# Cyclic carbonates as solvents in the dearomatization of refinery streams: experimental liquid-liquid equilibria, modelling, and simulation.

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## Abstract

Obtaining aromatic hydrocarbons from refinery streams is one of the most concerning issues that the petrochemical industry currently faces. Now, the presence of azeotropes between aromatic and non-aromatic compounds in gasoline fractions demands the employment of volatile organic solvents such as sulfolane to obtain benzene, toluene, and xylenes by liquid-liquid extraction. Several alternatives have been evaluated during the last decades to overcome the drawbacks related to the use of these solvents, being their replacement with ionic liquids one of the most promising so far. Nonetheless, the ionic liquids' complex synthesis routes and lack of availability at large production still limit their industrial implementation. Recently, cyclic carbonates have emerged as a double solution related to $CO_2$ fixation and designer solvents availability, the latter showing interesting extractive and physical properties which could reduce the environmental impact associated with the use of conventional solvents and ionic liquids in aromatic extraction processes. However, the availability of experimental data is scarce and only predictive models are available. In this work, firstly, the extractive properties of five cyclic carbonates (propylene, vinylethylene, glycerol, ethylene, and vinylene carbonates) were experimentally determined for wide composition ranges of several ternary systems {aliphatic/methylcycloalkane + aromatic + cyclic carbonate}. Afterwards, the NRTL, UNIFAC, and COSMO-SAC models, were used to fit or predict the liquid-liquid equilibria of those ternary systems. Finally, the aromatic extraction process from reformer gasoline with propylene carbonate as solvent was simulated in Aspen Plus with the COSMO-SAC model, comparing its performance with that of sulfolane to check its suitability at process scale.

**Keywords:** aromatic separation, liquid-liquid equilibrium, cyclic carbonates, NRTL, COSMO-SAC.

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# 1. INTRODUCTION

Nowadays, the separation of aromatic hydrocarbons from refinery streams such as naphtha and gasoline is mainly conducted by liquid-liquid extraction and extractive distillation employing volatile organic solvents i.e., sulfolane and *N*-formylmorpholine [1]. However, these processes reflect some intrinsic limitations regarding the use of these solvents. Apart from their toxicity, flammability, and partial volatility, the high energy requirements involved in the solvent recovery step and the necessity of further separations to achieve purity standards make it mandatory to put effort into the research of techno-economically efficient and environmentally friendly alternative processes. During the last decades, one of the most promising approaches released in the literature to overcome these drawbacks has been the replacement of organic solvents with ionic liquids [2–5]. Nevertheless, the limited availability and high price of ionic liquids together with the lack of suitable solutions for their liquid disposal are still concerning issues regarding the industrial implementation of these compounds.

In this context, cyclic carbonates have recently attracted the interest of the scientific community to face these challenges since they are one of the highlighted research lines related to $CO_2$ conversion processes [6]. Cyclic carbonates are characterized by low toxicity and ecotoxicity, high biodegradability, low viscosity [7], high solubility, low vapor pressure [7–9], and adequate extractive properties [10–12]. In addition, their large production at low cost makes cyclic carbonates suitable for being used as solvents in electrochemical, liquid-liquid extraction, synthesis, and catalysis operations to establish more sustainable processes reducing the environmental footprint.

For that reason, in this work, five different cyclic carbonates, namely propylene, vinylethylene, glycerol, ethylene, and vinylene carbonates, were selected to be evaluated as mass agents for the separation of {aliphatic + aromatic} and {methylcycloalkane + benzene} mixtures through the determination of the liquid-liquid equilibria for the ternary systems {aliphatic/methylcycloalkane + aromatic + cyclic carbonate}. The {aliphatic + aromatic} and {methylcycloalkane + benzene} mixtures are representative of reformer and pyrolysis gasolines which have been previously established in the literature as matrices to obtain aromatic hydrocarbons by liquid-liquid extraction and extractive distillation with ionic liquids [13–15]. In this way, the performance of the five selected cyclic carbonates can be fairly compared to those obtained with ionic liquids and conventional solvents.

Extractive properties of propylene carbonate have already been determined for some systems containing hydrocarbons, showing high distribution ratios and moderate selectivities through the aromatic compounds [16–21]. Moreover, COSMO-RS and COSMO-SAC calculations predicted similar separation performances between propylene carbonate and sulfolane for the separation of binary mixtures consisting of aromatics and aliphatics [22]. Ethylene carbonate has shown higher selectivity through the aromatics but a lower distribution ratio than propylene carbonate [23–26]. However, apart from these works, there is a lack of literature about using other cyclic carbonates as mass agents for separating of aromatic hydrocarbons.

Glycerol carbonate has been highlighted as a versatile compound due to its reactivity and the possibility of the valorization of waste glycerol [27,28]. {Glycerol carbonate + glycerol} mixtures have been tested as green solvents for sugarcane bagasse at lignocellulosic biomass treatment [29]. The use of glycerol as solvent in different processes is very widespread. It has been selected as one of the most relevant solvents because it is a renewable resource, reporting also high performance in the liquid-liquid extraction of aromatics [30]. In addition, the COSMO-RS predictions point out low distribution ratio and high selectivity values for glycerol carbonate compared with sulfolane [22].

Vinylene and vinylethylene carbonates have been studied as additives for electrolytes in lithium cells [31–36]. Recently, both carbonates come under the spotlight as they have been proposed as solvents for the separation of aromatics from naphtha streams [37]. COSMO-based predictions showed, on the one hand, low values of selectivity and distribution ratio for the vinylene carbonate and, on the other hand, an enhancement of the distribution ratio and the selectivity of vinylethylene carbonate compared to glycerol and ethylene carbonate, respectively. Since there is no further literature on the use of these carbonates for the extraction of aromatics, experimental liquid-liquid equilibrium data are needed.

Additionally, recent works using a multiscale computational program based on COSMO/Aspen methodology confirm the technical feasibility of several other cyclic carbonates in aliphatic/aromatic separations meeting the energy, equipment, and recovery requirements at process scale [22, 26, 37, 38]. Apart from COSMO predictions and scarce experimental data, there are no regression or predicting models that demonstrate competitiveness for these kinds of compounds.

