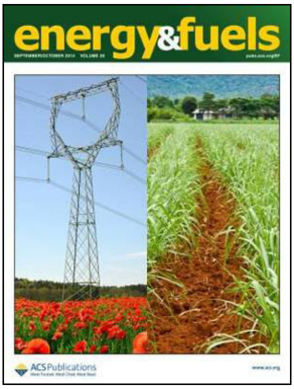
[32] A.R. Hansmeier, M. Minoves Ruiz, M. Meindersma, A.B. de Haan, Liquid–liquid equilibria for the three ternary systems (3-methyl-*N*-butylpyridinium dicyanamide + toluene + heptane), (1-butyl-3-methylimidazolium dicyanamide + toluene + heptane) and (1-butyl-3-methylimidazolium thiocyanate + toluene + heptane) at $T = (313.15$ and $348.15)$ K and $p = 0.1$ MPa, J. Chem. Eng. Data 55 (2010) 708–713.

[33] A.R. Ferreira, M.G. Freire, J.C. Ribeiro, F.M. Lopes, J.G. Crespo, J.A.P. Coutinho, Overview of the liquid–liquid equilibria of ternary systems composed of ionic liquid and aromatic and aliphatic hydrocarbons, and their modeling by COSMO-RS, Ind. Eng. Chem. Res. 51 (2012) 3483–3507.

[34] G.W. Meindersma, A.J.G. Podt, A.B. de Haan, Selection of ionic liquids for the extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures, Fuel Process. Technol. 87 (2005) 59–70.

[35] E.J. Henley, J.D. Seader, Equilibrium-Stage Separation Operations in Chemical Engineering, John Wiley and Sons, New York, 1981.

[36] F. Buchbender, F. Onink, G.W. Meindersma, A. de Haan, A. Pfenning, Simulation of aromatics extraction with an ionic liquid in a pilot-plant Kühni extractor based on single-drop experiments, Chem. Eng. Sci. 82 (2012) 167–176.



Energy & Fuels

Factor de impacto (2013): 2,73

Publicación 8:

Liquid−Liquid Extraction of BTEX from Reformer Gasoline Using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids

Marcos Larriba, Pablo Navarro, Julián García, Francisco Rodriguez

Energy and Fuels, 2014, 28, 6666-6676.

energy&fuels Article
pubs.acs.org/EF

Liquid–Liquid Extraction of BTEX from Reformer Gasoline Using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids

Marcos Larriba, Pablo Navarro, Julián García,* and Francisco Rodríguez

Department of Chemical Engineering, Complutense University of Madrid, E-28040 Madrid, Spain

ABSTRACT: Reformer gasoline is the main source for benzene, toluene, ethylbenzene, and xylenes (BTEX). Nowadays, the separation of BTEX is performed by liquid–liquid extraction using organic solvents such as sulfolane. Ionic liquids (ILs) have been recently proposed as potential replacements of sulfolane in the separation of aromatics from alkanes, being the binary IL mixture formed by the 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf_2N]) and the 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) one of the most promising IL-based solvents. In this work, we have studied the liquid–liquid extraction of BTEX from a reformer gasoline model using the {[4empy][Tf_2N] + [emim][DCA]} IL mixture with a [4empy][Tf_2N] mole fraction of 0.3 and sulfolane as solvents at temperatures between 303.2 and 323.2 K. The effects of temperature and solvent to feed ratio on the extractive properties have been studied to select the most appropriate conditions to extract BTEX using the IL mixture. From the experimental data, aromatic and aliphatic distribution ratios, aromatic/aliphatic selectivities, yields of extraction of aromatics and aliphatics, and relative purities of extracted aromatics have been calculated. The Kremser equation has also been used to simulate a countercurrent extraction column using both extraction solvents in the separation of BTEX from the reformer gasoline model.

1. INTRODUCTION

In the U.S.A., around 75% of BTEX is obtained by liquid–liquid extraction from reformer gasoline.[1] Most of the U.S. refineries use polyglycols or sulfolane as extraction solvents for recovering BTEX, being the Sulfolane process licensed by UOP the most currently used technology.[2,3] In this process, the separation of the aromatics is made in an extractor followed by an extractive stripper and an extract recovery distillation column. As a result of the high boiling point of the sulfolane (560 K), solvent regeneration and recovery of the extracted solutes have a high energy consumption.[4]

ILs are liquid salts at temperatures lower than 373.2 K, with their nonvolatile character being their most remarkable property. The use of ILs in desulfurization and dearomatization of fuels by liquid–liquid extraction has extensively studied in the past few years.[5−13] ILs have been revealed as potential replacements of sulfolane due to their exceptional properties. Because of their properties, ILs could simplify the aromatic separation process, reducing operating costs and process steps.[14−17] However, pure ILs have shown several drawbacks to be applied at industrial scale, such as high viscosities or extractive properties lower than the sulfolane in the extraction of aromatics from aliphatics.[17,18]

In our previous works, we have proposed the use of binary IL mixtures to finely tune the extractive and thermophysical properties of the IL-based solvents.[19−23] The {[4empy][Tf_2N] + [emim][DCA]} mixed solvent is the most promising IL mixture studied in the liquid–liquid extraction of aromatics from alkanes. The {[4empy][Tf_2N] + [emim][DCA]} mixture with a [4empy][Tf_2N] mole fraction (ϕ_1) of 0.3 has exhibited aromatic distribution ratios and aromatic/alkanes selectivities comparable to the sulfolane values in the extraction of toluene from *n*-heptane, 2,3-dimethylpentane, and cyclohexane,[20] and in the separation of toluene from *n*-hexane, *n*-octane, and *n*-nonane.[21] This binary IL mixture has also shown densities, dynamic viscosities, and surface tensions similar to the sulfolane values as can be observed in Table 1.[20,22,24,25] In addition, the {[4empy][Tf_2N] + [emim][DCA]} IL mixture with a ϕ_1 equal to 0.3 has presented an onset temperature of 560.7 K in a dynamic thermogravimetric analysis at a heating rate of 10 K·min^{-1}.[22] Therefore, this IL-based solvent has shown adequate extractive and physical properties and good thermal stability to be applied in an industrial process of liquid–liquid extraction of aromatics.

In this work, we have studied the performance of the {[4empy][Tf_2N] + [emim][DCA]} mixture with a [4empy][Tf_2N] mole fraction of 0.3 in the liquid–liquid extraction of BTEX from alkanes in a reformer gasoline model. Liquid–liquid extraction experiments have been made at 303.2, 313.2, and 323.2 K and atmospheric pressure, because this temperature range is the most usual in the separation of aromatics from alkanes using ILs.[17,18] Experiments under the same conditions have been performed using sulfolane as extraction solvent to be use as benchmark. The influence of the solvent to feed ratio on the extractive properties of the solvents has also been evaluated.

2. EXPERIMENTAL SECTION

2.1. Chemicals. [4empy][Tf_2N] and [emim][DCA] ILs were supplied by Iolitec GmbH with a mass fraction purity higher than 0.99 and 0.98, respectively. Water content in the ILs was 42 ppm in the [4empy][Tf_2N] and 1790 ppm in the [emim][DCA], whereas halide content was lower than 100 ppm in the [4empy][Tf_2N]) and lower than 2% in the [emim][DCA]. The structure of both ILs is shown in Figure 1. *n*-Hexane, *n*-heptane, *n*-octane, benzene, toluene, ethylbenzene, *p*-xylene, and sulfolane were purchased from Sigma-Aldrich.

Received: July 23, 2014
Revised: September 26, 2014
Published: September 28, 2014

dx.doi.org/10.1021/ef501671d | *Energy Fuels* 2014, 28, 6666−6676

Table 1. Densities (ρ), Dynamic Viscosities (μ), and Surface Tensions (σ) of the {[4empy][Tf_2N] (1) + [emim][DCA] (2)} IL Mixture with a [4empy][Tf_2N] Mole Fraction of 0.3 and Sulfolane as a Function of Temperature

	{[4empy][Tf_2N] + [emim][DCA]} at ϕ_1 = 0.3			sulfolane		
physical property	T (K)			T (K)		
	303.2	313.2	323.2	303.2	313.2	323.2
ρ (g·cm^{-3})	1.2576[a]	1.2499[a]	1.2422[a]	1.2620[b]	1.2532[b]	1.2444[b]
μ (m·Pa^{-1})	18.4[a]	13.9[a]	10.9[a]	10.8[b]	8.1[b]	6.4[b]
σ (mN m^{-1})	45.3[c]	44.1[c]	42.8[c]	47.9[d]	47.2[d]	46.6[d]

[a] From ref 20. [b] From ref 25. [c] From ref 22. [d] From ref 24.

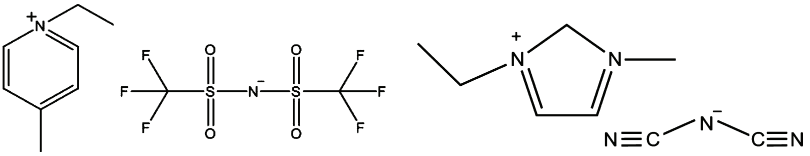


Figure 1. Structure of the ILs employed in this work. (Left) 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf_2N]) and (right) 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]).

The specifications of chemicals are presented in Table 2, together with the analysis method and the abbreviations of the compounds used in this work. Chemicals were employed as received without further purification. To avoid water absorption, ILs were handed in a glovebox filled with dry nitrogen and stored in a desiccator in their original bottles.

Table 2. Suppliers, Purities of Chemicals, Analysis Methods, and Abbreviations

chemical	supplier	mass fraction purity	analysis method	abbreviation
[4empy][Tf_2N][a]	Iolitec GmbH	0.99	NMR[c] and IC[d]	ILs
[emim][DCA][b]	Iolitec GmbH	0.98	NMR[c] and IC[d]	
n-hexane	Sigma-Aldrich	0.99	GC[e]	hexa
n-heptane	Sigma-Aldrich	0.997	GC[e]	hepta
n-octane	Sigma-Aldrich	0.99	GC[e]	octa
benzene	Sigma-Aldrich	0.995	GC[e]	benz
toluene	Sigma-Aldrich	0.995	GC[e]	tol
ethylbenzene	Sigma-Aldrich	0.998	GC[e]	etbenz
p-xylene	Sigma-Aldrich	0.99	GC[e]	*p*-xyl
sulfolane	Sigma-Aldrich	0.99	GC[e]	sulf

[a] [4empy][Tf_2N] = 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide. [b] [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide. [c] Nuclear Magnetic Resonance. [d] Ion chromatography. [e] Gas chromatography.

2.2. Reformer Gasoline Model. Franck and Stadelhofer published the mass composition of a typical reformer gasoline: benzene (5 wt %), toluene (24 wt %), ethylbenzene (4 wt %), xylenes and C_9–C_{10} aromatics (22 wt %), and nonaromatics (45 wt %).[1] To facilitate the analytical method, xylenes and C_9–C_{10} aromatics were represented in the reformer gasoline model by a 22 wt % of *p*-xylene, whereas the 45 wt % of nonaromatic was formed by a 15 wt % of *n*-hexane, *n*-heptane, and *n*-octane. The composition of the reformer gasoline model used in this work is shown in Table 3. In the preparation of the model, hydrocarbons were gravimetrically added using a Mettler Toledo XS 205 balance with a precision of ±1 × 10^{-5} g.

Table 3. Composition of the Reformer Gasoline Model

hydrocarbon	wt %
benzene	5.0
toluene	24.0
ethylbenzene	4.0
p-xylene	22.0
n-hexane	15.0
n-heptane	15.0
n-octane	15.0

2.3. Experimental Procedure and Analysis. Liquid–liquid equilibria (LLE) experiments were performed in 8 mL vials with screw caps using the {[4empy][Tf_2N] + [emim][DCA]} IL mixture with a [4empy][Tf_2N] mole fraction of 0.3 and sulfolane as solvents. The LLE was reached in a Labnet Vortemp 1550 shaking incubator at 303.2, 313.2, and 323.2 K for 5 h at 800 rpm. Later, vials were placed in a Labnet Accublock dry bath at a controlled temperature equal to the extraction temperature with a precision of ±0.1 K for 12 h to ensure the complete separation of the raffinate and extract phases. At each extraction temperature, vials were gravimetrically prepared at solvent to feed ratios in mass basis of 1.0, 2.0, 3.0, 4.0, and 5.0.

Raffinate and extract phases were analyzed by gas chromatography (GC) and headspace gas chromatography (HS-GC), respectively. Samples from raffinate phases were analyzed in triplicate using an Agilent 7890A gas chromatograph with a liquid autosampler Agilent 7693 and a flame ionization detector (FID). In the LLE experiments employing sulfolane as extraction solvent, the compositions of both phases were also measured by GC. A detailed description of this analytical method can be found elsewhere.[20,25] In our previous works, the presence of IL in the raffinate phase was assumed as negligible since signals corresponding to ILs were not found in ^{1}H NMR spectra.[19−21,25] In this work, we have also taken samples from raffinate phases of the LLE experiments using the ILs mixture to quantify the solubility of the ILs in the raffinate. We have used a Mettler Toledo TGA/DSC 1 thermogravimetric analyzer with a precision of ±0.1 K and ±10^{-3} mg to determine the IL mass fraction in raffinate by a thermogravimetric analysis (TGA). The volatile compounds were evaporated by an isothermal TGA at 393.2 K for 0.5 h, and the IL could be quantified as consequence of the nonvolatile character of the IL mixture and its thermal stability under these conditions. However,

Table 4. Experimental LLE on Mass Fraction (w) in the Liquid–Liquid Extraction of BTEX from the Reformer Gasoline Model using {[4empy][Tf_2N] + [emim][DCA]} at ϕ_1 = 0.3 and P = 0.1 MPa as Solvent as a Function of Temperature and Solvent to Feed Ratio (S/F)[a]

		raffinate phase							extract phase							
T (K)	S/F	w_{hexa}	w_{hepta}	w_{octa}	w_{benz}	w_{tol}	w_{etbenz}	$w_{p\text{-xyl}}$	w_{hexa}	w_{hepta}	w_{octa}	w_{benz}	w_{tol}	w_{etbenz}	$w_{p\text{-xyl}}$	w_{ILs}
303.2	1.0	0.1605	0.1663	0.1712	0.0374	0.2083	0.0430	0.2133	0.0011	0.0012	0.0008	0.0116	0.0472	0.0062	0.0299	0.9020
	2.0	0.1763	0.1838	0.1905	0.0301	0.1813	0.0401	0.1979	0.0011	0.0011	0.0008	0.0088	0.0387	0.0054	0.0260	0.9181
	3.0	0.1877	0.1991	0.2086	0.0248	0.1589	0.0373	0.1836	0.0011	0.0011	0.0008	0.0072	0.0329	0.0048	0.0232	0.9289
	4.0	0.2010	0.2136	0.2234	0.0211	0.1398	0.0341	0.1670	0.0012	0.0012	0.0009	0.0064	0.0300	0.0046	0.0218	0.9339
	5.0	0.2095	0.2250	0.2374	0.0182	0.1246	0.0315	0.1538	0.0012	0.0012	0.0008	0.0055	0.0265	0.0048	0.0213	0.9387
313.2	1.0	0.1602	0.1662	0.1711	0.0377	0.2089	0.0429	0.2130	0.0012	0.0013	0.0009	0.0109	0.0441	0.0058	0.0267	0.9091
	2.0	0.1730	0.1820	0.1986	0.0299	0.1801	0.0398	0.1966	0.0012	0.0013	0.0009	0.0083	0.0352	0.0051	0.0229	0.9251
	3.0	0.1890	0.2019	0.1953	0.0256	0.1628	0.0380	0.1874	0.0011	0.0012	0.0009	0.0068	0.0310	0.0046	0.0219	0.9325
	4.0	0.1967	0.2120	0.2252	0.0215	0.1415	0.0344	0.1687	0.0012	0.0013	0.0009	0.0061	0.0284	0.0044	0.0206	0.9371
	5.0	0.2116	0.2325	0.2319	0.0182	0.1234	0.0309	0.1515	0.0013	0.0014	0.0010	0.0055	0.0263	0.0041	0.0195	0.9409
323.2	1.0	0.1568	0.1652	0.1704	0.0381	0.2118	0.0432	0.2145	0.0011	0.0013	0.0010	0.0102	0.0420	0.0056	0.0265	0.9123
	2.0	0.1697	0.1813	0.1904	0.0309	0.1854	0.0407	0.2016	0.0013	0.0014	0.0010	0.0080	0.0349	0.0050	0.0234	0.9250
	3.0	0.1753	0.1932	0.2091	0.0253	0.1716	0.0379	0.1876	0.0011	0.0012	0.0009	0.0065	0.0301	0.0045	0.0213	0.9344
	4.0	0.1776	0.2043	0.2344	0.0215	0.1452	0.0365	0.1805	0.0012	0.0013	0.0010	0.0058	0.0277	0.0043	0.0204	0.9383
	5.0	0.1779	0.2031	0.2661	0.0173	0.1260	0.0351	0.1745	0.0013	0.0015	0.0011	0.0053	0.0262	0.0042	0.0198	0.9406

[a] Standard uncertainties (u) are $u(T)$ = 0.1 K, $u(P)$ = 1 kPa, $u(w_{hexa,raffinate})$ = 0.0005, $u(w_{hepta,raffinate})$ = 0.0006, $u(w_{octa,raffinate})$ = 0.0006, $u(w_{benz,raffinate})$ = 0.0004, $u(w_{tol,raffinate})$ = 0.0006, $u(w_{etbenz,raffinate})$ = 0.0004, $u(w_{p\text{-xyl},raffinate})$ = 0.0006, $u(w_{hexa,extract})$ = 0.0003, $u(w_{hepta,extract})$ = 0.0004, $u(w_{octa,extract})$ = 0.0003, $u(w_{benz,extract})$ = 0.0009, $u(w_{tol,extract})$ = 0.0009, $u(w_{etbenz,extract})$ = 0.0008, $u(w_{p\text{-xyl},extract})$ = 0.0008, $u(w_{ILs,extract})$ = 0.0010.