Bearing in mind the above, the liquid-liquid equilibria for ternary systems {aliphatic/methylcycloalkane + aromatic + cyclic carbonate} were experimentally determined here. Firstly, the extractive properties of propylene carbonate were determined at 303.2, 313.2, and 323.2 K for several ternary systems {aliphatic/methylcycloalkane + aromatic + propylene carbonate} to check the influence of temperature on the separation. Next, the study of the liquid-liquid equilibria was extended to the ternary systems containing the rest of the cyclic carbonates at 313.2 K. Then, the experimental liquid-liquid equilibria were compared with those obtained with three models based on different approaches: a classical thermodynamic fitting with the NRTL model, predictions with the group contribution model UNIFAC, and predictions with the COSMO-SAC model. After that, the NRTL and COSMO-SAC models were selected to simulate the extractor in Aspen Plus evaluating the performance of propylene, ethylene, and vinylene carbonates in the extraction of benzene, toluene, and *p*-xylene (BTX) from reformer gasoline. Finally, the whole process of liquid-liquid extraction of aromatics with propylene carbonate was simulated, comparing their performance and energy consumption with those of the conventional process using sulfolane as solvent.

## 2. EXPERIMENTAL SECTION

### *2.1. Chemicals*

The hydrocarbons and cyclic carbonates used in this work are shown in Tables 1 and 2, respectively, together with their most relevant properties. All were purchased from Sigma Aldrich, used without carrying out further purification and stored in a desiccator to avoid changes in their water content.

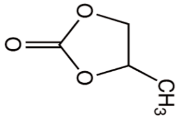
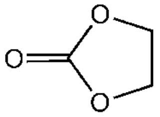
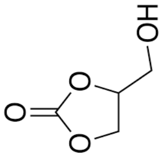
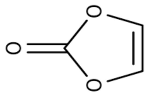
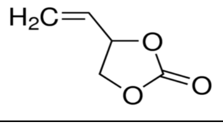
### *2.2. Determination of liquid-liquid equilibrium data*

Binary mixtures {*n*-hexane + benzene}, {*n*-heptane + toluene}, {*n*-octane + *p*-xylene}, {methylcyclopentane + benzene}, and {methylcyclohexane + benzene} were gravimetrically prepared with a Mettler Toledo XS 205 balance ($1\cdot10^{-5}$ g precision) according to the following aromatic/aliphatic ratios in mass basis: 5/95; 10/90; 20/80; 30/70; 40/60; 50/50; 60/40; 70/30. 1 mL of hydrocarbon binary mixture and 1 mL of cyclic carbonate were gravimetrically added to 8 mL vials and closed with screw caps. These vials were stirred at 800 rpm in a Labnet Vortemp 1550 incubator for 5 h at 303.2, 313.2, and 323.2 K until the liquid-liquid equilibrium was reached. Then, the vials were placed in a Labnet Accublock dry bath for 12 h at the same temperature for a complete separation between raffinate and extract phases. Once the phase separation was achieved, triplicate samples of the raffinate and extract phases were taken and analysed by gas chromatography and multiple headspace extraction (MHE), respectively, using an Agilent 7890A gas chromatograph coupled to an Agilent Headspace Injector 7697A. The detailed description of the analytical method can be found elsewhere [39].

**Table 1.** Hydrocarbons.

| Chemical | Purity / wt. % | Analysis method | Water content |
|---|---|---|---|
| *n*-Hexane | 99.0 | Gas chromatography | Anhydrous |
| *n*-Heptane | 99.7 | Gas chromatography | Anhydrous |
| *n*-Octane | 99.0 | Gas chromatography | Anhydrous |
| Methylcyclopentane | 99.0 | Gas chromatography | Anhydrous |
| Methylcyclohexane | 99.0 | Gas chromatography | Anhydrous |
| Benzene | 99.8 | Gas chromatography | Anhydrous |
| Toluene | 99.5 | Gas chromatography | Anhydrous |
| *p*-Xylene | 99.0 | Gas chromatography | Anhydrous |

**Table 2.** Cyclic carbonates.

| Chemical | Structure | Purity / wt.% | Analysis method | Water content / ppm |
|---|---|---|---|---|
| Propylene carbonate |  | 99.7 | Gas chromatography | Anhydrous |
| Ethylene carbonate |  | 99.0 | Gas chromatography | 10 |
| Glycerol carbonate |  | >90.0 | Gas chromatography | - |
| Vinylene carbonate |  | 99.0 | Gas chromatography | 100 |
| Vinylethylene carbonate |  | >90.0 | Gas chromatography | - |

*2.3. Modelling of the liquid-liquid equilibria*

Aspen Plus Properties V12.1 was used to adjust the experimental liquid-liquid equilibrium data to the NRTL model. In addition, the UNIFAC and COSMO-SAC predictive models were used to determine the liquid-liquid equilibrium of the ternary systems {aliphatic/methylcycloalkane + aromatic + cyclic carbonate}. Aspen Plus

Properties allowed to determine $\Delta g_{ij}/R$ and $\Delta g_{ji}/R$ binary interaction parameters of the NRTL model, provided the binary group interaction parameters for the UNIFAC model, and calculated the liquid-liquid equilibrium data with COSMO-SAC model from the COSMO volume and sigma profile of each compound. The non-randomness parameter ($\alpha_{ij}$) of NRTL model was set to 0.3 because of being the most common used in literature for similar systems [19]. The root mean square deviation (*rmsd*) was calculated according to the next expression:

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

where *i, l,* and *m* refer to the components, phases and tie lines, respectively; *x* is the mole fraction of each component and *k* is the tie line number.

### *2.4. Aspen Plus simulation methodology*

The liquid-liquid extraction column of BTX from reformer gasoline was simulated in Aspen Plus V12.1 with propylene, ethylene, and vinylene carbonates as solvents to compare their separation performance at process scale. These simulations were carried out with the NRTL and COSMO-SAC models to check the suitability of the COSMO-based predictions. Afterwards, the COSMO-SAC model was used to simulate the whole liquid-liquid extraction process with propylene carbonate, comparing the solvent and energy consumptions with those obtained in the conventional process using sulfolane as solvent. The flowsheet of the process can be found in Figure 1. After the liquid-liquid extraction column, aliphatics in the extract stream are removed in a stripping column and recirculated to the extractor. Finally, the purified extract stream is fed to a distillation column where the aromatics are recovered from the solvent, which is recirculated to the extraction column. Either hydrocarbons, cyclic carbonates or sulfolane can be found in Aspen Plus databases except for the glycerol carbonate which was added as a pseudocomponent. The liquid-liquid extraction column was simulated by an EXTRACT block working at 313.2 K and atmospheric pressure, while the RADFRAC model was used for the stripping and distillation columns, being the adjusted parameters the reboiler duty and distillate rate. Both recovery and purity of aromatics in the process were set to 99.9%, feeding 1000 t/h of reformer gasoline to the extraction column.

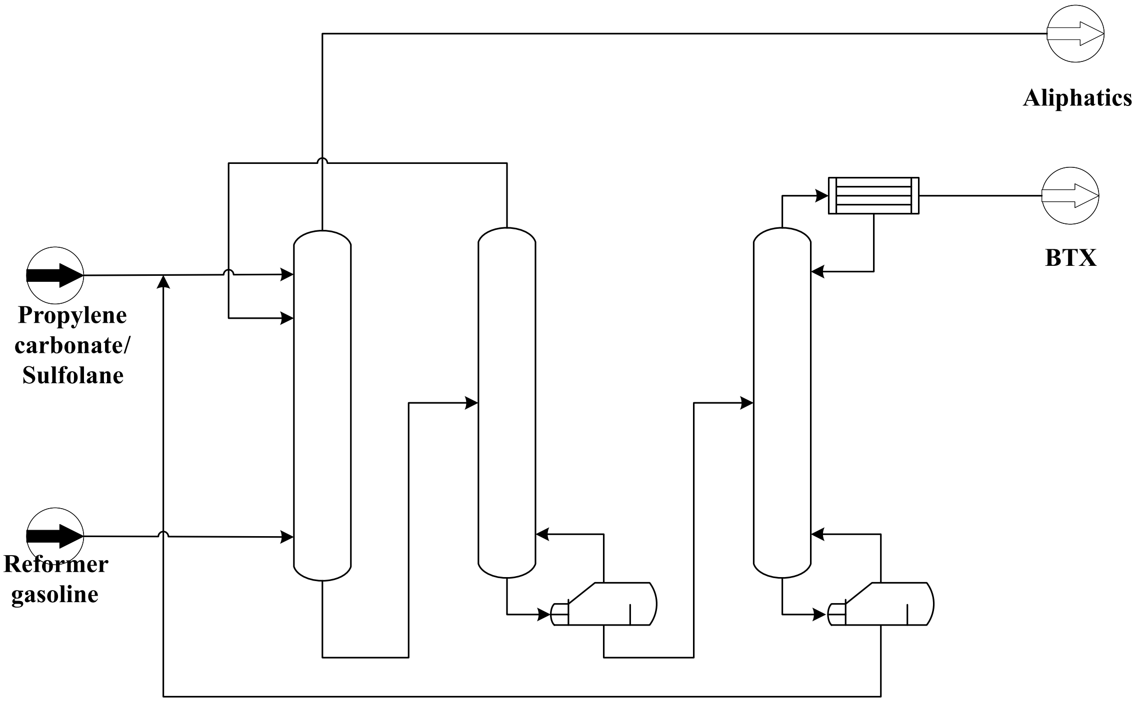


**Figure 1.** Flowsheet diagram of the liquid-liquid extraction process of BTX from reformer gasoline with propylene carbonate or sulfolane as solvents. EC = extraction column, SC = stripping column, DC = distillation column.

## 3. RESULTS AND DISCUSSION

### 3.1. Liquid-liquid equilibria for the ternary systems {aliphatic/methylcycloalkane + aromatic + cyclic carbonate}

The liquid-liquid equilibria for ternary systems {aliphatic/methylcycloalkane (1) + aromatic (2) + propylene carbonate (3)} were determined at 303.2, 313.2, and 323.2 K and atmospheric pressure. The aromatic mass distribution ratio ($D_2$) and selectivity through the aromatic compound ($S_{2,1}$) were determined from the experimental compositions of both liquid phases in equilibrium from the following equations:

$$D_2\left(\frac{g}{g}\right) = \frac{w_2^{II}}{w_2^{I}} \tag{2}$$

$$S_{2,1}\left(\frac{g}{g}\right) = \frac{w_2^{II}/w_2^{I}}{w_1^{II}/w_1^{I}} \tag{3}$$

where *w* is the mass fractions of hydrocarbons, superscripts I and II refer to raffinate and extract phases, and subscripts 1 and 2 to aliphatics and aromatics, respectively.

The aromatic distribution ratio and selectivity values of propylene carbonate for each ternary system {aliphatic/methylcycloalkane (1) + aromatic (2) + propylene carbonate

(3)} have been represented in Figure 2 as a function of the temperature and aromatic mole fraction in the raffinate phase. As can be seen, the aromatic distribution ratio and selectivity follow opposite trends when the aromatic mole fraction increases. A slight increment in the aromatic distribution ratio is noted while the selectivity sharply decreases. Quantitatively, the highest distribution ratio is obtained for benzene while the lowest is for *p*-xylene. That is, side alkane chains in the aromatic compound worsen their solubility in the solvent. These trends are completely in agreement with those previously published [17,20], as can be checked in Figure 2. In addition, the $S_{aromatic/aliphatic}$ is higher than the $S_{aromatic/methylcycloalkane}$ due to the higher similarity between methylcycloalkanes and aromatics in comparison with linear aliphatics and aromatics. On the other hand, aromatic distribution ratios are hardly altered between 303.2 and 323.2 K, while aromatic selectivities are negatively affected by this temperature increment, as reported previously for these kinds of systems [40–42]. Thus, attending to these results, 313.2 K was selected to extend the analysis of liquid-liquid equilibrium to ternary systems composed of the same hydrocarbons and the other four cyclic carbonates studied here.