Table 5. Experimental LLE on Mass Fraction (w) in the Liquid−Liquid Extraction of BTEX from the Reformer Gasoline Model using Sulfolane as Solvent at P = 0.1 MPa as a Function of Temperature and Solvent to Feed Ratio (S/F)[a]

		raffinate phase								extract phase							
T (K)	S/F	w_{hexa}	w_{hepta}	w_{octa}	w_{benz}	w_{tol}	w_{etbenz}	$w_{p\text{-}xyl}$	w_{sulf}	w_{hexa}	w_{hepta}	w_{octa}	w_{benz}	w_{tol}	w_{etbenz}	$w_{p\text{-}xyl}$	w_{sulf}
303.2	1.0	0.1636	0.1724	0.1801	0.0324	0.1868	0.0385	0.2007	0.0255	0.0056	0.0049	0.0041	0.0190	0.0770	0.0123	0.0556	0.8215
	2.0	0.1835	0.1970	0.2089	0.0245	0.1545	0.0337	0.1813	0.0166	0.0048	0.0042	0.0034	0.0138	0.0597	0.0100	0.0458	0.8583
	3.0	0.1986	0.2163	0.2312	0.0197	0.1307	0.0295	0.1620	0.0120	0.0046	0.0039	0.0032	0.0110	0.0489	0.0083	0.0389	0.8812
	4.0	0.2078	0.2294	0.2502	0.0164	0.1128	0.0263	0.1476	0.0095	0.0043	0.0036	0.0029	0.0090	0.0410	0.0071	0.0333	0.8988
	5.0	0.2109	0.2392	0.2708	0.0138	0.0985	0.0238	0.1356	0.0074	0.0049	0.0038	0.0028	0.0077	0.0356	0.0062	0.0295	0.9095
313.2	1.0	0.1626	0.1718	0.1792	0.0326	0.1860	0.0380	0.1971	0.0327	0.0073	0.0063	0.0053	0.0191	0.0783	0.0127	0.0578	0.8132
	2.0	0.1735	0.1931	0.2160	0.0243	0.1537	0.0342	0.1837	0.0215	0.0056	0.0051	0.0045	0.0139	0.0612	0.0104	0.0484	0.8509
	3.0	0.1911	0.2138	0.2380	0.0198	0.1303	0.0296	0.1622	0.0152	0.0054	0.0048	0.0041	0.0109	0.0494	0.0086	0.0403	0.8765
	4.0	0.1967	0.2255	0.2625	0.0164	0.1120	0.0265	0.1484	0.0120	0.0052	0.0045	0.0037	0.0090	0.0415	0.0073	0.0345	0.8943
	5.0	0.2036	0.2376	0.2788	0.0140	0.0984	0.0237	0.1341	0.0098	0.0055	0.0045	0.0036	0.0077	0.0359	0.0063	0.0303	0.9062
323.2	1.0	0.1577	0.1708	0.1801	0.0326	0.1855	0.0379	0.1957	0.0397	0.0083	0.0077	0.0067	0.0189	0.0800	0.0132	0.0608	0.8044
	2.0	0.1773	0.1961	0.2118	0.0249	0.1532	0.0331	0.1763	0.0273	0.0070	0.0065	0.0056	0.0139	0.0617	0.0105	0.0492	0.8456
	3.0	0.1889	0.2152	0.2392	0.0201	0.1292	0.0289	0.1576	0.0209	0.0057	0.0055	0.0049	0.0108	0.0499	0.0087	0.0415	0.8730
	4.0	0.1802	0.2263	0.2754	0.0163	0.1116	0.0265	0.1471	0.0166	0.0052	0.0050	0.0045	0.0088	0.0417	0.0074	0.0357	0.8917
	5.0	0.2061	0.2370	0.2778	0.0147	0.0985	0.0230	0.1286	0.0143	0.0051	0.0048	0.0071	0.0075	0.0360	0.0064	0.0311	0.9020

[a] Standard uncertainties (u) are $u(T) = 0.1$ K, $u(P) = 1$ kPa, $u(w_{hexa,raffinate}) = 0.0006$, $u(w_{hepta,raffinate}) = 0.0007$, $u(w_{octa,raffinate}) = 0.0006$, $u(w_{benz,raffinate}) = 0.0006$, $u(w_{tol,raffinate}) = 0.0009$, $u(w_{etbenz,raffinate}) = 0.0005$, $u(w_{p\text{-}xyl,raffinate}) = 0.0007$, $u(w_{sulf,raffinate}) = 0.0009$, $u(w_{hexa,extract}) = 0.0006$, $u(w_{hepta,extract}) = 0.0006$, $u(w_{octa,extract}) = 0.0005$, $u(w_{benz,extract}) = 0.0008$, $u(w_{tol,extract}) = 0.0008$, $u(w_{etbenz,extract}) = 0.0009$, $u(w_{p\text{-}xyl,extract}) = 0.0009$, $u(w_{sulf,extract}) = 0.0009$.

the presence of ILs has not been detected in these samples by thermogravimetric analyses. Because of this, the solubility of ILs in the raffinate phases was considered negligible.

To determine the composition of the extract phases in the LLE experiments employing the IL mixture as solvent, a multiple headspace extraction (MHE) method was employed. From each extract phase, three samples of approximately 100 μL were added to 20 mL closed vials and then analyzed by an Agilent 7890A GC coupled with an Agilent 7697A Headspace Sampler. A complete description of the MHE technique employed can be found elsewhere.[25,26] The uncertainty associated with the LLE compositions can be found in Tables 4 and 5 being calculated from the results obtained in the triplicate analyses.

3. RESULTS AND DISCUSSION

3.1. Experimental Results in the Liquid−liquid Extraction of BTEX from the Reformer Gasoline Model as a Function of Temperature and Solvent to Feed Ratio. Compositions of the raffinate and extract phases in the liquid−liquid extraction of BTEX from the reformer gasoline model at temperatures between 303.2 and 323.2 K and solvent to feed ratios from 1.0 to 5.0 using the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture at ϕ_1 = 0.3 as solvent are listed in Table 4. Experimental compositions in mass basis in the extraction of BTEX from the reformer gasoline model employing sulfolane can also be found in Table 5.

3.2. Distribution Ratios and Aromatic/aliphatic Selectivities. To evaluate the performance of the IL-based solvent in the extraction of BTEX from the reformer gasoline model, aliphatic and aromatic distribution ratios and aromatic/aliphatic selectivities have been calculated and compared to the experimental values using sulfolane. Values of aliphatic distribution ratios (D_{aliph}) have been calculated from the experimental compositions according to the following expression:

$$D_{\text{aliph}} = \frac{w_{\text{hexa}}^{\text{II}} + w_{\text{hepta}}^{\text{II}} + w_{\text{octa}}^{\text{II}}}{w_{\text{hexa}}^{\text{I}} + w_{\text{hepta}}^{\text{I}} + w_{\text{octa}}^{\text{I}}} \quad (1)$$

where w_i is the hydrocarbon mass fraction, I refers to the raffinate phase, and II indicates the extract phase. Values of D_{aliph} using the IL mixture are shown in Table 6, whereas the aliphatic distribution ratios employing sulfolane are listed in Table 7. Comparing the values obtained using both solvents, D_{aliph} for the IL-based solvent were substantially lower than those for the sulfolane. A lower aliphatic distribution ratio causes a higher value of aromatic/aliphatic selectivity and, consequently, a higher purity of the aromatic hydrocarbons extracted.

An increase in the extraction temperature has caused a slight increase in the D_{aliph} for both extraction solvents. This trend is in agreement with the results published by Hansmeier et al. in the liquid−liquid extraction of toluene from *n*-heptane using pure imidazolium and pyridinium-based ILs as solvents at 303.15 and 328.15 K.[27] As the solvent to feed ratio increased, the values of D_{aliph} were slightly lower. Therefore, to minimize the amount of aliphatics extracted, the selection of low temperatures and high values of solvent to feed ratio seems to be appropriated.

Aromatic distribution ratios (D_{arom}) have also been calculated from the LLE composition using the next equation:

Table 6. Aliphatic and Aromatic Distribution Ratios (D_i), Aromatic/aliphatic Selectivities ($\alpha_{\text{arom,aliph}}$), Yield of Extraction of Aromatics and Aliphatics (Yld_i), and Relative Purity of Extracted Aromatics in the Extract Phase (P_{arom}) using {[4empy][Tf$_2$N] + [emim][DCA]} at ϕ_1 = 0.3 as Solvent

T (K)	S/F	D_{aliph}	D_{arom}	$\alpha_{\text{arom,aliph}}$	Yld_{aliph} (%)	Yld_{arom} (%)	P_{arom} (%)
303.2	1.0	0.006	0.189	30.6	0.7	18.9	96.9
	2.0	0.005	0.176	32.2	1.4	30.9	96.3
	3.0	0.005	0.168	32.9	2.2	39.5	95.7
	4.0	0.005	0.173	34.1	3.1	48.8	95.1
	5.0	0.005	0.177	37.0	3.8	56.0	94.8
313.2	1.0	0.007	0.174	25.3	0.8	17.7	96.2
	2.0	0.006	0.160	25.7	1.7	28.8	95.4
	3.0	0.005	0.155	28.8	2.3	38.1	95.3
	4.0	0.005	0.163	30.1	3.3	46.9	94.6
	5.0	0.006	0.171	30.4	4.5	54.0	93.6
323.2	1.0	0.007	0.166	24.0	0.8	16.6	96.1
	2.0	0.007	0.155	23.0	1.7	27.9	95.1
	3.0	0.006	0.148	26.0	2.3	36.5	95.0
	4.0	0.006	0.152	27.1	3.3	45.0	94.4
	5.0	0.006	0.157	26.4	4.5	53.5	93.5

Table 7. Aliphatic and Aromatic Distribution Ratios (D_i), Aromatic/Aliphatic Selectivities ($\alpha_{\text{arom,aliph}}$), Yield of Extraction of Aromatics and Aliphatics (Yld_i), and Relative Purity of Extracted Aromatics in the Extract Phase (P_{arom}) Using Sulfolane as Solvent

T (K)	S/F	D_{aliph}	D_{arom}	$\alpha_{\text{arom,aliph}}$	Yld_{aliph} (%)	Yld_{arom} (%)	P_{arom} (%)
303.2	1.0	0.028	0.358	12.6	4.0	35.6	91.8
	2.0	0.021	0.328	15.6	6.4	54.1	91.2
	3.0	0.018	0.313	17.3	8.8	65.8	90.1
	4.0	0.016	0.298	19.0	10.8	72.2	89.3
	5.0	0.016	0.291	18.2	14.2	78.4	87.3
313.2	1.0	0.037	0.370	10.0	4.9	36.2	89.9
	2.0	0.026	0.338	12.9	7.8	56.2	89.8
	3.0	0.022	0.320	14.3	10.7	67.1	88.4
	4.0	0.020	0.304	15.6	13.0	74.4	87.3
	5.0	0.019	0.297	15.8	16.3	79.9	85.6
323.2	1.0	0.045	0.383	8.6	5.7	37.0	88.4
	2.0	0.033	0.349	10.7	9.3	57.1	87.6
	3.0	0.025	0.330	13.3	12.0	68.6	87.4
	4.0	0.022	0.311	14.4	14.5	75.8	86.4
	5.0	0.024	0.306	13.0	20.7	80.8	82.7

$$D_{\text{arom}} = \frac{w_{\text{benz}}^{\text{II}} + w_{\text{tol}}^{\text{II}} + w_{\text{etbenz}}^{\text{II}} + w_{p\text{-xyl}}^{\text{II}}}{w_{\text{benz}}^{\text{I}} + w_{\text{tol}}^{\text{I}} + w_{\text{etbenz}}^{\text{I}} + w_{p\text{-xyl}}^{\text{I}}} \quad (2)$$

Values of D_{arom} using the IL mixture are reported in Table 6, whereas the aromatic distribution ratios employing sulfolane are listed in Table 7. To facilitate the comparison between the extractive properties of both solvents, D_{arom} are represented in Figure 2 as a function of both temperature and solvent to feed ratio. As observed, aromatic distribution ratios using sulfolane were considerably higher than those of the IL mixture. Higher values of aromatic distribution ratios will cause a higher extraction yield of aromatics using sulfolane than that employing the IL mixture under the same conditions of temperature and solvent to feed ratio.

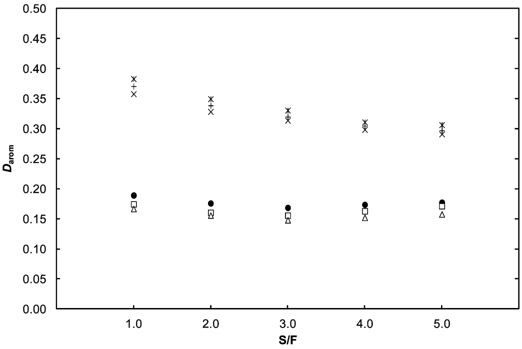


Figure 2. Aromatic distribution ratios as a function of temperature and solvent to feed ratio using {[4empy][Tf$_2$N] + [emim][DCA]} at ϕ_1 = 0.3 as solvent: ● 303.2 K; □ 313.2 K; Δ 323.2 K, and employing sulfolane as solvent: × 303.2 K; + 313.2 K; and * 323.2 K.

The highest values of D_{arom} for the IL-based solvent were achieved at the lowest temperature (303.2 K). Thus, the effect of temperature on the aromatic distribution ratios using the IL mixture was the contrary to the previously described effect of temperature on D_{aliph}. The same trend with the temperature was described by Hansmeier et al. in the toluene distribution ratios for several pure ILs in the extraction of toluene from heptane.[27] These results seem to be caused by the stronger molecular movements at higher temperatures that reduces the $\pi-\pi$ interactions between the aromatics and the IL. In addition, the results using the COSMO-RS (Conductor-like Screening Model for Real Solvents) to describe the liquid−liquid extraction of aromatics using ILs also predicted a decrease in the aromatic distribution ratios with increasing temperature.[28] However, the effect of temperature on D_{arom} using sulfolane was the opposite. The highest values of aromatic distribution ratios were obtained at the highest temperature (323.2 K). A similar trend was observed by Meindersma et al. in the liquid−liquid extraction of toluene from *n*-heptane employing sulfolane at 313.2 and 348.2 K.[29]

On the other hand, the effect of the solvent to feed ratio on the values of aromatic distribution ratios can also be studied in Figure 2. As seen, D_{arom} using the IL mixture at constant temperature hardly changed with the value of solvent to feed ratio, whereas D_{arom} employing sulfolane slightly decreased with increasing the solvent to feed ratio. This fact will allow to simulate a counter current extraction column using the Kremser Equation, because this equation is only valid if the solute distribution ratio can be assumed as constant.[30,31]

To conclude the comparative analysis between the extractive properties of the sulfolane and the IL mixture, experimental aromatic/aliphatic selectivities ($\alpha_{arom,aliph}$) in the liquid−liquid extraction of BTEX from the reformer gasoline model have been calculated as follows:

$$\alpha_{arom,aliph} = \frac{D_{arom}}{D_{aliph}} \tag{3}$$

Experimental values of $\alpha_{arom,aliph}$ using the IL-based solvent are listed in Table 6, whereas selectivities employing sulfolane are presented in Table 7. In Figure 3, aromatic/aliphatic selectivities as a function of temperature and solvent to feed ratio are graphically shown.

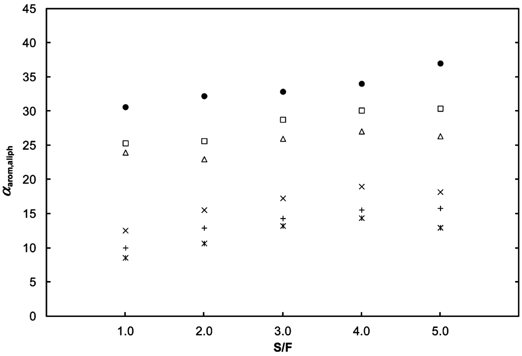


Figure 3. Aromatic/aliphatic selectivities as a function of temperature and solvent to feed ratio using {[4empy][Tf$_2$N] + [emim][DCA]} at ϕ_1 = 0.3 as solvent: ● 303.2 K; □ 313.2 K; Δ 323.2 K, and employing sulfolane as solvent: × 303.2 K; + 313.2 K; and * 323.2 K.

As can be observed, the highest values of $\alpha_{arom,aliph}$ were obtained using the IL-based solvent at 303.2 K and a solvent to feed ratio of 5.0. An increase in the extraction temperature caused a decrease in the value of $\alpha_{arom,aliph}$ for the IL mixture. This result is in agreement with the predictions using COSMO-RS made by Ferreira et al.[28] and with the experimental results published by Hansmeier et al. in the extraction of toluene from *n*-heptane using pure ILs.[27] The effect of temperature on $\alpha_{arom,aliph}$ employing sulfolane was the same as described for the IL mixture. This trend was also observed by Meindersma et al. in the separation of toluene from *n*-heptane using sulfolane at several temperatures.[29]

The influence of the solvent to feed ratio on the values of aromatic/aliphatic selectivities has been similar in both extraction solvents. An increase in the solvent to feed ratio has caused a slight increase in the values of $a_{arom,aliph}$ using the IL mixture, whereas the same influence has been observed in the sulfolane for solvent to feed ratios between 1.0 and 4.0, decreasing the aromatic/aliphatic selectivities at a solvent to feed ratio of 5.0.

3.3. Extraction Yield of Aromatics and Aliphatics and Relative Purity of Extracted Aromatics.

In addition to the study of the distribution ratios and the aromatic/aliphatic selectivities, extraction yield of aromatic and aliphatic hydrocarbons and the relative purity of aromatics in the extract phase have been calculated from the experimental results to evaluate the potential use of the IL mixture at industrial scale.