In Figures 3 and 4, the aromatic distribution ratio and selectivity of the five cyclic carbonates studied in this work for ternary systems {aliphatic/methylcycloalkane + benzene + cyclic carbonate} at 313.2 K and atmospheric pressure have been collected to compare their performance in the separation of aromatics from aliphatics and methylcycloalkanes. In addition, extractive properties of sulfolane found in the literature for the ternary systems {aliphatic + aromatic + sulfolane} are represented as a benchmark [43–45]. In both Figures 3 and 4, it can be observed that propylene carbonate and vinylene carbonate showed the highest aromatic distribution ratios either for aliphatic/aromatic or methylcycloalkane/benzene separations. What is more, higher values of toluene and *p*-xylene distribution ratios were reported with these two carbonates in comparison with those of sulfolane. In terms of aromatic selectivity, the highest values were provided by ethylene and glycerol carbonates for aliphatic/aromatic and methylcycloalkane/benzene separations, respectively. Comparing these selectivities with those provided by sulfolane, only ethylene carbonate overcame the performance of the conventional solvent, especially for the {benzene + *n*-hexane} mixture. On the contrary, vinylethylene carbonate provided the lowest aromatic selectivity.

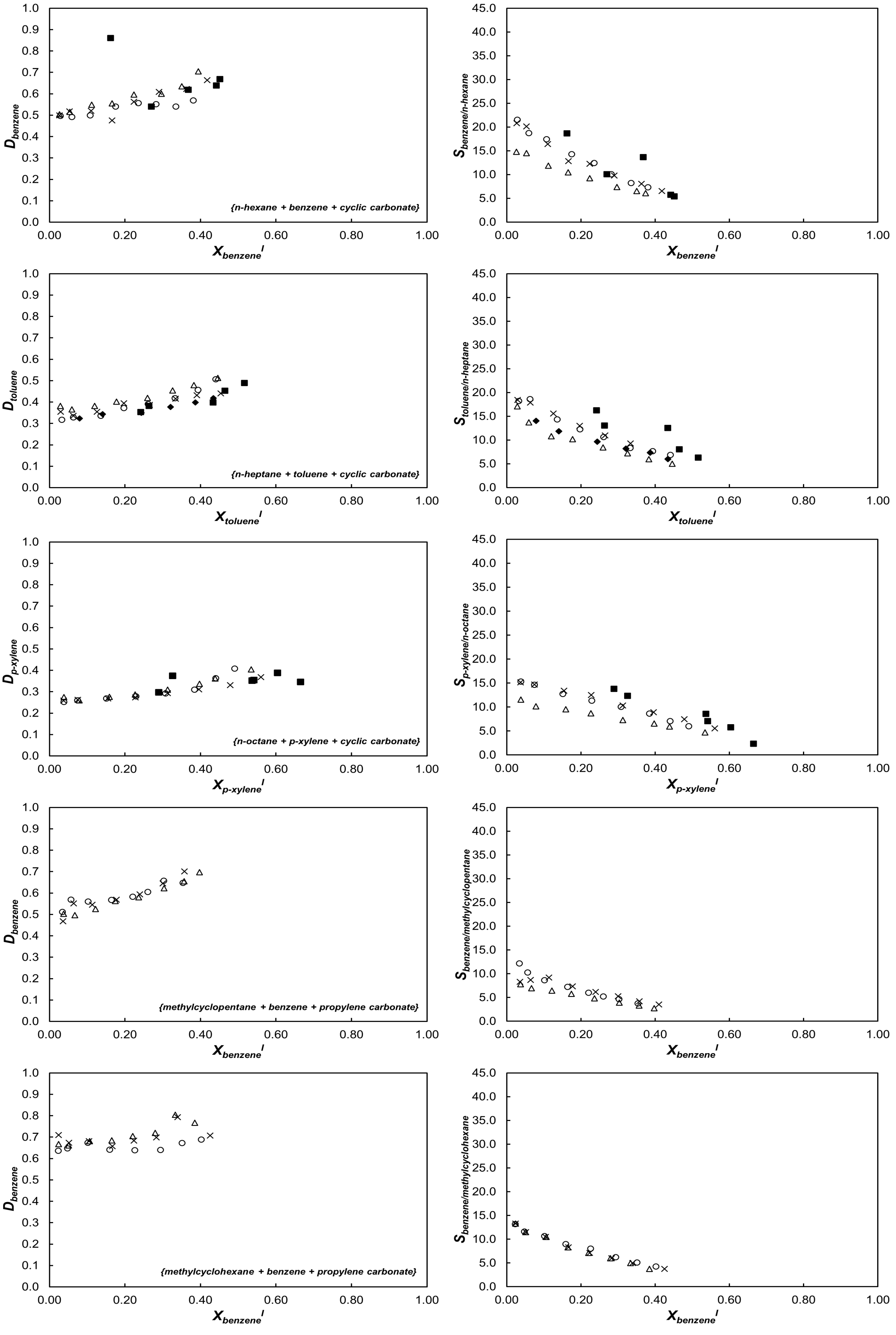


**Figure 2.** Mass-based aromatic distribution ratios and aromatic selectivities for ternary systems {aliphatic/methylcycloalkane (1) + aromatic (2) + propylene carbonate (3)} at $T$ = 303.2 (X), 313.2 (○), and 323.2 (Δ) K and $P$ = 0.1 MPa against aromatic mole fraction in the raffinate. ■ and ♦ symbols refer to data published in ref [17] and [20], respectively.

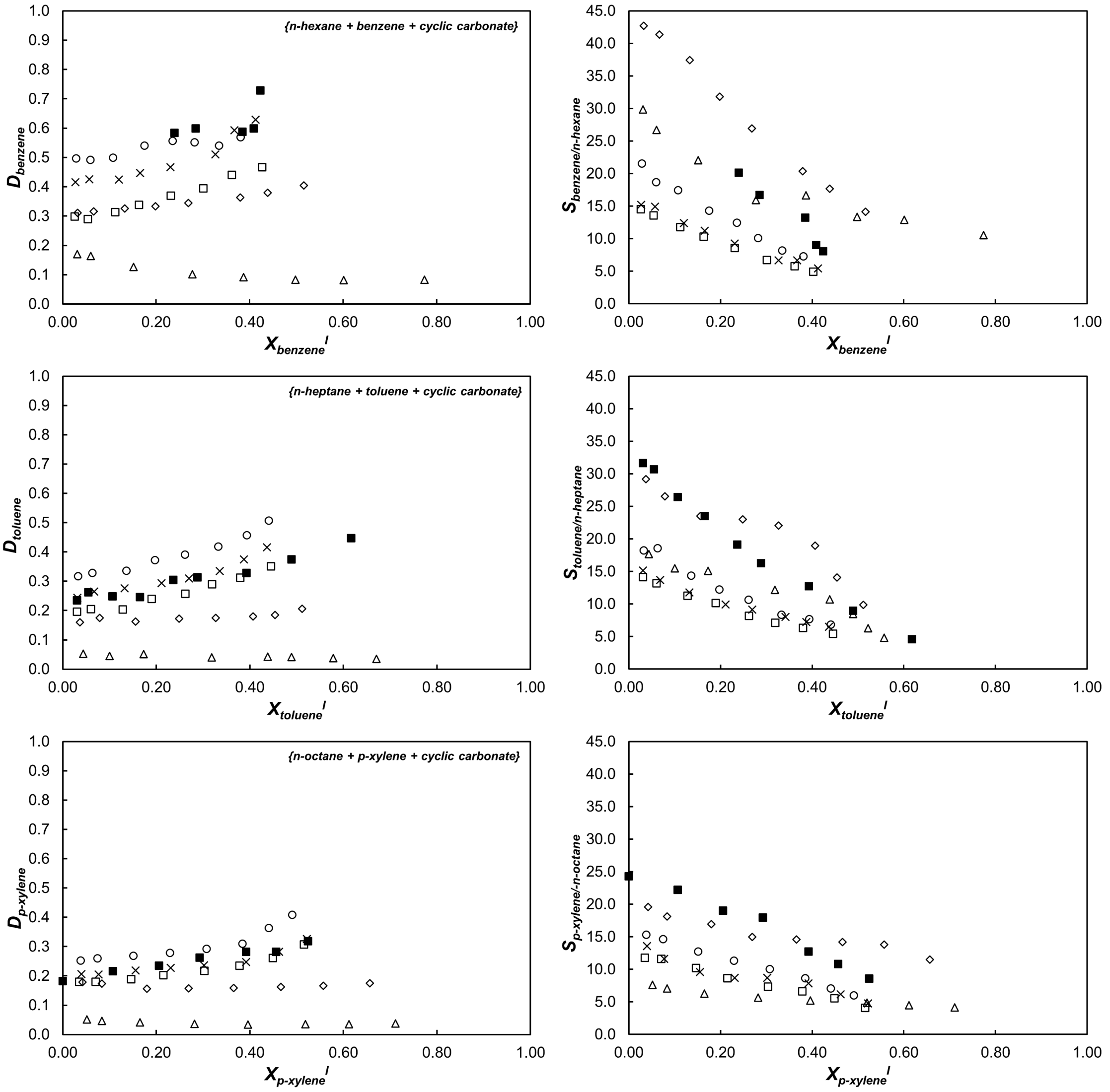


**Figure 3.** Mass-based aromatic distribution ratios and aromatic selectivities for the ternary systems {aliphatic (1) + aromatic (2) + organic carbonate (3)} at $T = 313.2$ K and $P = 0.1$ MPa against aromatic mole fraction in the raffinate phase: ○, propylene carbonate; □, vinylethylene carbonate; Δ, glycerol carbonate; ◊, ethylene carbonate; X, vinylene carbonate. ■ refers to extractive properties of sulfolane found in literature for these ternary systems [43–45].

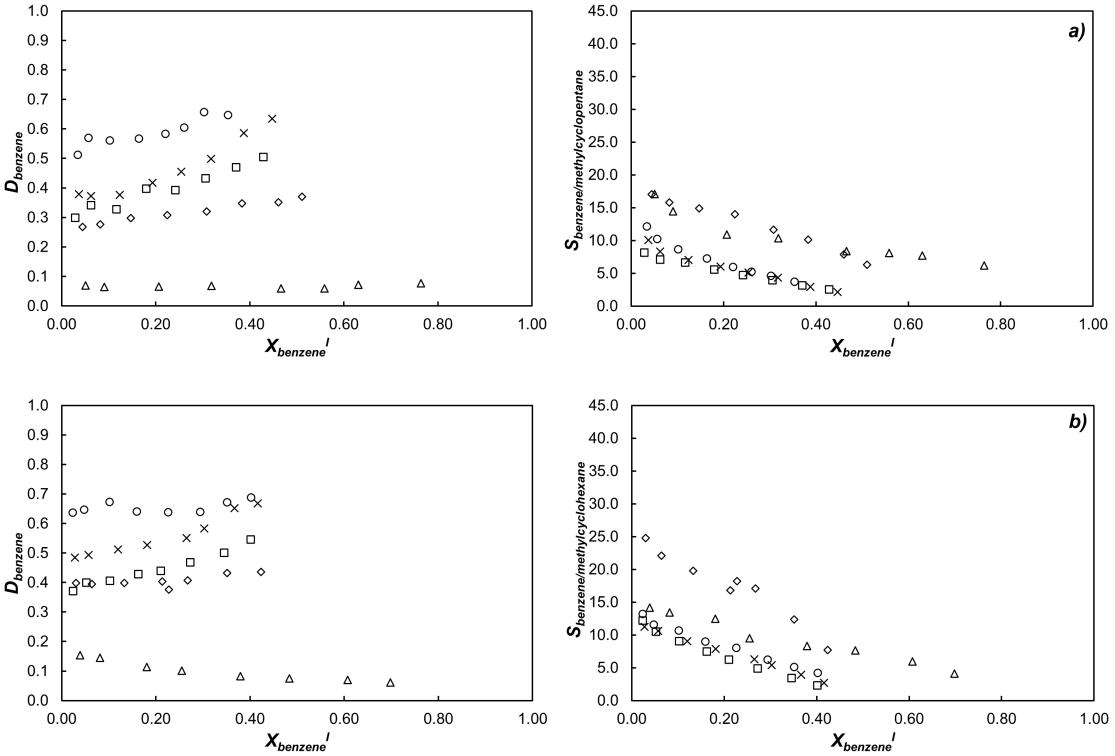


**Figure 4.** Mass-based aromatic distribution ratios and aromatic selectivities for the ternary systems {methylcyclopentane (1) + benzene (2) + organic carbonate (3)} (a) and {methylcyclohexane (1) + benzene (2) + organic carbonate (3)} (b) at $T = 313.2$ K and $P = 0.1$ MPa against aromatic mole fraction in the raffinate phase: ○, propylene carbonate; □, vinylethylene carbonate; Δ, glycerol carbonate; ◊, ethylene carbonate; X, vinylene carbonate.