To calculate the extraction yields, an overall mass balance in the vial was made taking into account the amount of each component in the feed added to vial and the experimental compositions of raffinate and extract phases showed in Tables 4 and 5. From this balance, the mass of each component in both phases was calculated. Experimental values of extraction yield of aliphatics (Yld_{aliph}) were determined as follows:

$$Yld_{aliph}(\%) = 100\frac{m_{hexa}^{II} + m_{hepta}^{II} + m_{octa}^{II}}{m_{hexa}^{feed} + m_{hepta}^{feed} + m_{octa}^{feed}} \tag{4}$$

where m_i is the hydrocarbon mass in grams in the feed or in the extract phase. Values of Yld_{aliph} employing the IL-based solvent are presented in Table 6, whereas the extraction yields of aliphatics for the sulfolane are shown in Table 7. Experimental extraction yields of aliphatics using both solvents as a function of solvent to feed ratio and at temperatures between 303.2 and 323.2 K are also plotted in Figure 4.

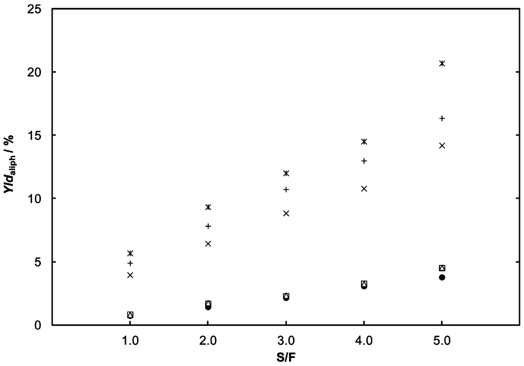


Figure 4. Extraction yields of aliphatics as a function of temperature and solvent to feed ratio using {[4empy][Tf$_2$N] + [emim][DCA]} at ϕ_1 = 0.3 as solvent: ● 303.2 K; ☐ 313.2 K; Δ 323.2 K, and employing sulfolane as solvent: × 303.2 K; + 313.2 K; and * 323.2 K.

In an industrial process of liquid−liquid extraction of aromatics from aliphatics, the extraction yield of aliphatics must be minimized to increase the purity of the aromatic hydrocarbon in the extract phase and to simplify the recovery of the aromatics from the solvent and their purification. As observed in Figure 4, values of Yld_{aliph} using sulfolane were substantially higher than those employing the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture at ϕ_1 = 0.3. An increase of the extraction temperature caused a significant increase of the Yld_{aliph} using sulfolane, but hardly affected the values using the IL mixture. A similar effect was also observed increasing the solvent to feed ratio.

From the results of the overall mass balance in the vials, the yield of extraction of aromatics (Yld_{arom}) was also calculated using the following expression:

$$Yld_{arom}(\%) = 100\frac{m_{benz}^{II} + m_{tol}^{II} + m_{etbenz}^{II} + m_{p\text{-}xyl}^{II}}{m_{benz}^{feed} + m_{tol}^{feed} + m_{etbenz}^{feed} + m_{p\text{-}xyl}^{feed}} \quad (5)$$

Experimental values of Yld_{arom} using the IL mixture are listed in Table 6 and the extraction yields of aromatics employing sulfolane are also presented in Table 7. In Figure 5, Yld_{arom} using both solvents at several temperatures and solvent to feed ratios are plotted.

As can be observed, values of Yld_{arom} for the sulfolane were substantially higher than those using the IL mixture over the whole range of temperatures and solvent to feed ratios. These results are the consequence of the higher aromatic distribution ratios for the sulfolane compared with those of the IL mixture. Because of this, the IL mixture will required a higher number of equilibrium stages to achieve the extraction yield of aromatics using sulfolane in a countercurrent extraction column employing the same mass flow of both solvents.

The influence of the solvent to feed ratio on the Yld_{arom} was similar in both extraction solvents. A higher value of solvent to feed ratio caused an increase in the value of the extraction yield of aromatics. However, the effect of temperature on Yld_{arom} using sulfolane was the opposite than that using the IL mixture. An increase in the extraction temperature at a solvent to feed ratio constant caused a slight increase in the Yld_{arom} using sulfolane but a small decrease in the value of the extraction yield of aromatics employing the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture at ϕ_1 = 0.3.

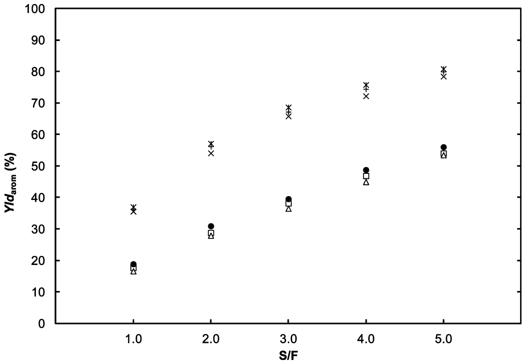


Figure 5. Extraction yields of aromatics as a function of temperature and solvent to feed ratio using {[4empy][Tf$_2$N] + [emim][DCA]} at ϕ_1 = 0.3 as solvent: ● 303.2 K; ☐ 313.2 K; Δ 323.2 K, and employing sulfolane as solvent: × 303.2 K; + 313.2 K; and * 323.2 K.

In addition to the extraction yield of the aromatic hydrocarbons, it is important to study the purity of the extracted solute to evaluate the performance of the extraction solvent. A higher purity of the aromatics extracted allows an easier purification process, reducing investment and operation costs of the regeneration unit. The relative purity of extracted aromatics in the extract phase (P_{arom}) was calculated from the hydrocarbon mass fraction in the extract phase as follows:

$$P_{arom}(\%) = 100\frac{w_{benz}^{II} + w_{tol}^{II} + w_{etbenz}^{II} + w_{p\text{-}xyl}^{II}}{(w_{hexa}^{II} + w_{hepta}^{II} + w_{octa}^{II}) + (w_{benz}^{II} + w_{tol}^{II} + w_{etbenz}^{II} + w_{p\text{-}xyl}^{II})} \quad (6)$$

Relative purities of aromatics in the extract phase using the IL mixture are presented in Table 6, whereas the values of P_{arom} employing sulfolane are listed in Table 7. As can be seen in Figure 6, the highest values of P_{arom} were achieved using the IL-based solvent at 303.2 K. These results are related to the values of aromatic/aliphatic selectivities previously described. Extracted aromatics by the IL mixture had a higher purity, since the IL-based solvent showed higher values of selectivity than those of sulfolane. Nevertheless, the influence of increasing the value of solvent to feed ratio caused an increase of the values of aromatic/aliphatic selectivity but the opposite trend was observed for the relative purity of the aromatics because the amount of aliphatics in the extract phase was higher. Employing both solvents, the highest values of P_{arom} were achieved at the lowest extraction temperature. However, the effect of temperature on the relative purity of extracted aromatics was higher in the values using sulfolane than in the case of the IL mixture.

The optimal conditions for extracting BTEX from the reformer gasoline model using the IL mixture have been selected considering the influence of temperature and solvent to feed ratio on the values of yields of extraction of aromatics and aliphatics and the relative purity of the aromatics in the extract phase. The most appropriate extraction temperature seems to be 303.2 K in order to achieve high values of yield extraction of aromatics and to obtain extracted BTEX with high

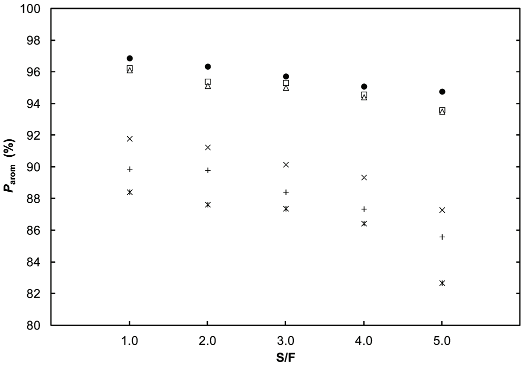


Figure 6. Relative purity of extracted aromatics in the extract phase as a function of temperature and solvent to feed ratio using {[4empy]-[Tf$_2$N] + [emim][DCA]} at ϕ_1 = 0.3 as solvent: ● 303.2 K; □ 313.2 K; Δ 323.2 K, and employing sulfolane as solvent: × 303.2 K; + 313.2 K; and * 323.2 K.

purity in the extract phase. On the other hand, a solvent to feed ratio of 5.0 has been selected to increase the yield of extraction of aromatics. A solvent to feed ratio of 5.0 was the optimal considering technical aspects. However, this value could be modified considering economic reasons to reduce investment or operating costs.

3.4. Simulation of a Countercurrent Extraction Column using the Kremser Equation. The Kremser Equation has been used to determine flows and compositions of the raffinate and extract phases in a countercurrent extraction column using the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture at ϕ_1 = 0.3 and sulfolane as extraction solvents in the separation of BTEX from the reformer gasoline model. In the application of the Kremser Equation to the liquid−liquid extraction, enthalpy balance equations are not required because temperature changes in an adiabatic extraction column are not significant.[30]

The Kremser Equation can be used to simulate an extraction column if the extract and raffinate phases are inmmiscible and if the distribution ratios can be considered constant.[31] As explained previously, values of aromatic and aliphatic distribution coefficients using the IL mixture were almost constant with temperature and solvent to feed ratios changes. By contrast, distribution ratios employing sulfolane were slightly affected by the temperature and the solvent to feed ratio, but they will be assumed as constant at 303.2 K and a solvent to feed ratio of 5.0 to compare the performance of both extraction solvents. In addition, sulfolane and the IL mixture formed two immiscible phases with the reformer gasoline model. Therefore, the Kremser Equation can be applied to simulate a counter current extraction column to extract BTEX employing sulfolane or the IL-based solvent.

The group method used in this work is analogous to the Kremser method applied to absorption. The extraction factor (E) and the reciprocal of $E(U)$ are the parameters used in the Kremser method in liquid−liquid extraction:

$$E_i = D_i\frac{V}{L} \tag{7}$$

$$U_i = \frac{1}{E_i} = \frac{L}{D_iV} \tag{8}$$

where D_i is the mass-based distribution ratio of each component, L is the raffinate mass flow, and V indicates the extract mass flow. Distribution ratios of the hydrocarbons and the solvents were calculated from the experimental composition showed in Tables 4 and 5 at 303.2 K and a solvent to feed ratio of 5.0.

To perform the simulation of the extraction column, a feed of the reformer gasoline model flow equal to 1000 t/h was used as basis of calculation. As a consequence of the selected solvent to feed ratio of 5.0, the solvent flow was fixed to 5000 t/h. Subsequently, the number of the equilibrium stages in the countercurrent was fixed. Considering the values of the distribution ratios of the components, individual flows in raffinate and extract phases were estimated. Then, an iterative method was applied performing total balances for each component in the extractor to calculate the individual flows in raffinate and extract streams. This iterative method was developed using Microsoft Excel. A complete description of the equations used in the Kremser method applied to liquid−liquid extraction can be found elsewhere.[30]

According to Gary et al., extraction yields in the sulfolane process are equal to or better than 99.9, 99.0, and 97.0% for benzene, toluene, and mixed xylenes, respectively, with the mixed xylenes formed by *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene.[2,3] Because of this, the influence of the number of equilibrium stages (N_s) on the extraction yield of the aromatics has been studied in order to find the N_s that provides the previously cited values of aromatic recovery using the IL-based solvent. Individual extraction yields of the BTEX using the IL mixture and sulfolane are plotted in Figure 7 as a function of the number of equilibrium stages. Extraction yields of each hydrocarbon have been calculated as the relationship between the individual flow in the extract stream and in the feed.

As seen in Figure 7, at a constant number of equilibrium stages the order in the extraction yield was the following: benzene > toluene > ethylbenzene > *p*-xylene, since an increase in the aromatic alkyl chain substituted length causes a decrease in the distribution ratio and in the solubility of the aromatic hydrocarbons in ILs.[28] Comparing the results obtained using the IL-based solvent and sulfolane, a higher extraction yield was achieved using sulfolane because the experimental aromatic distribution ratios of this organic solvent were higher than those of the IL mixture. As can be observed, extraction yields of benzene and toluene using the IL mixture were equal to 100% at N_s higher than 14. Hence, this IL-based solvent could be applied in the extraction of aromatics from industrial streams with high content of both aromatics. Target values of individual extraction yield previously indicated for benzene, toluene, and xylenes were successfully achieved using the IL mixture employing 24 equilibrium stages. A fully extraction of all aromatics using sulfolane were achieved using 16 equilibrium stages. Therefore, the replacement of the sulfolane process by a hypothetical process employing the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture could imply an extraction column with a higher number of stages.

In Table 8, flows and compositions of the feed, solvent, extract, and raffinate streams are presented at 303.2 K and a solvent to feed of 5.0. Values using sulfolane were calculated with a N_s of 16, whereas the results using the IL mixture were obtained with a number of equilibrium stages of 24. An important advantage of the IL-based solvent with respect to the sulfolane is the negligible solubility of the ILs in the raffinate stream. As can be seen in Table 8, the sulfolane content in

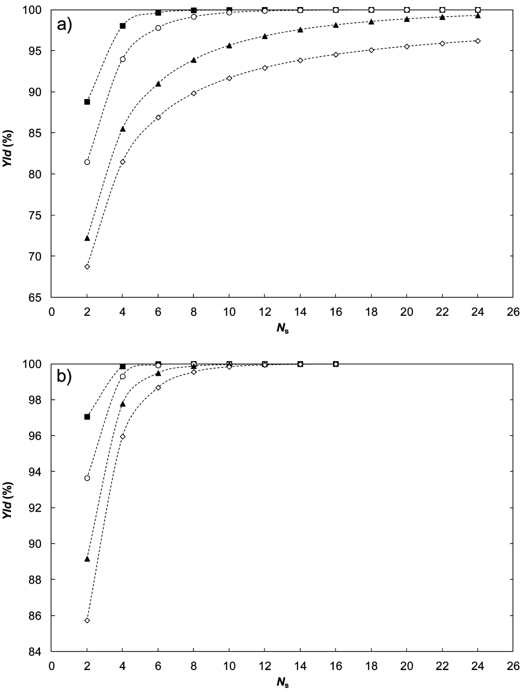


Figure 7. Extraction yield of aromatic hydrocarbons using the (a) {[4empy][Tf_2N] + [emim][DCA]} at ϕ_1 = 0.3 IL mixture and (b) using sulfolane as solvents: ■ benzene; ○ toluene; ▲ ethylbenzene; ◇ *p*-xylene at 303.2 K and a solvent to feed ratio of 5.0 as a function of the number of equilibrium stages in the countercurrent extraction column. Dashed lines are to guide the eye.

Table 8. Results of the Simulation of a Countercurrent Extraction Column using the Kremser Equation at S/F = 5.0 and *T* = 303.2 K

extraction solvent: {[4empy][Tf_2N] + [emim][DCA]} at ϕ_1 = 0.3; N_s = 24				
	feed	solvent	raffinate phase	extract phase
flow (t/h)	1000.0	5000.0	445.9	5554.1
benzene (wt %)	5.00	0.00	0.00	0.90
toluene (wt %)	24.00	0.00	0.00	4.32
ethylbenzene (wt %)	4.00	0.00	0.06	0.72
p-xylene (wt %)	22.00	0.00	1.87	3.81
aromatics (wt %)	55.00	0.00	1.93	9.75
n-hexane (wt %)	15.00	0.00	32.55	0.09
n-heptane (wt %)	15.00	0.00	32.58	0.08
n-octane (wt %)	15.00	0.00	32.95	0.06
n-alkanes (wt %)	45.00	0.00	98.07	0.23
binary IL mixture (wt %)	0.00	100.00	0.00	90.02

extraction solvent: sulfolane. N_s = 16				
	feed	solvent	raffinate phase	extract phase
flow (t/h)	1000.0	5000.0	405.9	5594.1
benzene (wt %)	5.00	0.00	0.00	0.89
toluene (wt %)	24.00	0.00	0.00	4.29
ethylbenzene (wt %)	4.00	0.00	0.00	0.72
p-xylene (wt %)	22.00	0.00	0.00	3.93
aromatics (wt %)	55.00	0.00	0.00	9.83
n-hexane (wt %)	15.00	0.00	31.36	0.41
n-heptane (wt %)	15.00	0.00	33.26	0.27
n-octane (wt %)	15.00	0.00	34.57	0.17
n-alkanes (wt %)	45.00	0.00	99.19	0.85
sulfolane (wt %)	0.00	100.00	0.81	89.32

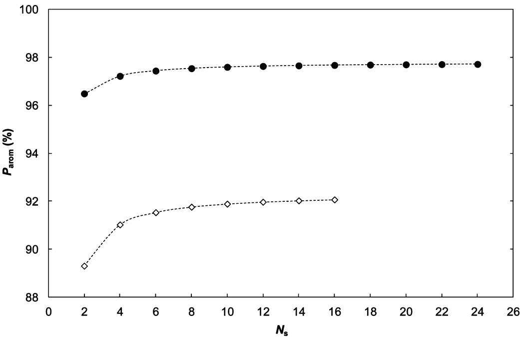


Figure 8. Relative purities of the aromatics in the extract phase at 303.2 K and a solvent to feed ratio of 5.0 as a function of the number of equilibrium stages in the countercurrent extraction column. ●, using the [4empy][Tf_2N] + [emim][DCA]} at ϕ_1 = 0.3 IL mixture; ◇, employing sulfolane as solvent. Dashed lines are to guide the eye.

raffinate phase was 0.81%. Because of this, a raffinate wash column has to be used in the sulfolane process to recover and recycle the sulfolane dissolved in the hydrocarbons to the extractor.[32]

Relative purities of the extracted aromatic hydrocarbons using both extraction solvents are graphically shown in Figure 8. Represented values were calculated using eq 6. As observed, the relative purity of the extracted aromatics by the IL mixture was substantially higher than that using sulfolane. This fact would simply the subsequent step of recovery and purification of the aromatic hydrocarbons. Moreover, as a consequence of the nonvolatile character of the IL-based solvent the recovery of the BTEX could be achieved by a flash distillation or by stripping at moderate temperatures,[14] instead of the extractive stripper and the recovery distillation column currently used in the sulfolane process.[32] According to the work of Meindersma et al., the energy requirement of a liquid–liquid extraction process of aromatics from aliphatics using an IL-based solvent could be substantially lower than that of the sulfolane process because of the simpler recovery of the solvent. In addition, the investment costs could be 35% lower using ILs in the liquid–liquid extraction of aromatics instead of sulfolane.[32]

4. CONCLUSIONS

In this work, we have studied the liquid–liquid extraction of benzene, toluene, ethylbenzene, and xylenes from a reformer gasoline model using the {[4empy][Tf_2N] + [emim][DCA]} IL mixture with a [4empy][Tf_2N] mole fraction of 0.3. The influence of temperature and solvent to feed ratio on BTEX extraction has been studied. Extraction experiments have also been performed employing sulfolane to make a comparative analysis between the extractive properties of both solvents.

From the experimental results of the liquid–liquid extraction of BTEX from the reformer gasoline model, aromatic and aliphatic distribution ratios, aromatic/aliphatic selectivities, yields of extraction of aromatic and aliphatics, and relative purities of extracted aromatics have been calculated. The IL mixture has shown higher values of aromatic/aliphatic selectivities and purity of the extracted aromatics than those using sulfolane. By contrast, the sulfolane has exhibited higher distribution ratios and extraction yields of aromatic and aliphatic hydrocarbons. Considering the influence of temperature and solvent to feed ratio on the extractive properties, both 303.2 K and a solvent to feed ratio of 5.0 have been selected as the optimal conditions to extract BTEX using the IL mixture.

To complete the study, the Kremser equation has been used to simulate a countercurrent extraction column using both extraction solvents at 303.2 K in the separation of BTEX from the reformer gasoline model. An hypothetical process using the {[4empy][Tf_2N] + [emim][DCA]} IL mixture would need an extractor with a higher number of equilibrium stages than that using sulfolane, but the BTEX extracted would have a purity considerably higher than those extracted by the sulfolane, simplifying the purification process of the solutes. The liquid−liquid extraction of aromatics from a real fuel should be used in future studies employing the IL mixture proposed in this work to adequately design an industrial process of aromatic extraction.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +34 91 394 51 19. Fax: +34 91 394 42 43. Email: jgarcia@quim.ucm.es.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to the Ministerio de Economía y Competitividad (MINECO) of Spain and the Comunidad Autónoma de Madrid for financial support of Projects CTQ2011-23533 and S2009/PPQ-1545, respectively. Marcos Larriba thanks Ministerio de Educación, Cultura y Deporte for awarding him an FPU grant (Reference AP-2010-0318), and Pablo Navarro also thanks MINECO for awarding him an FPI grant (Reference BES-2012-052312).

■ REFERENCES

(1) Franck, H. G.; Staldelhofer, J. W. *Industrial Aromatic Chemistry*; Springer-Verlag: Berlin, 1988.

(2) Gary, J.; Handwerk, G.; Kaiser, M. *Petroleum Refining Technology and Economics*, 5th ed.; CRC Press: Boca Raton, FL, 2007.

(3) Meyers, R. A. *Handbook of Petroleum Refining Processes*, 3rd ed.; McGraw-Hill: New York, 2004.

(4) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Selection of Ionic Liquids for the Extraction of Aromatic Hydrocarbons from Aromatic/Aliphatic Mixtures. *Fuel Process. Technol.* **2005**, *87*, 59−70.

(5) Fang, W.; Shao, D.; Lu, X.; Guo, Y.; Xu, L. Extraction of Aromatics from Hydrocarbon Fuels Using N-Alkyl Piperazinium-Based Ionic Liquids. *Energy Fuels* **2012**, *26*, 2154−2160.

(6) Aparicio, S.; Atilhan, M. Nanoscopic Vision on Fuel Dearomatization Using Ionic Liquids: The Case of Piperazine-Based Fluids. *Energy Fuels* **2013**, *27*, 2515−2527.

(7) Zhang, J.; Huang, C.; Chen, B.; Ren, P.; Lei, Z. Extraction of Aromatic Hydrocarbons from Aromatic/Aliphatic Mixtures Using Chloroaluminate Room-Temperature Ionic Liquids. *Energy Fuels* **2007**, *21*, 1724−1730.

(8) Huang, C.; Chen, B.; Zhang, J.; Liu, Z.; Li, Y. Desulfurization of Gasoline by Extraction with New Ionic Liquids. *Energy Fuels* **2004**, *18*, 1862−1864.

(9) Ko, N. H.; Lee, J. S.; Huh, E. S.; Lee, H.; Jung, K. W.; Kim, H. S.; Cheong, M. Extractive Desulfurization Using Fe-Containing Ionic Liquids. *Energy Fuels* **2008**, *22*, 1687−1690.

(10) Gao, H.; Li, Y.; Wu, Y.; Luo, M.; Li, Q.; Xing, J.; Liu, H. Extractive Desulfurization of Fuel Using 3-Methylpyridinium-Based Ionic Liquids. *Energy Fuels* **2009**, *23*, 2690−2694.

(11) Li, Z.; Li, C.; Chi, Y.; Wang, A.; Zhang, Z.; Li, H.; Liu, Q.; Welz-Biermann, U. Extraction Process of Dibenzothiophene with New Distillable Amine-Based Protic Ionic Liquids. *Energy Fuels* **2012**, *26*, 3723−3727.

(12) Wang, Q.; Lei, L.; Zhu, J.; Yang, B.; Li, Z. Deep Desulfurization of Fuels by Extraction with 4-Dimethylaminopyridinium-Based Ionic Liquids. *Energy Fuels* **2013**, *27*, 4617−4623.

(13) Lu, X.; Yue, L.; Hu, M.; Cao, Q.; Xu, L.; Guo, Y.; Hu, S.; Fang, W. Piperazinium-Based Ionic Liquids with Lactate Anion for Extractive Desulfurization of Fuels. *Energy Fuels* **2014**, *28*, 1774−1780.

(14) Anjan, S. T. Ionic Liquid for Aromatic Extraction: Are They Ready? *Chem. Eng. Prog.* **2006**, *102*, 30−39.

(15) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room Temperature Ionic Liquids as Novel Media for 'Clean' Liquid−Liquid Extraction. *Chem. Commun.* **1998**, *16*, 1765−1766.

(16) Selvan, M. S.; McKinley, M. D.; Dubois, R. H.; Atwood, J. L. Liquid−Liquid Equilibria for Toluene + Heptane + 1-Ethyl-3-methylimidazolium Triiodide and Toluene + Heptane + 1-Butyl-3-methylimidazolium Triiodide. *J. Chem. Eng. Data* **2000**, *45*, 841−845.

(17) Meindersma, G. W.; Hansmeier, A. R.; de Haan, A. B. Ionic Liquids for Aromatics Extraction. Present Status and Future Outlook. *Ind. Eng. Chem. Res.* **2010**, *49*, 7530−7540.

(18) Meindersma, G. W.; de Haan, A. B. Cyano-Containing Ionic Liquids for the Extraction of Aromatic Hydrocarbons from an Aromatic/Aliphatic Mixture. *Sci. China Chem.* **2012**, *55*, 1488−1499.

(19) Larriba, M.; Navarro, P.; García, J.; Rodríguez, F. Liquid−Liquid Extraction of Toluene from *n*-Heptane by {[emim][TCM] + [emim][DCA]} Binary Ionic Liquid Mixtures. *Fluid Phase Equilib.* **2014**, *364*, 48−54.

(20) Larriba, M.; Navarro, P.; García, J.; Rodríguez, F. Separation of Toluene from *n*-Heptane, 2,3-Dimethylpentane, and Cyclohexane Using Binary Mixtures of [4empy][Tf_2N] and [emim][DCA] Ionic Liquids as Extraction Solvents. *Sep. Purif. Technol.* **2013**, *120*, 392−401.

(21) Larriba, M.; Navarro, P.; García, J.; Rodríguez, F. Liquid−Liquid Extraction of Toluene from *n*-Alkanes Using {[4empy][Tf_2N] + [emim][DCA]} Ionic Liquid Mixtures. *J. Chem. Eng. Data* **2014**, *59*, 1692−1699.

(22) Navarro, P.; Larriba, M.; García, J.; Rodríguez, F. Thermal Stability, Specific Heats, and Surface Tensions of ([emim][DCA] + [4empy][Tf_2N]) Ionic Liquid Mixtures. *J. Chem. Thermodyn.* **2014**, *76*, 152−160.

(23) Navarro, P.; Larriba, M.; García, J.; Rodríguez, F. Thermal Stability and Specific Heats of {[emim][DCA] + [emim][TCM]} Mixed Ionic Liquids. *Thermochim. Acta* **2014**, *588*, 22−27.

(24) Kelayeh, S. A.; Jalili, A. H.; Ghotbi, C.; Hosseini-Jenab, M.; Taghikhani, V. Densities, Viscosities, and Surface Tensions of Aqueous Mixtures of Sulfolane + Triethanolamine and Sulfolane + Diisopropanolamine. *J. Chem. Eng. Data* **2011**, *56*, 4317−4324.

(25) Larriba, M.; Navarro, P.; García, J.; Rodríguez, F. Liquid−Liquid Extraction of Toluene from Heptane Using [emim][DCA], [bmim]-[DCA], and [emim][TCM] Ionic Liquids. *Ind. Eng. Chem. Res.* **2013**, *52*, 2714−2720.

(26) Kolb, B.; Ettre, L. S. *Static Headspace-Gas Chromatography: Theory and Practice*; Wiley-VCH: New York, 1997.

(27) Hansmeier, A. R.; Minoves Ruiz, M.; Meindersma, G. W.; de Haan, A. B. Liquid−Liquid Equilibria for the Three Ternary Systems (3-Methyl-*N*-butylpyridinium Dicyanamide + Toluene + Heptane), (1-Butyl-3-methylimidazolium Dicyanamide + Toluene + Heptane) and (1-Butyl-3-methylimidazolium Thiocyanate + Toluene + Heptane) at T = (313.15 and 348.15) K and p = 0.1 MPa. *J. Chem. Eng. Data* **2010**, *55*, 708.

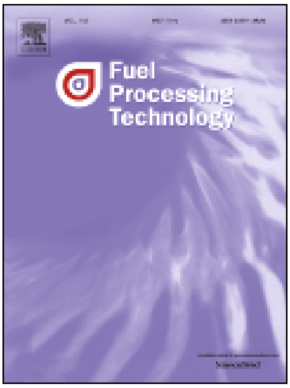
(28) Ferreira, A. R.; Freire, M. G.; Ribeiro, J. C.; Lopes, F. M.; Crespo, J. G.; Coutinho, J. A. P. Overview of the Liquid−Liquid Equilibria of Ternary Systems Composed of Ionic Liquid and Aromatic and Aliphatic Hydrocarbons, and Their Modeling by COSMO-RS. *Ind. Eng. Chem. Res.* **2012**, *51*, 3483−3507.

(29) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Ternary Liquid−Liquid Equilibria for Mixtures of Toluene + *n*-Heptane + an Ionic Liquid. *Fluid Phase Equilib.* **2006**, *247*, 158−168.

(30) Henley, E. J.; Seader, J. D. *Equilibrium-Stage Separation Operations in Chemical Engineering*; John Wiley and Sons: New York, 1981.

(31) Buchbender, F.; Onink, F.; Meindersma, W.; de Haan, A.; Pfenning, A. Simulation of Aromatics Extraction with an Ionic Liquid in a Pilot-Plant Kühni Extractor Based on Single-Drop Experiments. *Chem. Eng. Sci.* **2012**, *82*, 167−176.

(32) Meindersma, G. W.; de Haan, A. B. Conceptual Process Design for Aromatic/aliphatic Separation with Ionic Liquids. *Chem. Eng. Res. Des.* **2008**, *86*, 745−752.



Fuel Processing Technology

Factor de impacto (2013): 3,02

Publicación 9:

Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid-liquid extraction using a binary mixture of [4empy][Tf$_2$N] and [emim][DCA] ionic liquids

Marcos Larriba, Pablo Navarro, Emilio J. González, Julián García, Francisco Rodriguez

Fuel Processing Technology, 2015, DOI: 10.1016/j.fuproc.2015.03.009.

ARTICLE IN PRESS
FUPROC-04483; No of Pages 14

Fuel Processing Technology xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy][Tf_2N] and [emim][DCA] ionic liquids

Marcos Larriba, Pablo Navarro, Emilio J. González, Julián García *, Francisco Rodríguez

Department of Chemical Engineering, Complutense University of Madrid, E-28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 17 December 2014
Received in revised form 20 February 2015
Accepted 13 March 2015
Available online xxxx

Keywords:
Liquid–liquid extraction
Dearomatization
Ionic liquids
Pyrolysis gasoline
Simulation of a countercurrent column

ABSTRACT

In Europe and Japan, benzene, toluene, and xylenes (BTX) are usually obtained by liquid–liquid extraction from pyrolysis gasolines using organic solvents such as sulfolane. In the last few years, ionic liquids (ILs) have been studied as potential substitutes of conventional solvents in the extraction of BTX from alkanes. In this paper, we have studied the dearomatization of pyrolysis gasolines obtained by mild and severe cracking using the binary IL mixture composed of the 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf_2N]) and the 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) and also employing sulfolane to compare the performance of both extraction solvents. To choose the most appropriate conditions of temperature and solvent to feed ratio to perform the extraction of BTX from pyrolysis gasolines, several extractive properties have been estimated from the experimental results employing the IL mixture and sulfolane. Simulations of countercurrent extraction columns in the dearomatization of both pyrolysis gasolines have also been made using the Kremser equation. The dearomatization of pyrolysis gasolines by the {[4empy][Tf_2N] + [emim][DCA]} IL mixture would require a higher number of equilibrium stages in the extractor than that employing sulfolane. By contrast, the purity of extracted aromatics would be substantially greater using the IL-based solvent, simplifying the subsequent purification of the BTX.

1. Introduction

Benzene, toluene, and xylenes (BTX) are mainly obtained from pyrolysis and reformer gasolines and coke oven benzole. In the USA, reformer gasoline is the major raw material for BTX, whereas the pyrolysis gasoline is the most important source of aromatics in Japan and Europe [1]. Recovery of aromatics is performed by liquid–liquid extraction, the UOP Sulfolane Process being the most widely used method at industrial scale [2,3]. However, the Sulfolane Process has several drawbacks such as the high energy consumption in the solvent regeneration and the need to recover the sulfolane dissolved in the raffinate stream [4].

ILs have been extensively studied in the dearomatization, denitrogenation, and desulfuration of liquid fuels, showing good extractive properties and a nonvolatile nature that could reduce investment and operating costs of the extraction units [4–16]. A wide number of pure ILs have been specifically applied in the liquid–liquid extraction of benzene, toluene, or xylenes from binary mixtures with an aliphatic hydrocarbon [4,11]. However, only a very limited number of pure ILs have exhibited extractive and physical properties comparable to sulfolane values. For that reason, we have proposed the use of binary IL mixtures in order to obtain an IL-based solvent with intermediate extractive and physical properties between those of the ILs forming the mixture and comparable or higher than the sulfolane values [17–19].

In our previous works, we studied 34 pure ILs and 6 binary IL mixtures in the separation of an aromatic hydrocarbon from an aliphatic hydrocarbon, studying the liquid–liquid equilibria data of systems (aliphatic + aromatic + IL). Among the IL mixtures studied so far in the liquid–liquid extraction of BTX, the mixture composed of {[4empy][Tf_2N] and [emim][DCA]} ILs has been the most promising mixed solvent considering its extractive and physical properties. The {[4empy][Tf_2N] + [emim][DCA]} mixture with a [4empy][Tf_2N] mole fraction (x_1) equal to 0.3 showed extractive properties higher or similar to sulfolane values in the separation of toluene from binary mixtures with *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, 2,3-dimethylpentane, or cyclohexane, and in the extraction of benzene, ethylbenzene, or xylenes from *n*-heptane [18,20,21]. Moreover, this IL mixture has shown densities, viscosities, surface tensions, and thermal stability comparable to those of sulfolane [18,22,23].

In our most recently published work, we have studied the performance of the {[4empy][Tf_2N] + [emim][DCA]} IL mixture with a x_1 of 0.3 in the extraction of benzene, toluene, ethylbenzene, and *p*-xylene from a reformer gasoline model. The IL mixture exhibited yields of extraction of aromatics slightly lower than the sulfolane values and purities of extracted aromatics considerably higher than those using sulfolane [24].

---

* Corresponding author. Tel.: +34 91 394 51 19; fax: +34 91 394 42 43.
E-mail address: jgarcia@quim.ucm.es (J. García).

http://dx.doi.org/10.1016/j.fuproc.2015.03.009
0378-3820/© 2015 Elsevier B.V. All rights reserved.

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009

In this paper, we have studied the liquid–liquid extraction of BTX from two pyrolysis gasoline models obtained by mild and severe cracking using the {[4empy][Tf_2N] + [emim][DCA]} mixture with a x_1 of 0.3. To analyze the influence of temperature on the extractive properties of the IL-based solvent, the liquid–liquid extraction has been performed at 303.2 K, 313.2 K, and 323.2 K and atmospheric pressure, being these temperature values the most common in the separation of BTX from alkanes using IL-based solvents [4,11]. The effect of the solvent to feed ratio (S/F) on the BTX extraction has also been studied performing liquid–liquid extraction experiments at S/F ratios between 1.0 and 5.0. The extraction of BTX from the pyrolysis gasoline models have also been made employing sulfolane as extraction solvent to perform a comparative analysis between the extractive properties of both solvents.