According to recent works regarding COSMO-SAC calculations, there is a clear relationship between carbonate polarity and its extractive properties. That is, the higher carbonate polarity the higher aromatic selectivity and the lower aromatic distribution ratio [22]. Here, the polar character of the five solvents could be defined from their dielectric constants which follow the next trend: propylene carbonate < ethylene carbonate < vinylethylene carbonate < glycerol carbonate < vinylene carbonate [46–48]. From the experimentally obtained results, the highest benzene selectivity for ternary systems {methylcycloalkane + benzene + organic carbonate} is represented by glycerol carbonate. Although it presents the second highest dielectric constant, glycerol carbonate presents a hydroxyl group in its structure which provides it a second dipole moment and the possibility of hydrogen bonding [49,50]. However, glycerol carbonate is, by far, the cyclic carbonate that presents the lowest values of aromatic distribution ratio for all the ternary systems evaluated.

On the other hand, propylene carbonate shows the lowest polar character among the five carbonates analyzed [51], providing the highest aromatic distribution ratios. Up to here, the experimental results presented in this work agree with those previously reported with COSMO-SAC [22, 26, 37]. Nevertheless, ethylene carbonate shows low aromatic distribution ratios but the highest aromatic selectivity for ternary systems {aliphatic + aromatic + organic carbonate}, being clearly less polar than glycerol and vinylene carbonates which could be explained by the lack of ramifications and double bonds in the ethylene carbonate's structure. The performances of ethylene carbonate and sulfolane in the aliphatic/aromatic separation are quite similar in terms of aromatic selectivity, showing ethylene carbonate slightly lower aromatic distribution ratios which is due to the lower polarity of sulfolane [47]. In addition, the high aromatic distribution ratio shown by vinylene carbonate can be explained for this same reason, especially for its double bond which increases its affinity for the aromatics. In brief, although the premise that the polarity of the cyclic carbonates plays a dominant role in the separation of aromatic hydrocarbons from aliphatics and methylcycloalkanes could be a good starting point to predict their performance as solvents, an eye must be kept on the carbonate structure to avoid steric hindrance mainly due to ramifications. Moreover, it is mandatory to obtain experimental data to confirm the data predicted by COSMO-SAC or other models.

In light of the above, propylene, vinylene, and ethylene carbonates were selected since they represent extreme behaviors in the separation of aromatic hydrocarbons from aliphatics and methylcycloalkanes. Propylene carbonate provided the highest aromatic distribution ratio while ethylene carbonate was the best in terms of selectivity. Vinylene carbonate, on the other hand, showed equilibrate extractive properties.

### 3.2. Modeling of the liquid-liquid equilibrium data with UNIFAC, COSMO-SAC and NRTL models.

In Figures 5-9, ternary liquid-liquid equilibrium diagrams for ternary systems {aliphatic/methylcycloalkane + aromatic + cyclic carbonate} have been collected, together with the data obtained with three thermodynamic approaches: NRTL, UNIFAC, and COSMO-SAC models. The experimental data have been collected in Tables S1-S7 in the Supporting Information As can be seen in Figures 5-9, UNIFAC is not able to reproduce the liquid-liquid equilibria of these ternary systems. Problems related to UNIFAC describing systems formed by hydrocarbons and propylene carbonate have been previously reported with deviations between experimental and predicted values for mole fractions higher than 40%, especially for propylene carbonate mole fractions in the raffinate phase [52]. In addition, the UNIFAC model is unable to predict two liquid phases in equilibrium for some systems, contrary to experimental observations. Therefore, UNIFAC model is discarded as an available option to obtain accurate data of systems composed of hydrocarbons and cyclic carbonates. This can be correlated to the lack of experimental information regarding cyclic carbonate's phase equilibria and, thus, the absence of validated binary interaction parameters for UNIFAC groups.

On the other hand, as mentioned before, the COSMO-SAC model has been recently used to simulate the aromatic separation from naphtha and fuel streams by liquid-liquid extraction or extractive distillation with organic carbonates. It is widely known that COSMO-SAC quantitative predictions of liquid-liquid equilibria of systems containing hydrocarbons with ionic liquids or deep eutectic solvents are not very accurate, being more useful for establishing tendencies in extractive properties and narrowing the number of suitable solvents for a concrete separation [53–56]. However, in Figures 5-9, one can see that COSMO-SAC predictions of the liquid-liquid equilibria of ternary systems {aliphatic/methylcycloalkane + aromatic + cyclic carbonate} are precise, being the mean root deviation between experimental and predicted values of mole fractions lower than 0.09.

Therefore, the COSMO-SAC model is confirmed as a great tool for accurately predicting the behavior of systems composed of hydrocarbons and cyclic carbonates, obtaining much better results than those previously published for systems formed by hydrocarbons and other neoteric solvents, i.e. ionic liquids or deep eutectic solvents [57–59]. This fact supposes a great advance in computational calculations based on the COSMO-SAC model to determine extractive properties of cyclic carbonates without the necessity of experimental support. However, a regression model like NRTL is still more accurate as can be seen in Figures 5 – 9. The *rmsd* for the NRTL model never overcome a value of 0.05 in the composition of both phases in equilibrium, agreeing well with some works that have been previously published in the literature [16,17]. The NRTL parameters and *rmsd* values have been collected in Tables S8 and S9 in the Supporting Information for checking purposes. In a nutshell, the COSMO-SAC model provides reliable liquid-liquid equilibrium data for ternary systems {aliphatic/methylcycloalkane + aromatic + cyclic carbonate} showing slightly higher deviations than NRTL regression model but avoiding time-consuming experiments and modeling of the data. However, the alkyl chain length variation in the hydrocarbon is not well-captured by COSMO-SAC when non-aromatic solubility is not negligible, imposing that COSMO-SAC suitability is somewhat deteriorated by less selective liquid-liquid systems.