2. Materials and methods

2.1. Materials

The ILs [4empy][Tf_2N] and [emim][DCA] were supplied by Iolitec GmbH (Germany) with a mass fraction purity higher than 0.99 and 0.98, respectively. The presence of halides was lower than 100 ppm in the ([4empy][Tf_2N]) and lower than 2% in the [emim][DCA], whereas the water content was 42 ppm in the case of the [4empy][Tf_2N] and 1790 ppm for the [emim][DCA]. *n*-Hexane, *n*-heptane, *n*-octane, benzene, toluene, *p*-xylene, and sulfolane were purchased from Sigma-Aldrich (USA). Chemicals were employed as received without further purification. The ILs were handled in a glovebox filled with dry nitrogen and all chemicals were stored in a desiccator to prevent water absorption. In Table 1, mass fractions purities of the chemicals are listed along with the abbreviations of the compounds used in this paper.

2.2. Pyrolysis gasoline models

Franck and Stadelhofer [1] published the composition in mass basis of the pyrolysis gasolines as a function of the severity of the cracking. A typical pyrolysis gasoline obtained by mild cracking has the following composition: benzene (22.0 wt.%), toluene (17.5 wt.%), ethylbenzene, xylenes and styrene (11.5 wt.%), and non-aromatics (49.0 wt.%). On the other hand, according to Franck and Stadelhofer the composition of a typical pyrolysis gasoline obtained by severe cracking is: benzene (33.8 wt.%), toluene (19.4 wt.%), ethylbenzene, xylenes and styrene (13.0 wt.%), and non-aromatics (33.9 wt.%) [1]. To simplify the experimental procedure and the analytical method, the content of ethylbenzene, xylenes, and styrene were represented in the models by *p*-xylene. In addition, the non-aromatic content in the gasoline from mild cracking was formed by a 16.3 wt.% of *n*-hexane, 16.3 wt.% of *n*-heptane, and 16.3 wt.% of *n*-octane, whereas the non-aromatics were represented by an 11.3 wt.% of each *n*-alkane in the gasoline model from severe cracking. Compositions of the pyrolysis gasoline models obtained by mild and severe cracking employed in this work are presented in Table 2. In the preparation of the gasoline models, aromatic and aliphatic hydrocarbons were added using a Mettler Toledo XS 205 balance with a precision of $\pm 1 \cdot 10^{-5}$ g to determine the composition of the model by mass.

Table 1
Suppliers, purities of chemicals, and abbreviations.

Chemical	Supplier	Mass fraction purity	Analysis method	Abbreviation
[4empy][Tf_2N][a]	Iolitec GmbH	0.99	NMR[b] and IC[c]	ILs
[emim][DCA][d]	Iolitec GmbH	0.98	NMR[b] and IC[c]	
n-Hexane	Sigma-Aldrich	0.99	GC[e]	hexa
n-Heptane	Sigma-Aldrich	0.997	GC[e]	hepta
n-Octane	Sigma-Aldrich	0.99	GC[e]	octa
Benzene	Sigma-Aldrich	0.995	GC[e]	benz
Toluene	Sigma-Aldrich	0.995	GC[e]	tol
p-Xylene	Sigma-Aldrich	0.99	GC[e]	p-xyl
Sulfolane	Sigma-Aldrich	0.99	GC[e]	sulf

[a] [4empy][Tf_2N] = 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide.
[b] Nuclear magnetic resonance.
[c] Ion chromatography.
[d] [emim][DCA] = 1-ethyl-3-methylimidazolium dicyanamide.
[e] Gas chromatography.

2.3. Dearomatization by liquid–liquid extraction. Experimental procedure and analysis

To study the performance of the {[4empy][Tf_2N] + [emim][DCA]} IL mixture with a [4empy][Tf_2N] mole fraction of 0.3 as aromatic extraction solvent, liquid–liquid equilibria (LLE) experiments were made in 8 mL vials with screw caps using a Labnet Vortemp 1550 shaking incubator at 303.2 K, 313.2 K, and 323.2 K for 5 h at 800 rpm. To achieve a complete separation of the extract and raffinate phases in LLE, vials were then placed in a Labnet Accublock dry bath for 12 h at the LLE temperature controlled with a precision of ±0.1 K. At each experimental temperature, vials were gravimetrically prepared at S/F ratios in mass basis of 1.0, 2.0, 3.0, 4.0, and 5.0 using a Mettler Toledo XS 205 balance. LLE experiments using sulfolane under the same conditions were also performed to be used as benchmarks.

Raffinate phases were analyzed in triplicate by gas chromatography (GC) employing an Agilent 7890A gas chromatograph coupled with a liquid autosampler Agilent 7693 and a flame ionization detector (FID). In the experiments using sulfolane as solvent, the compositions of both raffinate and extract phases were also determined by GC. A complete description of the analytical method can be found elsewhere [18,25].

In our recently published papers on the liquid–liquid extraction of aromatics using the {[4empy][Tf_2N] + [emim][DCA]} IL mixture, signals corresponding to ILs were not found in ^1H NMR spectra from samples of raffinate phases and, therefore, the presence of ILs in this phase was considered negligible [18,20,21].

Samples from extract phases in the LLE experiments using the IL mixture as extraction solvent were analyzed by the multiple headspace extraction (MHE) technique. Three samples of approximately 100 L from each extract phase were added to 20 mL vials to be analyzed in an Agilent 7890A GC coupled with an Agilent 7697A Headspace Sampler. A detailed description of the MHE method used in this work can be found elsewhere [18,25,26]. Standard uncertainties of the compositions are listed in SI Tables 1 to 4 in the supplementary data.

Table 2
Composition of the pyrolysis gasoline models obtained by mild and severe cracking in mass basis.

Model of pyrolysis gasoline obtained by mild cracking

Hydrocarbon	w_i
n-Hexane	0.163
n-Heptane	0.163
n-Octane	0.163
Benzene	0.220
Toluene	0.176
p-Xylene	0.115

Model of pyrolysis gasoline obtained by severe cracking

Hydrocarbon	w_i
n-Hexane	0.113
n-Heptane	0.113
n-Octane	0.113
Benzene	0.338
Toluene	0.193
p-Xylene	0.130

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009

3. Results and discussion

3.1. Liquid–liquid extraction of BTX from pyrolysis gasoline models as a function of solvent to feed ratio and temperature

Experimental compositions of the raffinate and extract phases in mass basis in the dearomatization of the pyrolysis gasolines models using the {[4empy][Tf_2N] + [emim][DCA]} IL mixture as extraction solvent as a function of temperature and S/F ratio are presented in SI Tables 1 and 2 in the supplementary data. Experimental results employing sulfolane in the liquid–liquid extraction of BTX from the pyrolysis gasoline models at temperatures from 303.2 K to 323.2 K and S/F ratios between 1.0 and 5.0 are also listed in SI Tables 3 and 4 in the supplementary data.

3.2. Aromatic and aliphatic distribution ratios and aromatic/aliphatic selectivities

To perform a comparative analysis between the experimental results obtained in the liquid–liquid extraction of BTX using sulfolane or the {[4empy][Tf_2N] + [emim][DCA]} IL mixture, aromatic and aliphatic distribution ratios and aromatic/aliphatic selectivities have been calculated.

From the experimental compositions of raffinate and extract phases, aliphatic distribution ratios (D_{aliph}) have been determined as follows:

$$D_{\text{aliph}} = \frac{w^{\text{II}}_{\text{hexa}} + w^{\text{II}}_{\text{hepta}} + w^{\text{II}}_{\text{octa}}}{w^{\text{I}}_{\text{hexa}} + w^{\text{I}}_{\text{hepta}} + w^{\text{I}}_{\text{octa}}} \qquad (1)$$

where w_i is the mass fraction of the hydrocarbon, I denotes the raffinate phase, and II refers to the extract phase. Experimental values of aliphatic distribution ratios employing the IL mixture are listed in Table 3 as a function of temperature, S/F ratio, and pyrolysis gasoline model, whereas the values of D_{aliph} using sulfolane under the same conditions are presented in Table 4. As can be seen, values of D_{aliph} for the IL-based solvent are substantially smaller than those employing sulfolane. This fact implies that the solubility of the aliphatic hydrocarbons is lower in the IL mixture and, therefore, the aromatic hydrocarbons could be extracted with a greater purity than in the case of the sulfolane. Values of D_{aliph} in the dearomatization of the pyrolysis gasoline model obtained by mild cracking were somewhat lower than those of the gasoline from severe cracking employing both solvents.

The effect of temperature on the values of D_{aliph} was similar in the results using the IL mixture and sulfolane, slightly increasing the aliphatic distribution ratio with temperature. To conclude, an increase in the S/F ratio caused a slight decrease in the values of D_{aliph} using IL mixture, whereas the effect of the S/F ratio on the aliphatic distribution ratios for the sulfolane was more pronounced obtaining the lowest values of D_{aliph} at the highest solvent to feed ratio. Therefore, a solvent to feed ratio of 5.0 and a temperature of 303.2 K seem to be adequate to reduce the solubility of the aliphatic hydrocarbons in both extraction solvents.

Aromatic distribution ratios (D_{arom}) have been calculated from the experimental compositions of raffinate and extract phases employing the following expression:

$$D_{\text{arom}} = \frac{w^{\text{II}}_{\text{benz}} + w^{\text{II}}_{\text{tol}} + w^{\text{II}}_{\text{p-xyl}}}{w^{\text{I}}_{\text{benz}} + w^{\text{I}}_{\text{tol}} + w^{\text{I}}_{\text{p-xyl}}} \qquad (2)$$

Table 3
Aliphatic and aromatic distribution ratios (D_i), aromatic/aliphatic selectivities ($\alpha_{\text{arom,aliph}}$), yield of extraction of aromatics and aliphatics (Yld_i), and relative purity of extracted aromatics in the extract phase (P_{arom}) using {[4empy][Tf_2N] + [emim][DCA]} at $x_1 = 0.3$ as solvent.

Model of pyrolysis gasoline obtained by mild cracking

T/K	S/F	D_{aliph}	D_{arom}	$\alpha_{\text{arom,aliph}}$	Yld_{aliph}/%	Yld_{arom}/%	P_{arom}/%
303.2	1.0	0.006	0.235	38.0	0.8	22.3	96.7
	2.0	0.006	0.233	41.5	1.6	36.8	96.1
	3.0	0.005	0.226	43.1	2.4	45.8	95.3
	4.0	0.005	0.227	44.6	3.2	52.9	94.6
	5.0	0.005	0.226	44.5	4.1	58.1	93.7
313.2	1.0	0.007	0.230	32.6	0.9	22.0	96.2
	2.0	0.006	0.219	35.0	1.7	35.2	95.5
	3.0	0.006	0.216	38.2	2.5	44.5	94.9
	4.0	0.005	0.213	39.0	3.4	51.0	94.1
	5.0	0.005	0.212	41.0	4.2	56.1	93.4
323.2	1.0	0.007	0.212	30.2	0.9	20.2	96.0
	2.0	0.006	0.202	33.1	1.7	32.8	95.3
	3.0	0.006	0.193	33.8	2.5	40.3	94.4
	4.0	0.006	0.199	35.0	3.6	49.0	93.6
	5.0	0.006	0.202	34.1	4.8	54.9	92.4

Model of pyrolysis gasoline obtained by severe cracking

T/K	S/F	D_{aliph}	D_{arom}	$\alpha_{\text{arom,aliph}}$	Yld_{aliph}/%	Yld_{arom}/%	P_{arom}/%
303.2	1.0	0.009	0.261	30.6	1.3	26.5	97.6
	2.0	0.007	0.257	35.7	2.5	43.1	97.2
	3.0	0.006	0.243	39.4	3.5	51.5	96.6
	4.0	0.006	0.240	41.5	4.7	57.7	96.0
	5.0	0.005	0.234	46.0	5.5	61.1	95.6
313.2	1.0	0.009	0.243	26.9	1.3	24.9	97.4
	2.0	0.008	0.231	29.4	2.6	39.9	96.7
	3.0	0.006	0.218	33.6	3.6	47.9	96.3
	4.0	0.006	0.218	36.1	4.9	53.2	95.5
	5.0	0.006	0.217	37.9	6.1	60.0	95.1
323.2	1.0	0.010	0.231	22.8	1.4	23.6	97.0
	2.0	0.008	0.222	27.4	2.6	38.5	96.6
	3.0	0.007	0.208	28.6	4.0	46.7	95.9
	4.0	0.007	0.200	30.7	5.1	52.2	95.3
	5.0	0.006	0.197	34.4	6.1	53.9	94.6

Table 4
Aliphatic and aromatic distribution ratios (D_i), aromatic/aliphatic selectivities ($\alpha_{\text{arom,aliph}}$), yield of extraction of aromatics and aliphatics (Yld_i), and relative purity of extracted aromatics in the sulfolane-rich phase (P_{arom}) using sulfolane as solvent.

Model of pyrolysis gasoline obtained by mild cracking

T/K	S/F	D_{aliph}	D_{arom}	$\alpha_{\text{arom,aliph}}$	Yld_{aliph}/%	Yld_{arom}/%	P_{arom}/%
303.2	1.0	0.028	0.458	16.1	4.1	41.5	91.4
	2.0	0.021	0.424	20.1	6.7	60.4	90.5
	3.0	0.017	0.398	23.2	8.5	70.0	89.6
	4.0	0.014	0.386	26.9	9.9	76.5	89.0
	5.0	0.014	0.375	27.6	12.0	80.8	87.7
313.2	1.0	0.034	0.459	13.5	5.5	44.9	89.6
	2.0	0.025	0.425	17.2	8.4	62.8	88.8
	3.0	0.021	0.398	19.3	10.1	71.1	88.1
	4.0	0.017	0.389	22.6	11.7	77.1	87.3
	5.0	0.017	0.378	22.3	14.9	81.1	85.2
323.2	1.0	0.041	0.462	11.3	6.1	43.0	88.2
	2.0	0.029	0.426	14.8	9.1	61.1	87.6
	3.0	0.023	0.403	17.4	11.9	71.5	86.4
	4.0	0.021	0.390	18.7	14.6	78.0	84.9
	5.0	0.019	0.383	20.4	16.9	82.9	83.7

Model of pyrolysis gasoline obtained by severe cracking

T/K	S/F	D_{aliph}	D_{arom}	$\alpha_{\text{arom,aliph}}$	Yld_{aliph}/%	Yld_{arom}/%	P_{arom}/%
303.2	1.0	0.055	0.551	10.0	10.4	56.8	91.4
	2.0	0.030	0.462	15.2	13.0	72.3	91.6
	3.0	0.024	0.434	18.2	16.4	82.0	90.7
	4.0	0.021	0.427	20.8	19.5	86.5	89.7
	5.0	0.017	0.406	23.6	21.2	88.6	89.1
313.2	1.0	0.067	0.544	8.1	12.2	54.5	89.8
	2.0	0.038	0.476	12.5	15.9	72.5	89.9
	3.0	0.028	0.445	16.0	18.9	81.2	89.4
	4.0	0.022	0.423	19.0	21.2	86.4	88.9
	5.0	0.018	0.407	22.4	22.0	87.2	88.6
323.2	1.0	0.080	0.546	6.8	14.5	55.1	88.1
	2.0	0.047	0.481	10.3	19.1	72.7	88.2
	3.0	0.032	0.441	13.6	22.1	82.2	87.9
	4.0	0.025	0.420	16.6	24.1	85.8	87.4
	5.0	0.021	0.420	20.3	25.6	88.1	87.1

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009

Experimental aromatic distribution ratios using the IL mixture as a function of temperature and S/F ratio are listed in Table 3, whereas values of D_{arom} for the sulfolane are shown in Table 4. To compare the values of D_{arom} in the dearomatization of the pyrolysis gasoline models using both solvents, experimental values using sulfolane and the IL mixture are graphically shown in Fig. 1.

As seen, D_{arom} for the sulfolane were substantially higher than those using the IL-based solvent in the BTX extraction from both pyrolysis gasoline models. Greater aromatic distribution ratios would imply better yields of extraction of aromatics using sulfolane than the IL-based solvent. Values of D_{arom} obtained in the liquid–liquid extraction of BTX from the pyrolysis gasoline model from mild cracking using the IL mixture were very slightly smaller than those in the dearomatization of the gasoline obtained from severe cracking. Also, comparing the aromatic distribution ratios in the liquid–liquid extraction of BTX from both gasoline models using sulfolane, values of D_{arom} for the pyrolysis gasoline from severe cracking were significantly higher than those in the aromatic extraction from gasoline from mild cracking. These facts can be related to the higher BTX content in the pyrolysis gasoline obtained by severe cracking (66.1 wt.%) than in the gasoline from mild cracking (51.1 wt.%).

As can be observed in the values of D_{arom} represented in Fig. 1, the extraction temperature affected the aromatic distribution ratios using the IL-based solvent, obtaining the highest values of D_{arom} at the lowest temperature (303.2 K). This effect of temperature on the solubility of BTX in the IL mixture was previously observed in the dearomatization of a reformer gasoline model [24]. In addition, simulations made using the COSMO-RS (Conductor-like Screening Model for Real Solvents) also predicted a decrease in the values of D_{arom} with temperature as a consequence of the stronger molecular movements that reduce the π–π interactions between the BTX and the IL-based solvent [27]. An increase in the S/F ratio caused a decrease in the values of D_{arom} using sulfolane, whereas the aromatic distribution ratios for the IL mixture were almost constant with the change of the solvent to feed ratio.

From the experimental values of aromatic and aliphatic distribution ratios, aromatic/aliphatic selectivities ($\alpha_{arom,aliph}$) in the liquid–liquid

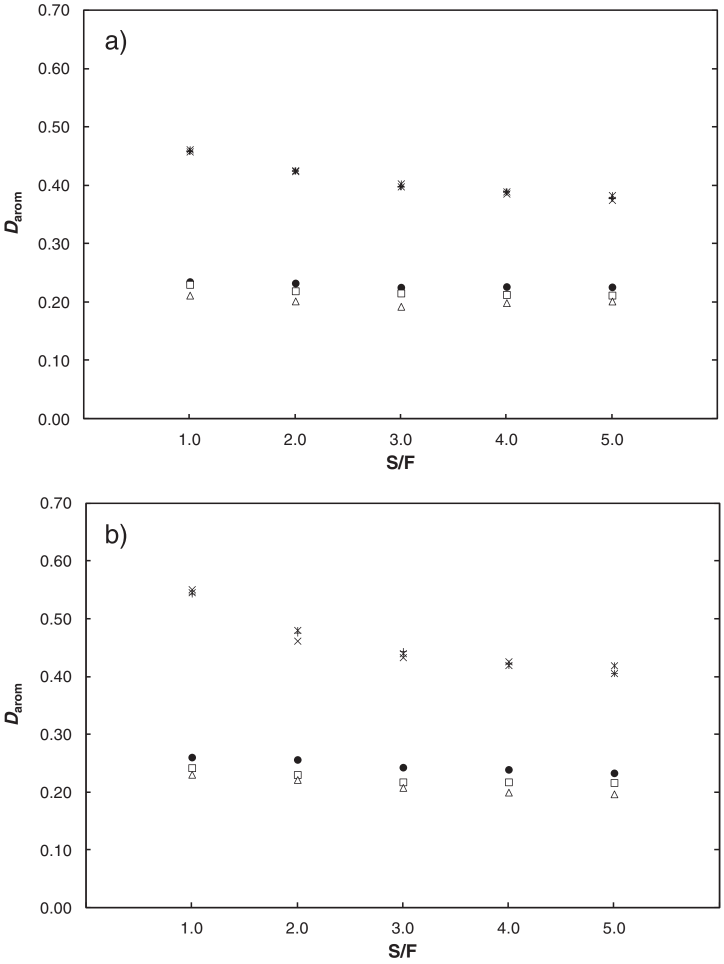


Fig. 1. Aromatic distribution ratios as a function of temperature and solvent/feed ratio. a) Model of pyrolysis gasoline obtained by mild cracking and b) model of pyrolysis gasoline obtained by severe cracking. Results using {[4empy][Tf$_2$N] + [emim][DCA]} at $x_1 = 0.3$ as solvent: ●, 303.2 K; □, 313.2 K; △, 323.2 K, and using sulfolane as solvent:×, 303.2 K; +, 313.2 K; and *, 323.2 K.

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009

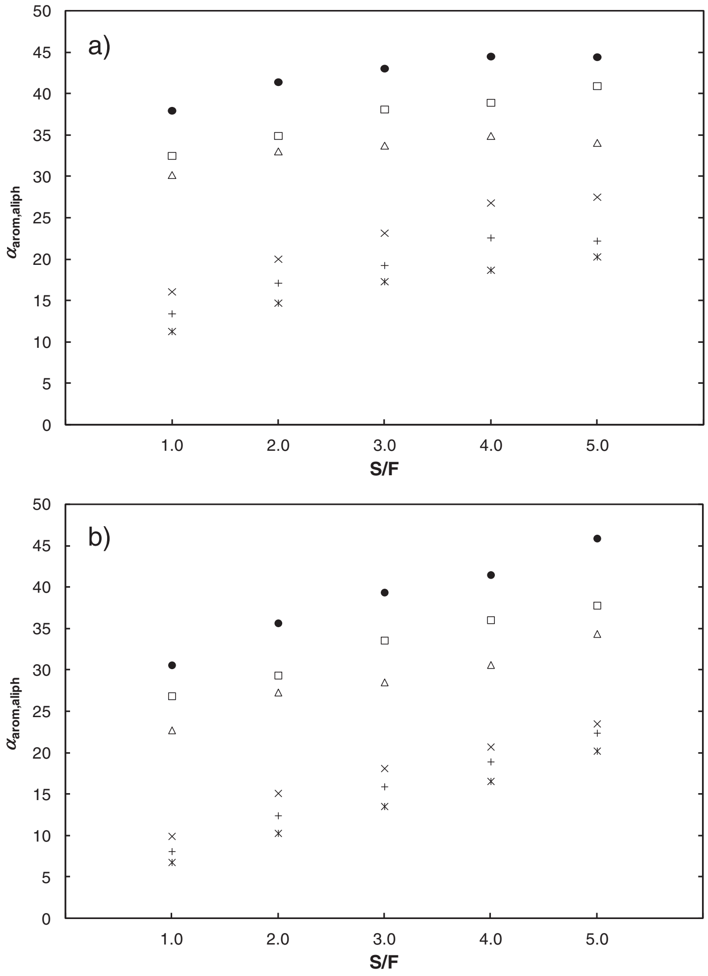


Fig. 2. Aromatic/aliphatic selectivities as a function of temperature and solvent/feed ratio. a) Model of pyrolysis gasoline obtained by mild cracking and b) model of pyrolysis gasoline obtained by severe cracking. Results using {[4empy][Tf$_2$N] + [emim][DCA]} at $x_1 = 0.3$ as solvent: ●, 303.2 K; □, 313.2 K; Δ, 323.2 K, and using sulfolane as solvent: ×, 303.2 K; +, 313.2 K; and *, 323.2 K.

extraction of BTX from the pyrolysis gasoline models have been calculated as follows:

$$\alpha_{arom,aliph} = \frac{D_{arom}}{D_{aliph}} \quad (3)$$

Values of aromatic/aliphatic selectivities using the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture are presented in Table 3 and $\alpha_{arom,aliph}$ for the sulfolane are shown in Table 4. In Fig. 2, values of $\alpha_{arom,aliph}$ as a function of temperature and solvent to feed ratio for both extraction solvent are also plotted. As observed, aromatic/aliphatic selectivities using the IL mixture were almost double than those using sulfolane at the same temperature and S/F ratio. These high values of selectivity would imply a higher purity of the BTX extracted, simplifying the purification steps of the aromatics. On the other hand, values of $\alpha_{arom,aliph}$ in the BTX extraction from the pyrolysis gasoline obtained by mild cracking were slightly higher than those for the gasoline from severe cracking using both extraction solvents, because of the greater content of BTX in this gasoline. This trend is in agreement with the experimental results and the predictions by COSMO-RS in the liquid–liquid extraction of aromatics from n-alkanes, decreasing the values of aromatic/aliphatic selectivities as the aromatic content in the raffinate phase increases [27].

The temperature influence on the values of $\alpha_{arom,aliph}$ was the same in both extraction solvents, achieving the highest values of aromatic/aliphatic selectivity at the lowest temperature (303.2 K). The same effect was predicted by the COSMO-RS model [27]. An increase in the value of S/F ratio also caused an increase in the $\alpha_{arom,aliph}$ using sulfolane and the IL-based solvent at constant temperature. Therefore, to achieve high values of aromatic/aliphatic selectivities in the dearomatization of both pyrolysis gasoline models a high value of S/F ratio and a low temperature should be chosen.

3.3. Extraction yields and relative purity of aromatics in the extract phase

In addition to the extractive properties of the solvents, such as distribution ratios and selectivities, from an industrial point of view it is important to quantify the extraction yields of the solutes and

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009

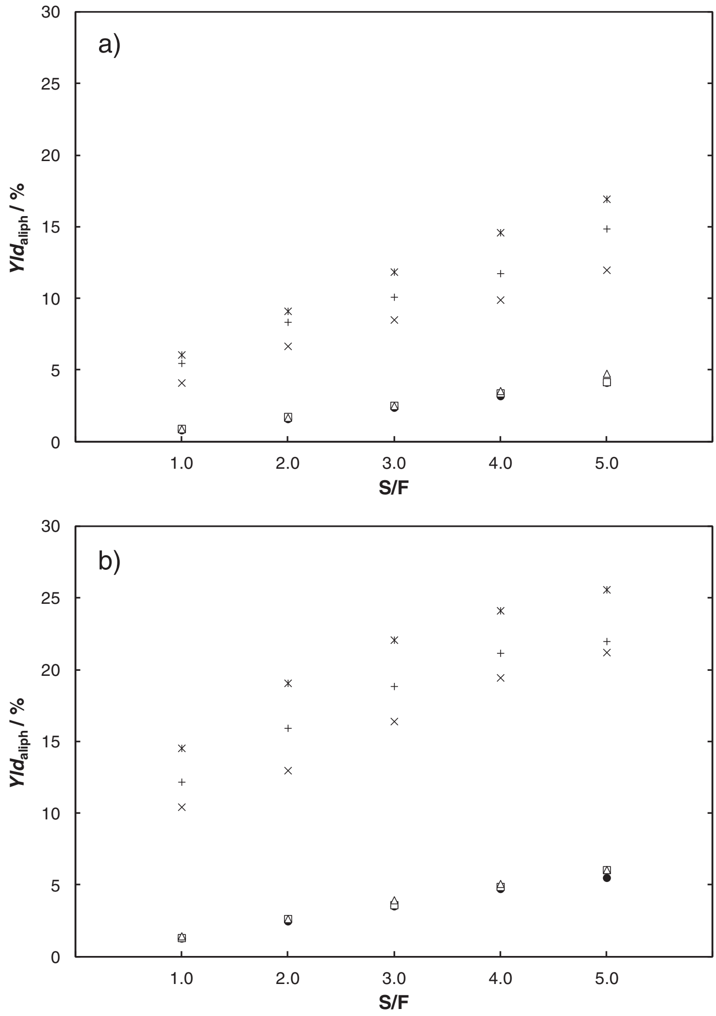


Fig. 3. Yield of extraction of aliphatics as a function of temperature and solvent/feed ratio. a) Model of pyrolysis gasoline obtained by mild cracking and b) model of pyrolysis gasoline obtained by severe cracking. Results using {[4empy][Tf$_2$N] + [emim][DCA]} at $x_1 = 0.3$ as solvent: ●, 303.2 K; □, 313.2 K; Δ, 323.2 K, and using sulfolane as solvent: ×, 303.2 K; +, 313.2 K; and *, 323.2 K.

the purities of the solutes extracted. Experimental yields of extraction of aliphatics (Yld_{aliph}) were calculated according to the following equation:

$$Yld_{aliph}\ (\%) = 100\frac{m^{II}_{hexa} + m^{II}_{hepta} + m^{II}_{octa}}{m^{feed}_{hexa} + m^{feed}_{hepta} + m^{feed}_{octa}} \qquad (4)$$

where m_i indicates the mass of the hydrocarbon in the feed or in the extract phase. To determine the mass of each hydrocarbon in raffinate and extract phases, an overall mass balance was performed considering the amount of each hydrocarbon added to vial with the feed and the experimental compositions of raffinate and extract phases. Experimental values of extraction yields of aliphatics using the IL mixture are listed in Table 3, whereas the Yld_{aliph} employing the sulfolane are presented in Table 4. To make an analysis of the effect of temperature and S/F ratio on the values of yield of extraction of aliphatics using both extraction solvents, experimental values of Yld_{aliph} are plotted in Fig. 3.

As can be seen, yields of extraction of aliphatics using sulfolane were considerably higher than those employing the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture at constant temperature and solvent to feed ratio. A higher yield of extraction of aliphatics would imply a lower relative purity of the BTX extracted and a more complicated purification unit of the aromatics.

An increase in the extraction temperature caused a significant rise in the values of Yld_{aliph} employing sulfolane, whereas the influence of temperature on the extraction yields of aliphatics using the IL mixture was negligible. Similar results were found in the study on the influence of the S/F ratio on the values of Yld_{aliph} using both extraction solvents;

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009

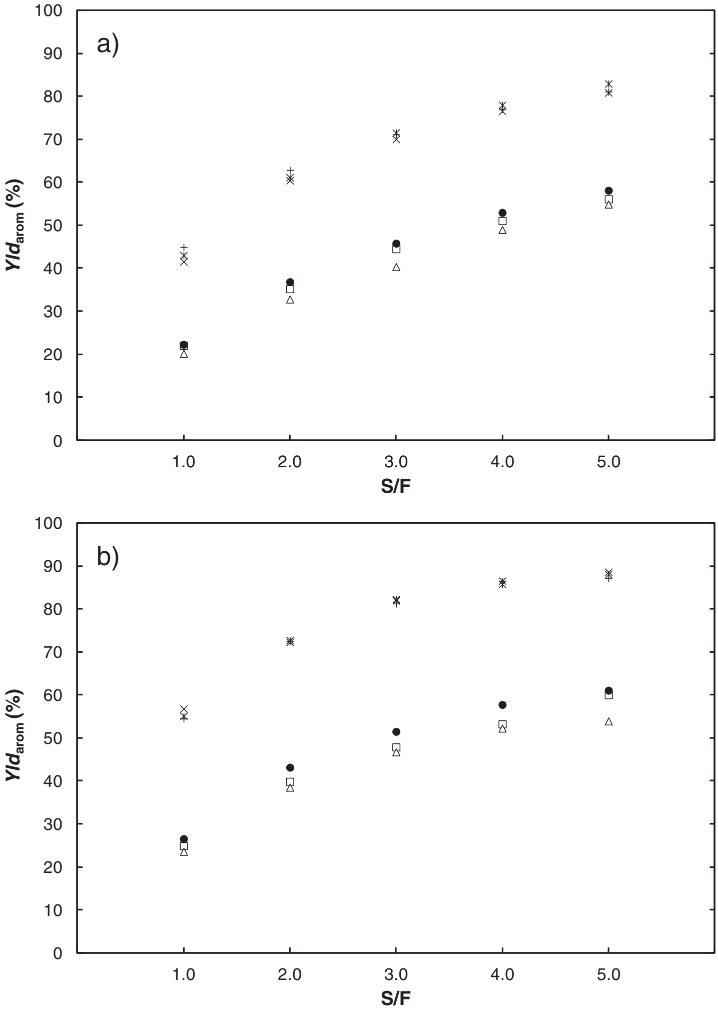


Fig. 4. Yield of extraction of aromatics as a function of temperature and solvent/feed ratio. a) Model of pyrolysis gasoline obtained by mild cracking and b) model of pyrolysis gasoline obtained by severe cracking. Results using {[4empy][Tf_2N] + [emim][DCA]} at $x_1 = 0.3$ as solvent: ●, 303.2 K; □, 313.2 K; △, 323.2 K, and using sulfolane as solvent: ×, 303.2 K; +, 313.2 K; and *, 323.2 K.

Yld_{aliph} increased with S/F ratio more strongly in the sulfolane values than in the yields of extraction of aliphatics using the {[4empy][Tf_2N] + [emim][DCA]} IL mixture.

Values of yields of extraction of aromatics (Yld_{arom}) were also obtained as follows, considering the mass of each hydrocarbon in the feed and the hydrocarbon mass determined by an overall mass balance in the vials:

$$\mathrm{Yl}d_{\mathrm{arom}}\ (\%) = 100\,\frac{m^{\mathrm{II}}_{\mathrm{benz}} + m^{\mathrm{II}}_{\mathrm{tol}} + m^{\mathrm{II}}_{\mathrm{p\text{-}xyl}}}{m^{\mathrm{feed}}_{\mathrm{benz}} + m^{\mathrm{feed}}_{\mathrm{tol}} + m^{\mathrm{feed}}_{\mathrm{p\text{-}xyl}}} \tag{5}$$

Experimental Yld_{arom} using the IL-based solvent can be found in Table 3, whereas the yields of extraction of aromatics for the sulfolane are shown in Table 4. Values of Yld_{arom} using the {[4empy][Tf_2N] + [emim][DCA]} IL mixture and sulfolane in the liquid–liquid extraction of BTX from the pyrolysis gasoline models as a function of temperature and S/F ratio are plotted in Fig. 4.

As seen, Yld_{arom} for the sulfolane were substantially greater than the values employing the IL mixture at constant temperature and S/F ratio and in both gasoline models. As a consequence of this result, the liquid–liquid extraction of BTX from pyrolysis gasolines in a countercurrent extraction column using the IL-based solvent would need a higher number of equilibrium stages to reach a similar extraction yield of aromatics than using sulfolane. Comparing the values of Yld_{arom} in the dearomatization of the pyrolysis gasolines, extraction yields of aromatics were slightly higher in the case of the gasoline obtained by severe cracking than those in the experiments with pyrolysis gasoline from mild cracking. This result is due to the greater content of benzene (33.8 wt.%) in the gasoline from severe cracking than in the other gasoline model (22.0 wt.%), since the benzene is the most soluble BTX as a consequence of its higher aromatic character [21].

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009

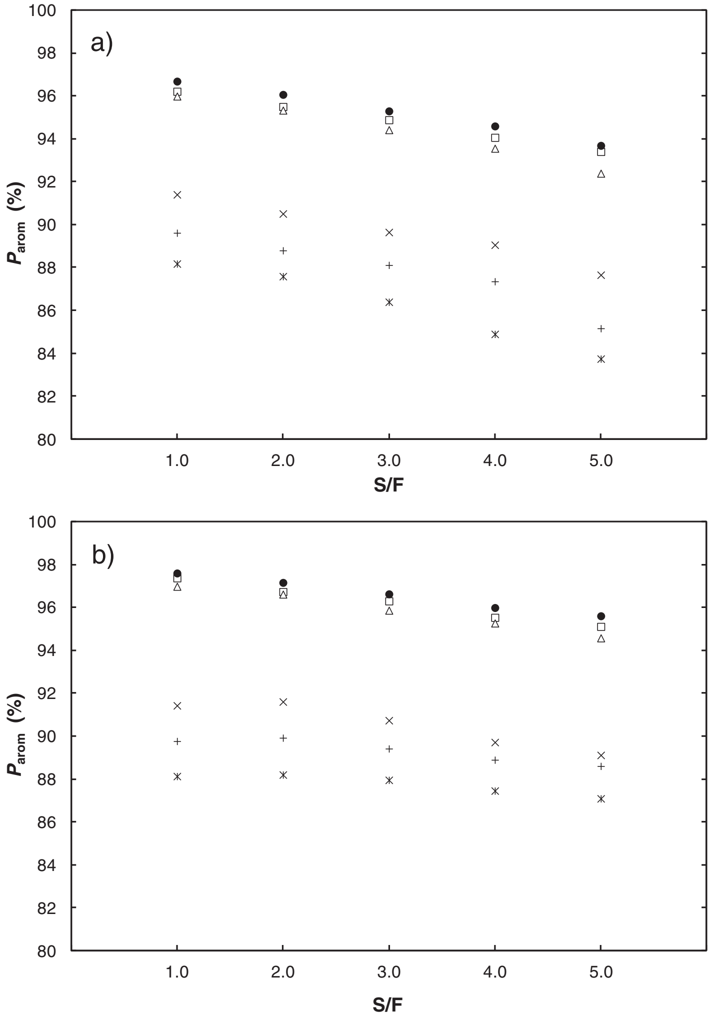


Fig. 5. Relative purity of extracted aromatics in the extract phase as a function of temperature and solvent/feed ratio. a) Model of pyrolysis gasoline obtained by mild cracking and b) model of pyrolysis gasoline obtained by severe cracking. Results using {[4empy][Tf_2N] + [emim][DCA]} at $x_1 = 0.3$ as solvent: ●, 303.2 K; □, 313.2 K; Δ, 323.2 K, and using sulfolane as solvent: ×, 303.2 K; +, 313.2 K; and *, 323.2 K.