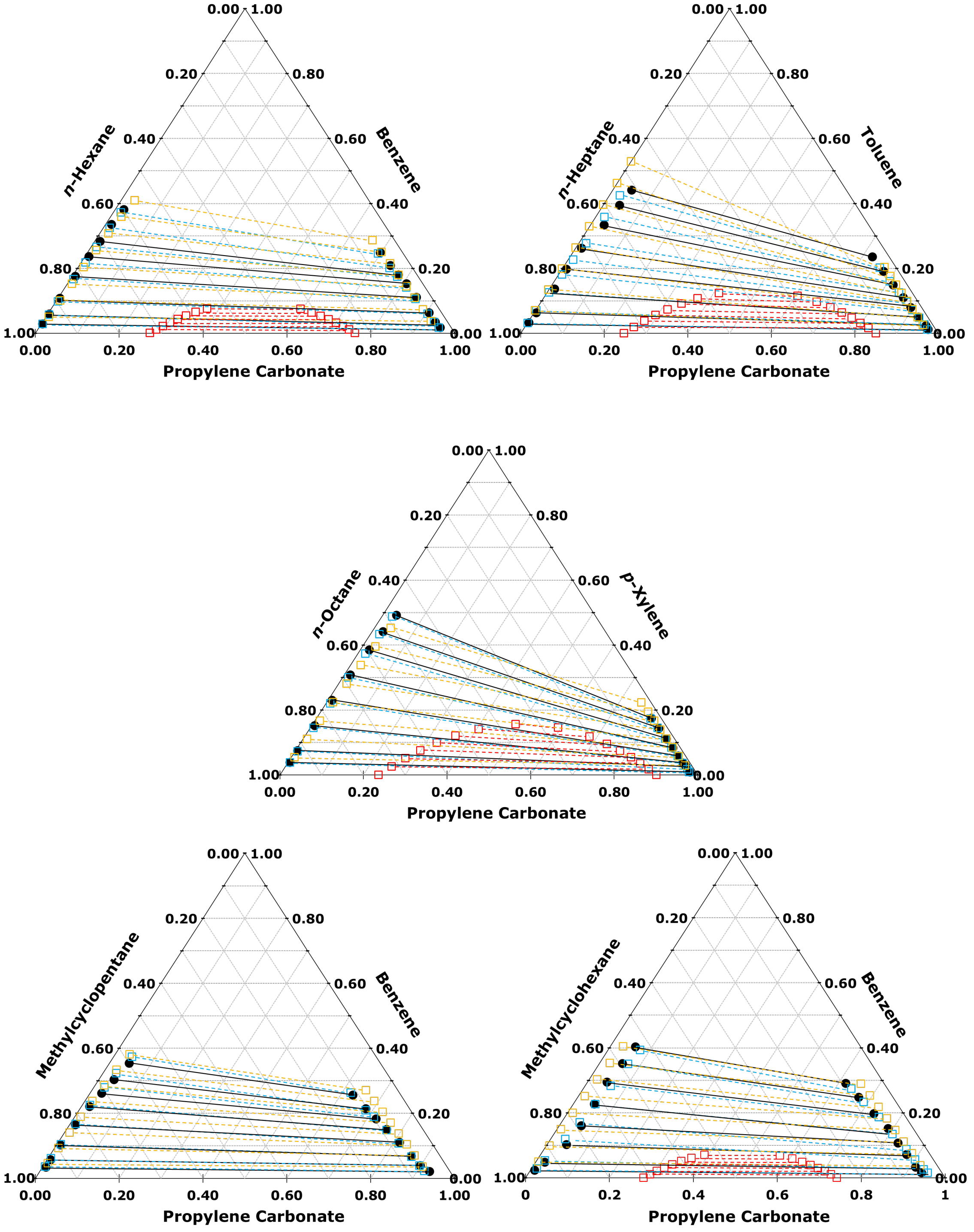


**Figure 5.** Liquid-liquid equilibria for the ternary systems {aliphatic/methylcycloalkane (1) + aromatic (2) + propylene carbonate (3)} at $T = 313.2$ K and $P = 0.1$ MPa. Solid lines and full black points represent experimental tie-lines and points, whereas dashed lines and empty squares are the regressed data using the NRTL (blue), COSMO-SAC (yellow) and UNIFAC (red) models.