The temperature effect on the values of Yld_{arom} was relatively slight using both extraction solvents, achieving the highest values of extraction yields of aromatics at 303.2 K in the case of the IL mixture and at 323.2 K using sulfolane. To conclude, the extraction yields of aromatics increased as the S/F ratio rose using both extraction solvents in the extraction of BTX from the two gasoline models. Hence, in order to obtain high values of Yld_{arom} in the dearomatization of the pyrolysis gasoline models obtained by mild or severe cracking using the {[4empy][Tf_2N] + [emim][DCA]} mixture a temperature of 303.2 K and a S/F ratio of 5.0 seem to be the most adequate conditions.

In addition to the extraction yields, it is important to quantify the purity of the solute extracted, since this value will determine the necessary steps in the purification of the solutes. The relative purity of extracted BTX in the extract phase (P_{arom}) was determined from the experimental compositions of the extract phase in mass basis using the next expression:

$$P_{\text{arom}}\ (\%) = 100\frac{w^{\text{II}}_{\text{benz}}+w^{\text{II}}_{\text{tol}}+w^{\text{II}}_{p\text{-xyl}}}{\left(w^{\text{II}}_{\text{hexa}}+w^{\text{II}}_{\text{hepta}}+w^{\text{II}}_{\text{octa}}\right)+\left(w^{\text{II}}_{\text{benz}}+w^{\text{II}}_{\text{tol}}+w^{\text{II}}_{p\text{-xyl}}\right)} \qquad (6)$$

Experimental values of P_{arom} using the IL mixture and sulfolane are listed in Tables 3 and 4, respectively. To study the effects of temperature and S/F ratio on the relative purity of the extracted aromatics, the results using sulfolane and the IL mixture in the dearomatization of both pyrolysis gasoline models are graphically shown in Fig. 5.

As observed, values of P_{arom} for the {[4empy][Tf_2N] + [emim][DCA]} mixture were greater than those using sulfolane over the whole range of temperature and S/F ratio in the two pyrolysis gasolines. This fact would

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009

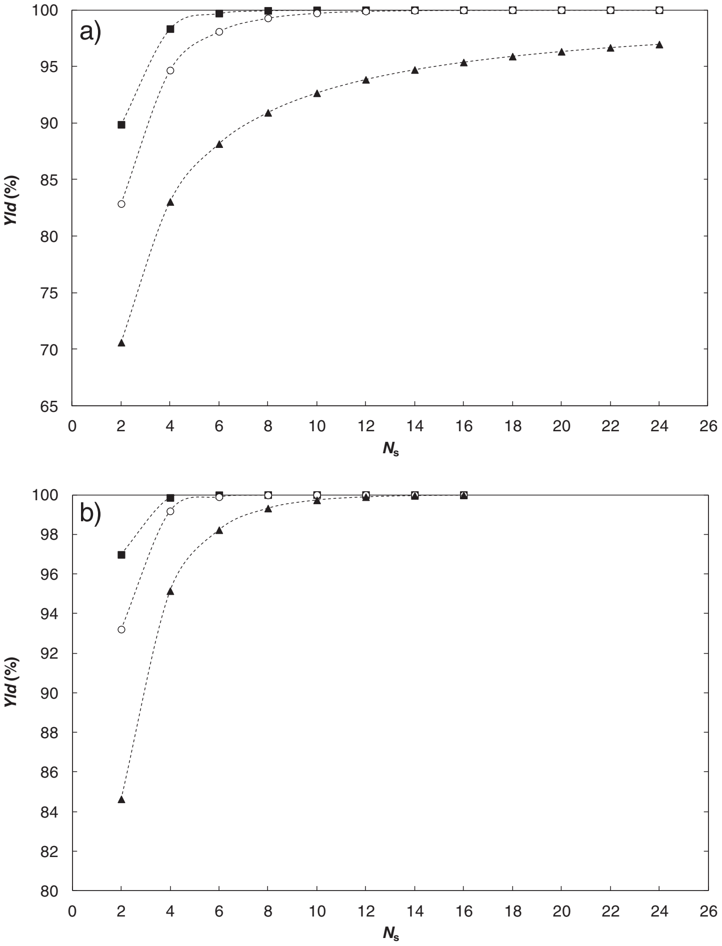


Fig. 6. Extraction yield of aromatic hydrocarbons from the pyrolysis gasoline obtained by mild cracking as a function of the number of equilibrium stages in the countercurrent extraction column using the (a) {[4empy][Tf_2N] + [emim][DCA]} at $x_1 = 0.3$ IL mixture and (b) using sulfolane as solvents: ■, benzene; ○, toluene; ▲, *p*-xylene at 303.2 K and a solvent to feed ratio of 5.0. Dashed lines are to guide the eye.

simplify the purification unit of the extracted BTX and it would reduce the amount of aliphatics in the extract stream.

A rise in the extraction temperature caused a decrease in the values of P_{arom} using both extraction solvents, being more pronounced the effect in the case of the sulfolane. The negative influence of temperature on the purity of the extracted aromatics is due to the higher dependence of temperature of the extraction yield of aliphatics than in the case of aromatics. The effect of increasing the S/F ratio also caused a decrease in the P_{arom} using sulfolane and the IL mixture as a result of the greater extraction yields of aliphatics at high values of solvent to feed ratio.

Once the influence of the temperature and S/F ratio on extraction yields and relative purities of the BTX extracted have been analyzed, the optimal conditions to perform the dearomatization of the pyrolysis gasoline models using the IL mixture have been selected. A temperature of 303.2 K was chosen to achieve high values of extraction yields of aromatics and relative purity of the BTX extracted and to reduce the extraction yields of aliphatics. A S/F ratio of 5.0 was also selected in order to ensure high values of extraction yields of BTX.

3.4. Simulations of countercurrent extraction columns by the Kremser equation

To complete the study, simulations of countercurrent extraction columns in the dearomatization of both pyrolysis gasoline models obtained by mild and severe cracking have been performed using the Kremser equation [28]. This equation has been used to determine the influence of the number of equilibrium stages in the flow and composition of the raffinate and extract streams, the extraction yield of aromatics, and in the purity of the BTX extracted. Simulations have been made from the experimental results of the liquid–liquid extraction of BTX using {[4empy][Tf_2N] + [emim][DCA]} IL mixture at $x_1 = 0.3$ and sulfolane at the optimal conditions of 303.2 K and a S/F of 5.0.

A liquid–liquid extraction column can be simulated using the Kremser equation if raffinate and extract phases are immiscible and if the solute distribution ratios can be considered constant under the conditions used in the simulation [29]. In the experimental liquid–liquid extraction of BTX from the pyrolysis gasoline models using sulfolane

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009

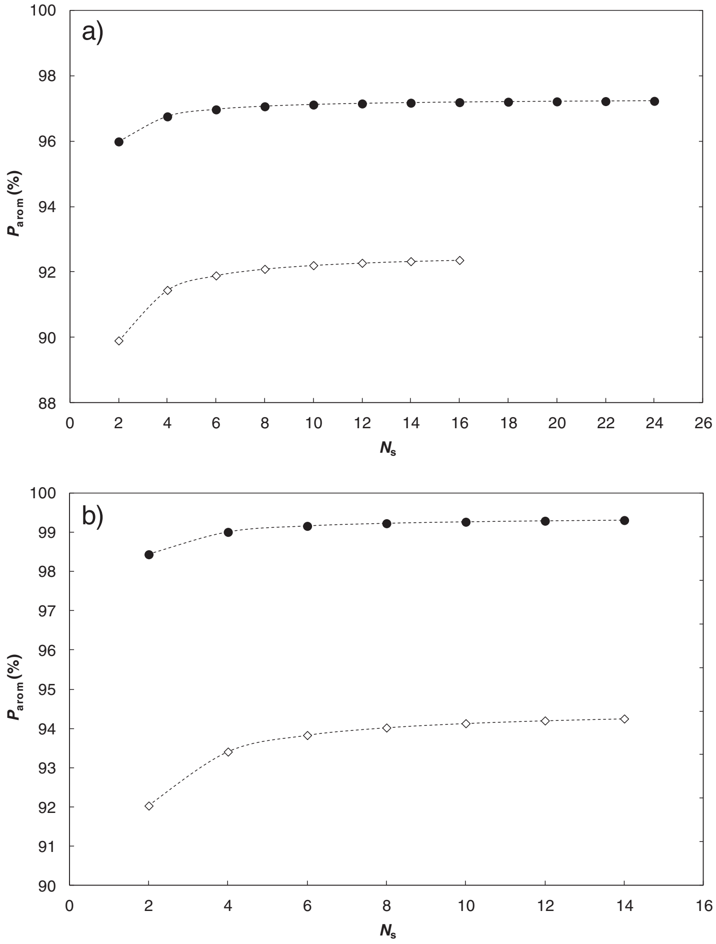


Fig. 7. Relative purities of the aromatics in the extract phase from (a) pyrolysis gasoline from mild cracking and (b) pyrolysis gasoline obtained by severe cracking as a function of the number of equilibrium stages in the countercurrent extraction column at 303.2 K and a solvent to feed ratio of 5.0. ●, using the {[4empy][Tf$_2$N] + [emim][DCA]} at $x_1 = 0.3$ IL mixture; and ◊, employing sulfolane as solvent. Dashed lines are to guide the eye.

and the IL mixture two immiscible phases were found. On the other hand, as explained in the discussion on the results shown in Fig. 1, the values of aromatic distribution ratios using the IL mixture were almost constant over the whole range of temperatures and S/F ratios. However, although the aromatic distribution ratios of sulfolane were slightly affected by the temperature and S/F ratio, in order to compare the simulations using both extraction solvents, D_{arom} using sulfolane have been assumed constant in the simulation of the column at 303.2 K and S/F ratio of 5.0. Finally, as the enthalpy changes in an adiabatic liquid–liquid extraction column are not significant, enthalpy balance equations cannot be considered in the simulation of an extraction column using the Kremser equation [28].

3.4.1. Simulation of countercurrent extraction column in the liquid–liquid extraction of BTX from a pyrolysis gasoline obtained by mild cracking

First, the Kremser equation have been used to simulate countercurrent extraction columns in the dearomatization of the pyrolysis gasoline model obtained by mild cracking using the IL mixture and sulfolane at 303.2 K and S/F ratio of 5.0. The group method of Kremser to simulate a liquid–liquid extraction column is analogous to the Kremser method used in absorption. The extraction factor (E) and the reciprocal of E (U) have been calculated according to the following expressions:

$$E_i = D_i \frac{V}{L} \tag{7}$$

$$U_i = \frac{1}{E_i} = \frac{L}{D_i V} \tag{8}$$

where D_i indicates the distribution ratio of each hydrocarbon in mass basis, L denotes the mass flow of the raffinate stream, whereas V is the mass flow of the extract stream. From the experimental compositions gathered in SI Tables 1 and 2 in the supplementary data at 303.2 K and S/F ratio equal to 5.0, the value of D_i of each component was calculated.

As basis of calculation in the simulations, a flow of 1000 t/h of the pyrolysis gasoline model from mild or severe cracking was fixed. All the simulations were performed using a S/F ratio of 5.0; therefore, the value of the solvent flow was 5000 t/h. To estimate the flows of each component in raffinate and extract streams, the number of the

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009

Table 5
Results of the simulation of countercurrent extraction columns using the Kremser equation in the liquid–liquid extraction of aromatics from a model of pyrolysis gasoline obtained by mild cracking at S/F = 5.0 and T = 303.2 K.

Extraction solvent: {[4empy][Tf$_2$N] + [emim][DCA]} at x_1 = 0.3. N_s = 24.

	Feed	Solvent	Raffinate phase	Extract phase
Flow (t/h)	1000.0	5000.0	478.0	5522.0
Benzene (wt.%)	22.00	0.00	0.00	3.98
Toluene (wt.%)	17.60	0.00	0.00	3.19
p-Xylene (wt.%)	11.50	0.00	0.73	2.02
Aromatics (wt.%)	51.10	0.00	0.73	9.19
n-Hexane (wt.%)	16.30	0.00	32.95	0.10
n-Heptane (wt.%)	16.30	0.00	32.98	0.10
n-Octane (wt.%)	16.30	0.00	33.35	0.06
n-Alkanes (wt.%)	48.90	0.00	99.27	0.26
Binary IL mixture (wt.%)	0.00	100.00	0.00	90.55

Extraction solvent: sulfolane. N_s = 8.

	Feed	Solvent	Raffinate phase	Extract phase
Flow (t/h)	1000.0	5000.0	447.1	5552.9
Benzene (wt.%)	22.00	0.00	0.00	3.96
Toluene (wt.%)	17.60	0.00	0.01	3.17
p-Xylene (wt.%)	11.50	0.00	0.18	2.06
Aromatics (wt.%)	51.10	0.00	0.19	9.19
n-Hexane (wt.%)	16.30	0.00	31.97	0.36
n-Heptane (wt.%)	16.30	0.00	33.28	0.26
n-Octane (wt.%)	16.30	0.00	34.31	0.17
n-Alkanes (wt.%)	48.90	0.00	99.56	0.79
Sulfolane (wt.%)	0.00	100.00	0.25	90.02

equilibrium stages (N_s) in the liquid–liquid extraction column was fixed and mass balances of each component were made by using an iterative method implemented in Microsoft Excel. A fully description of the Kremser method used in this work to simulate a liquid–liquid extraction column can be found elsewhere [28].

The aim of the simulations using the IL mixture was to determine the number of equilibrium stages that allows us to achieve the typical values of aromatics recoveries in the UOP Sulfolane Process at industrial scale. Extraction yields in the dearomatization process using sulfolane are 99.9% for benzene, 99.0% for toluene, and 97.0% for mixed xylenes [2].

In Fig. 6, individual extraction yields of benzene, toluene, and *p*-xylene are graphically shown as a function of N_s. These values of extraction yields in the simulations have been calculated as the percentage relationship between the flow of each component in the extract stream and in the feed stream introduced to the extraction column. As can be observed, the greatest value of extraction yield at a constant value of N_s was obtained for the benzene, followed by the toluene and the *p*-xylene. This trend is due to the decrease of solubility of aromatics in ILs as the molecular weight of the aromatic increases [27]. To achieve the target values of extraction yield of benzene (99.9%) and toluene (99.0%) using the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture were required at least 10 equilibrium stages. However, as a result of the lower solubility of the *p*-xylene, an extraction yield of *p*-xylene higher than 97.0% was just achieved using 24 equilibrium stages.

Extraction yields in the simulation of the liquid–liquid extraction of BTX from the pyrolysis gasoline model from mild cracking using sulfolane are also plotted in Fig. 6. As seen, higher extraction yields of BTX were obtained using sulfolane than those employing the IL mixture at a constant value of N_s because the experimental values of aromatic distribution ratios and extraction yields of BTX were greater using the conventional solvent. The target values of extraction yield of benzene, toluene, and *p*-xylene were achieved with at least 8 equilibrium stages. Hence, a liquid–liquid extraction process using the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture could achieve the required values of BTX extraction yields but using an extraction column with a higher number of equilibrium stages than that employing sulfolane.

In addition to the extraction yields of BTX, the purities of the extracted solutes must be considered. Using Eq. (6), values of relative purities of the extracted BTX have been calculated and plotted in Fig. 7. As can be observed, the relative purity of the extracted BTX using the IL mixture was considerably higher than the purity employing sulfolane, as a consequence of the greater values of aromatic/aliphatic selectivity for the IL-based solvent. A higher purity of the solutes implies a more simplified unit of purification of the BTX and lower investment and operating costs. Furthermore, the BTX recovery from the ILs could be performed by a flash distillation or by stripping at low temperatures, because of the nonvolatile nature of the IL-based solvent [7]. This easier operation would replace the extractive stripper and the recovery distillation column currently used in the UOP Sulfolane Process for the purification of extracted BTX and regeneration of the solvent [5].

Flows and compositions of each stream obtained in the simulation of the countercurrent extraction columns using the IL mixture and sulfolane in the dearomatization of the pyrolysis gasoline from mild cracking at 303.2 K and S/F ratio equal to 5.0 are listed in Table 5. The simulation using the IL-based solvent was made with a number of equilibrium stages of 24 to achieve the target values of extraction yields of BTX, whereas the simulation of the extraction employing sulfolane was performed with a N_s of 8 because of the same reason. As can be observed, the sulfolane was presented in raffinate stream in 0.25% whereas the IL-based solvent solubility in the hydrocarbons was negligible, this fact being an important advantage of the IL mixture with respect to conventional solvents. Because of this, in a hypothetical process employing the IL-based solvent the raffinate wash column employed in the Sulfolane Process to recover the sulfolane dissolved in the raffinate would be unnecessary [5].

3.4.2. Simulation of countercurrent extraction column in the liquid–liquid extraction of BTX from a pyrolysis gasoline from severe cracking

Countercurrent extraction columns in the dearomatization of the pyrolysis gasoline model from severe cracking using the IL mixture and sulfolane at 303.2 K and S/F ratio equal to 5.0 have also been simulated by the Kremser method. The goal of the simulations was analogous to that of the dearomatization of the other pyrolysis gasoline; the number of equilibrium stages was modified in order to determine the value of N_s that provides values of extraction yield higher than 99.9% for benzene, 99.0% for toluene, and 97.0% for *p*-xylene.

Individual extraction yields of benzene, toluene, and *p*-xylene as a function of the number of equilibrium stages using the IL mixture are shown in Fig. 8. As in the case of the pyrolysis gasoline from mild cracking, the highest value of extraction yield at constant value of N_s were obtained for the benzene, followed by the toluene and the *p*-xylene. The target values of extraction yield of benzene (99.9%) and toluene (99.0%) were achieved using the IL mixture with a value of N_s higher than 6. However, to obtain an extraction yield of *p*-xylene higher than 97.0% were required at least 14 equilibrium stages. This number is lower than the necessary N_s to obtain the target values of extraction yields of BTX in the pyrolysis gasoline from mild cracking, because the aromatic distribution ratios using the IL mixture in the dearomatization of the gasoline from severe cracking were slightly greater than those in the gasoline obtained by mild cracking.

In Fig. 8, individual extraction yields using sulfolane are also plotted. As seen, the number of equilibrium stages to obtain the target values of yields was between 4 and 6, this value being substantially lower than that using the IL-based solvent. Therefore, the number of equilibrium stages in the extraction column using the ILs for the dearomatization of the pyrolysis gasoline from severe cracking would be greater than those employing sulfolane.

Purities of the extracted BTX using both extraction solvents are plotted in Fig. 7. As in the case of the pyrolysis gasoline from mild cracking, the extracted aromatics by the ILs had a considerably greater purity than those extracted by sulfolane, as a result of the higher values of aromatic/aliphatic selectivities for the IL-based solvent. Thus, the

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009

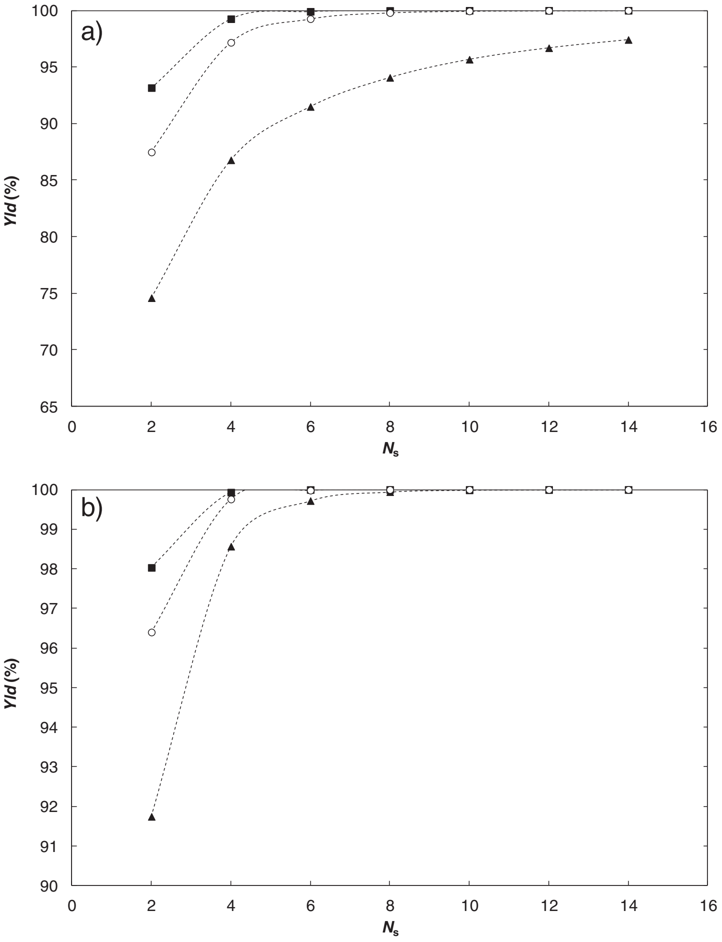


Fig. 8. Extraction yield of aromatic hydrocarbons from the pyrolysis gasoline obtained by severe cracking as a function of the number of equilibrium stages in the countercurrent extraction column employing the using the (a) {[4empy][Tf$_2$N] + [emim][DCA]} at $x_1 = 0.3$ IL mixture and (b) using sulfolane as solvents: ■, benzene; ○, toluene; ▲, *p*-xylene at 303.2 K and a solvent to feed ratio of 5.0. Dashed lines are to guide the eye.

purification of BTX extracted by the IL mixture would be easier than that of the BTX extracted employing sulfolane. At a constant number of equilibrium stages, higher purities of the aromatics were obtained in the dearomatization of the pyrolysis gasoline obtained by severe cracking than in that obtained by mild cracking because of the lower percentage of aliphatics in the pyrolysis gasoline from severe cracking.

Results of the simulations of countercurrent extractions columns in the dearomatization of the pyrolysis gasoline model from severe cracking are presented in Table 6. The simulation using the IL-based solvent was performed with a N_s equal to 14, whereas the simulation employing sulfolane was made with a number of equilibrium stages of 6, to compare the performance of the solvents under the conditions that allow to reach the target values of yields of BTX extraction. As can be seen, the percentage content of aliphatics in the extract stream using the IL-based solvent were lower but a greater amount of *p*-xylene was presented in the raffinate stream employing the IL mixture. In addition, the sulfolane was dissolved in the aliphatic hydrocarbons, obtaining a percentage content of this solvent equal to 0.50% in the raffinate stream.

To sum up, an industrial process of dearomatization of pyrolysis gasolines using the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture at $x_1 = 0.3$ would need an extraction column with a higher number of equilibrium stages than that using sulfolane. However, the purity of the extracted BTX using this IL mixture would be substantially greater than those extracted by the sulfolane and the purification unit would be more simplified as a consequence of the higher purity of the solutes and the nonvolatile nature of the IL-based solvents. As a result of the simpler recovery of the extraction solvent and the mild operating conditions in the extraction and purification units, the investment costs of a liquid–liquid extraction of BTX process employing ILs could be 35% lower than those employing sulfolane and the operating cost could be also smaller [5].

4. Conclusions

In this paper, we have studied the extraction of BTX from two pyrolysis gasoline models obtained by mild and severe cracking employing the {[4empy][Tf$_2$N] + [emim][DCA]} IL mixture with a [4empy][Tf$_2$N] mole fraction of 0.3 as extraction solvent. To study the effects of temperature and S/F ratio on several extractive properties, liquid–liquid extraction experiments have been made at temperatures

Table 6
Results of the simulation of countercurrent extraction columns using the Kremser equation in the liquid–liquid extraction of aromatics from a model of pyrolysis gasoline obtained by severe cracking at S/F = 5.0 and $T = 303.2$ K.

Extraction solvent: {[4empy][Tf_2N] + [emim][DCA]} at $x_1 = 0.3$. $N_s = 14$.

	Feed	Solvent	Raffinate phase	Extract phase
Flow (t/h)	1000.0	5000.0	331.5	5668.5
Benzene (wt.%)	33.80	0.00	0.00	5.96
Toluene (wt.%)	19.30	0.00	0.00	3.40
p-Xylene (wt.%)	13.00	0.00	1.02	2.24
Aromatics (wt.%)	66.10	0.00	1.02	11.60
n-Hexane (wt.%)	11.30	0.00	32.80	0.07
n-Heptane (wt.%)	11.30	0.00	32.89	0.07
n-Octane (wt.%)	11.30	0.00	33.29	0.05
n-Alkanes (wt.%)	33.90	0.00	98.98	0.19
Binary IL mixture (wt.%)	0.00	100.00	0.00	88.21

Extraction solvent: Sulfolane. $N_s = 6$.

	Feed	Solvent	Raffinate phase	Extract phase
Flow (t/h)	1000.0	5000.0	297.4	5702.6
Benzene (wt.%)	33.80	0.00	0.00	5.93
Toluene (wt.%)	19.30	0.00	0.01	3.38
p-Xylene (wt.%)	13.00	0.00	0.12	2.27
Aromatics (wt.%)	66.10	0.00	0.13	11.58
n-Hexane (wt.%)	11.30	0.00	33.51	0.23
n-Heptane (wt.%)	11.30	0.00	33.25	0.25
n-Octane (wt.%)	11.30	0.00	32.61	0.28
n-Alkanes (wt.%)	33.90	0.00	99.37	0.76
Sulfolane (wt.%)	0.00	100.00	0.50	87.66

from 303.2 K to 323.2 K and S/F ratios between 1.0 and 5.0. To perform a comparison between the performance of the IL mixture and that of the most employed aromatic extraction solvent; experiments under the same conditions have also been made employing sulfolane as solvent.

To choose the most appropriate conditions of temperature and S/F ratio to perform the dearomatization of the pyrolysis gasolines, aliphatic and aromatic distribution ratios, aromatic/aliphatic selectivities, extraction yields of aromatics and aliphatics, and relative purities of extracted BTX have been calculated from the experimental compositions employing both extraction solvents. To ensure high values of purity of the extracted BTX and high extraction yields of aromatics a temperature of 303.2 K and S/F ratio of 5.0 were selected.

From the experimental results, countercurrent extraction columns in the dearomatization of the two pyrolysis gasoline model have been simulated using the Kremser equation under the optimal conditions of S/F ratio and temperature employing the IL mixture and sulfolane. The number of equilibrium stages in the extractor has been optimized to reach the extraction yields of benzene, toluene, and xylene achieved by the UOP Sulfolane Process. According to the results of the simulations, the dearomatization of pyrolysis gasolines by the {[4empy][Tf_2N] + [emim][DCA]} IL mixture would require a higher number of equilibrium stages in the extractor than that employing sulfolane. By contrast, extracted aromatics would have a considerably greater purity using the IL-based than those employing sulfolane. Considering the purities of the extracted BTX and the nonvolatile nature of the IL-based solvents, the purification unit in a dearomatization process using the IL mixture would have lower investment and operating costs.

Acknowledgments

The authors are grateful to Ministerio de Economía y Competitividad (MINECO) of Spain and Comunidad Autónoma de Madrid for financial support of Projects CTQ2011-23533 and S2013/MAE-2800, respectively. Marcos Larriba thanks Ministerio de Educación, Cultura y Deporte for awarding him an FPU grant (Reference AP-2010-0318), Pablo Navarro thanks MINECO for awarding him an FPI grant (Reference BES-2012-052312), and Emilio J. González also thanks MINECO for awarding him a Juan de la Cierva Contract (Reference JCI-2012-12005).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.fuproc.2015.03.009.

References

[1] H.G. Franck, J.W. Staldelhofer, Industrial Aromatic Chemistry, Springer-Verlag, New York, 1988.
[2] J. Gary, G. Handwerk, M. Kaiser, Petroleum Refining Technology and Economics, CRC Press, Boca Raton, FL, 2007.
[3] R.A. Meyers, Handbook of Petroleum Refining Processes, McGraw-Hill, New York, 2004.
[4] G.W. Meindersma, A.R. Hansmeier, A.B. de Haan, Ionic liquids for aromatics extraction. Present status and future outlook, Ind. Eng. Chem. Res. 49 (2010) 7530–7540.
[5] G.W. Meindersma, A.B. de Haan, Conceptual process design for aromatic/aliphatic separation with ionic liquids, Chem. Eng. Res. Des. 86 (2008) 745–752.
[6] G.W. Meindersma, A.J.G. Podt, A.B. de Haan, Selection of ionic liquids for the extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures, Fuel Process. Technol. 87 (2005) 59–70.
[7] S.T. Anjan, Ionic liquid for aromatic extraction: are they ready? Chem. Eng. Prog. 102 (2006) 30–39.
[8] Y. Nie, C. Li, H. Meng, Z. Wang, N,N-dialkylimidazolium dialkylphosphate ionic liquids: their extractive performance for thiophene series compounds from fuel oils versus the length of alkyl group, Fuel Process. Technol. 89 (2008) 978–983.
[9] R. Anantharaj, T. Banerjee, COSMO-RS based predictions for the desulphurization of diesel oil using ionic liquids: effect of cation and anion combination, Fuel Process. Technol. 92 (2011) 39–52.
[10] C.D. Wilfred, C.F. Kiat, Z. Man, M.A. Bustam, M.I.M. Mutalib, C.Z. Phak, Extraction of dibenzothiophene from dodecane using ionic liquids, Fuel Process. Technol. 93 (2012) 85–89.
[11] G.W. Meindersma, A.B. de Haan, Cyano-containing ionic liquids for the extraction of aromatic hydrocarbons from an aromatic/aliphatic mixture, Sci. China Chem. 55 (2012) 1488–1499.
[12] G.O. Yahaya, F. Hamad, A. Bahamdan, V.V.R. Tammana, E.Z. Hamad, Supported ionic liquid membrane and liquid–liquid extraction using membrane for removal of sulfur compounds from diesel/crude oil, Fuel Process. Technol. 113 (2013) 123–129.
[13] U. Maity, J.K. Basu, S. Sengupta, Performance study of extraction and oxidation–extraction coupling processes in the removal of thiophenic compounds, Fuel Process. Technol. 121 (2014) 119–124.
[14] S.A. Dharaskar, K.L. Wasewar, M.N. Varma, D.Z. Shende, K.K. Tadi, C.K. Yoo, Synthesis, characterization, and application of novel trihexyl tetradecyl phosphonium bis (2,4,4-trimethylpentyl) phosphinate for extractive desulfurization of liquid fuel, Fuel Process. Technol. 123 (2014) 1–10.
[15] I. Dominguez, E.J. González, A. Dominguez, Liquid extraction of aromatic/cyclic aliphatic hydrocarbon mixtures using ionic liquids as solvent: Literature review and new experimental LLE data, Fuel Process. Technol. 125 (2014) 207–216.
[16] G.C. Laredo, N.V. Likhanova, I.V. Lijanova, B. Rodriguez-Heredia, J.J. Castillo, P. Perez-Romo, Synthesis of ionic liquids and their use for extracting nitrogen compounds from gas oil feeds towards diesel fuel production, Fuel Process. Technol. 130 (2015) 38–45.
[17] S. García, M. Larriba, J. García, J.S. Torrecilla, F. Rodríguez, Liquid–liquid extraction of toluene from n-heptane using binary mixtures of N-butylpyridium tetrafluoroborate and N-butylpyridinium bis(trifluoromethylsulfonyl)imide ionic liquids, Chem. Eng. J. 180 (2012) 210–215.
[18] M. Larriba, P. Navarro, J. García, F. Rodríguez, Separation of toluene from *n*-heptane, 2,3-dimethylpentane, and cyclohexane using binary mixtures of [4empy][Tf_2N] and [emim][DCA] ionic liquids as extraction solvents, Sep. Purif. Technol. 120 (2013) 392–401.
[19] M. Larriba, P. Navarro, J. García, F. Rodríguez, Liquid–liquid extraction of toluene from *n*-heptane by {[emim][TCM] + [emim][DCA]} binary ionic liquid mixtures, Fluid Phase Equilib. 364 (2014) 48–54.
[20] M. Larriba, P. Navarro, J. García, F. Rodríguez, Liquid–liquid extraction of toluene from *n*-alkanes using {[4empy][Tf_2N] + [emim][DCA]} ionic liquid mixtures, J. Chem. Eng. Data 59 (2014) 1692–1699.
[21] M. Larriba, P. Navarro, J. García, F. Rodríguez, Extraction of benzene, ethylbenzene, and xylenes from *n*-heptane using binary mixtures of [4empy][Tf2N] and [emim][DCA] ionic liquids, Fluid Phase Equilib. 38 (2014) 1–10.
[22] P. Navarro, M. Larriba, J. García, F. Rodríguez, Thermal stability, specific heats, and surface tensions of ([emim][DCA] + [4empy][Tf_2N]) ionic liquid mixtures, J. Chem. Thermodyn. 76 (2014) 152–160.
[23] P. Navarro, M. Larriba, E. Rojo, J. García, F. Rodríguez, Thermal properties of cyano-based ionic liquids, J. Chem. Eng. Data 58 (2013) 2187–2193.
[24] M. Larriba, P. Navarro, J. García, F. Rodríguez, Liquid–liquid extraction of BTEX from reformer gasoline using binary mixtures of [4empy][Tf_2N] and [emim][DCA] ionic liquids, Energy Fuels 28 (2014) 6666–6676.
[25] M. Larriba, P. Navarro, J. García, F. Rodríguez, Liquid–liquid extraction of toluene from heptane using [emim][DCA], [bmim][DCA], and [emim][TCM] ionic liquids, Ind. Eng. Chem. Res. 52 (2013) 2714–2720.

[26] B. Kolb, L.S. Ettre, Static Headspace-Gas Chromatography: Theory and Practice, Wiley-VCH, New York, 1997.
[27] A.R. Ferreira, M.G. Freire, J.C. Ribeiro, F.M. Lopes, J.G. Crespo, J.A.P. Coutinho, Overview of the liquid–liquid equilibria of ternary systems composed of ionic liquid and aromatic and aliphatic hydrocarbons, and their modeling by COSMO-RS, Ind. Eng. Chem. Res. 51 (2012) 3483–3507.
[28] E.J. Henley, J.D. Seader, Equilibrium-Stage Separation Operations in Chemical Engineering, John Wiley and Sons, New York, 1981.
[29] F. Buchbender, F. Onink, G.W. Meindersma, A. de Haan, A. Pfenning, Simulation of aromatics extraction with an ionic liquid in a pilot-plant Kühni extractor based on single-drop experiments, Chem. Eng. Sci. 82 (2012) 167–176.

Please cite this article as: M. Larriba, et al., Dearomatization of pyrolysis gasolines from mild and severe cracking by liquid–liquid extraction using a binary mixture of [4empy]..., Fuel Processing Technology (2015), http://dx.doi.org/10.1016/j.fuproc.2015.03.009