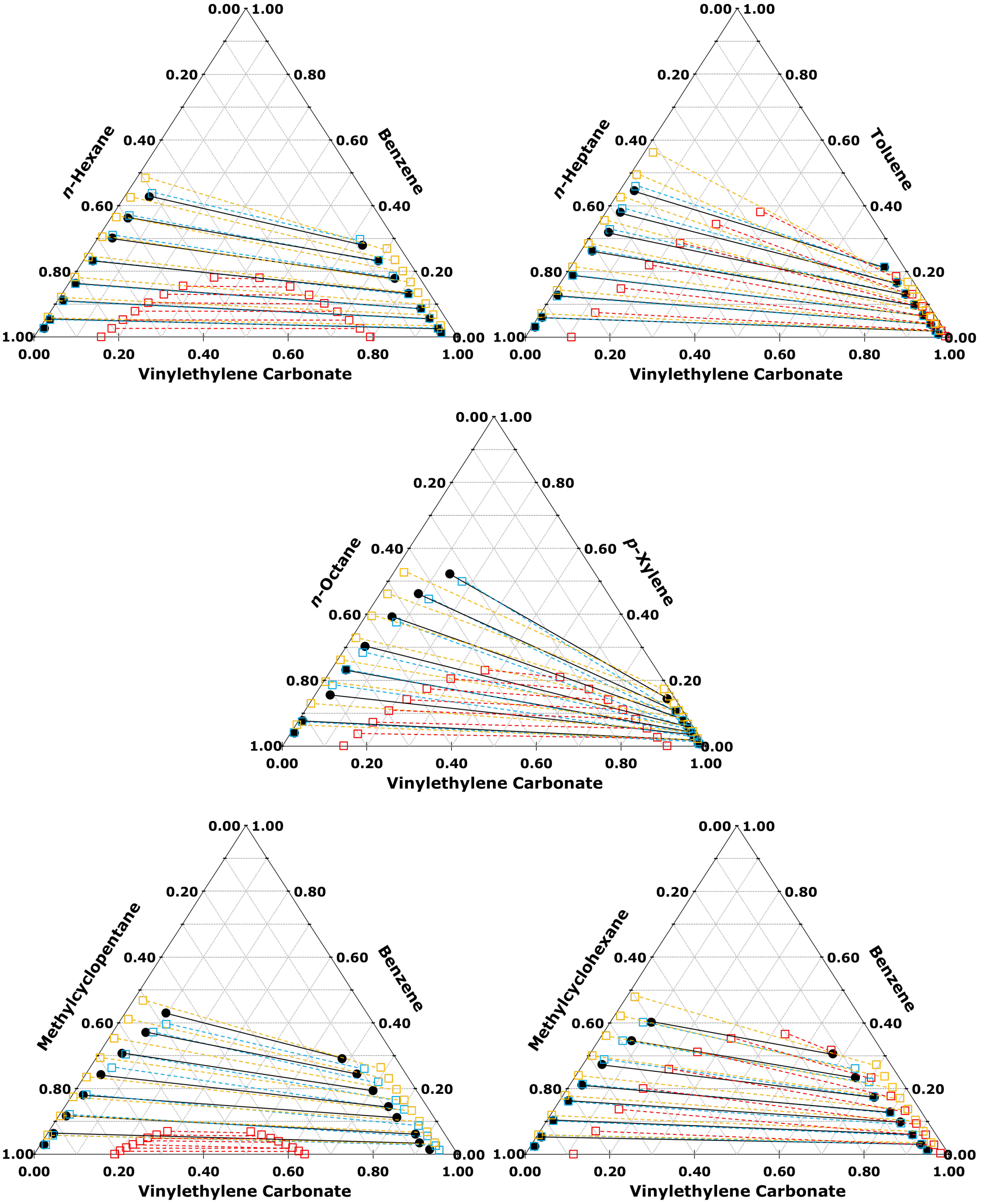


**Figure 6.** Liquid-liquid equilibria for the ternary systems {aliphatic/methylcycloalkane (1) + aromatic (2) + vinylethylene carbonate (3)} at $T = 313.2$ K and $P = 0.1$ MPa. Solid lines and full black points represent experimental tie-lines and points, whereas dashed lines and empty squares are the regressed data using the NRTL (blue), COSMO-SAC (yellow) and UNIFAC (red) models.

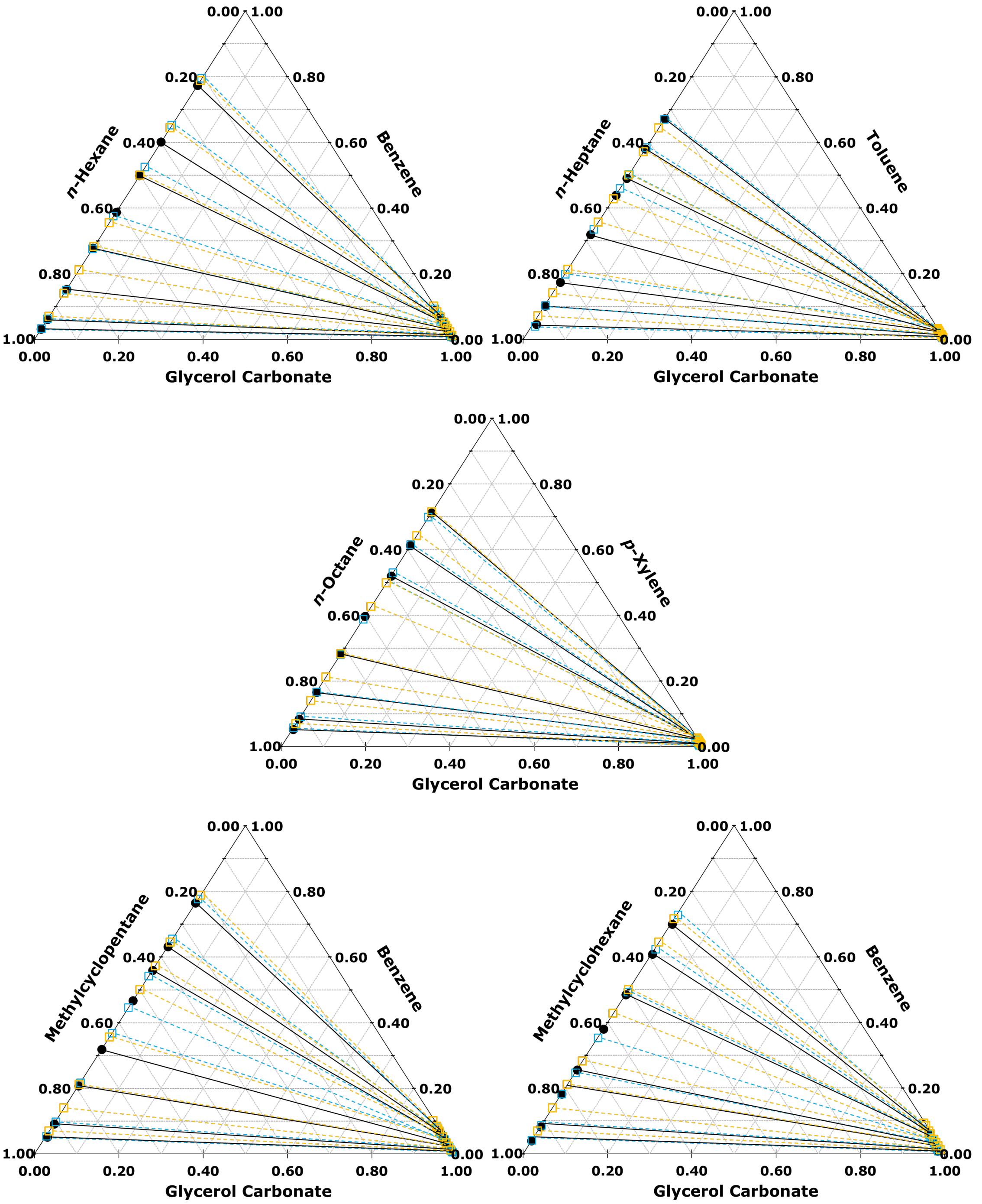


**Figure 7.** Liquid-liquid equilibria for the ternary systems {aliphatic/methylcycloalkane (1) + aromatic (2) + glycerol carbonate (3)} at $T = 313.2$ K and $P = 0.1$ MPa. Solid lines and full black points represent experimental tie-lines and points, whereas dashed lines and empty squares are the regressed data using the NRTL (blue) and COSMO-SAC (yellow).

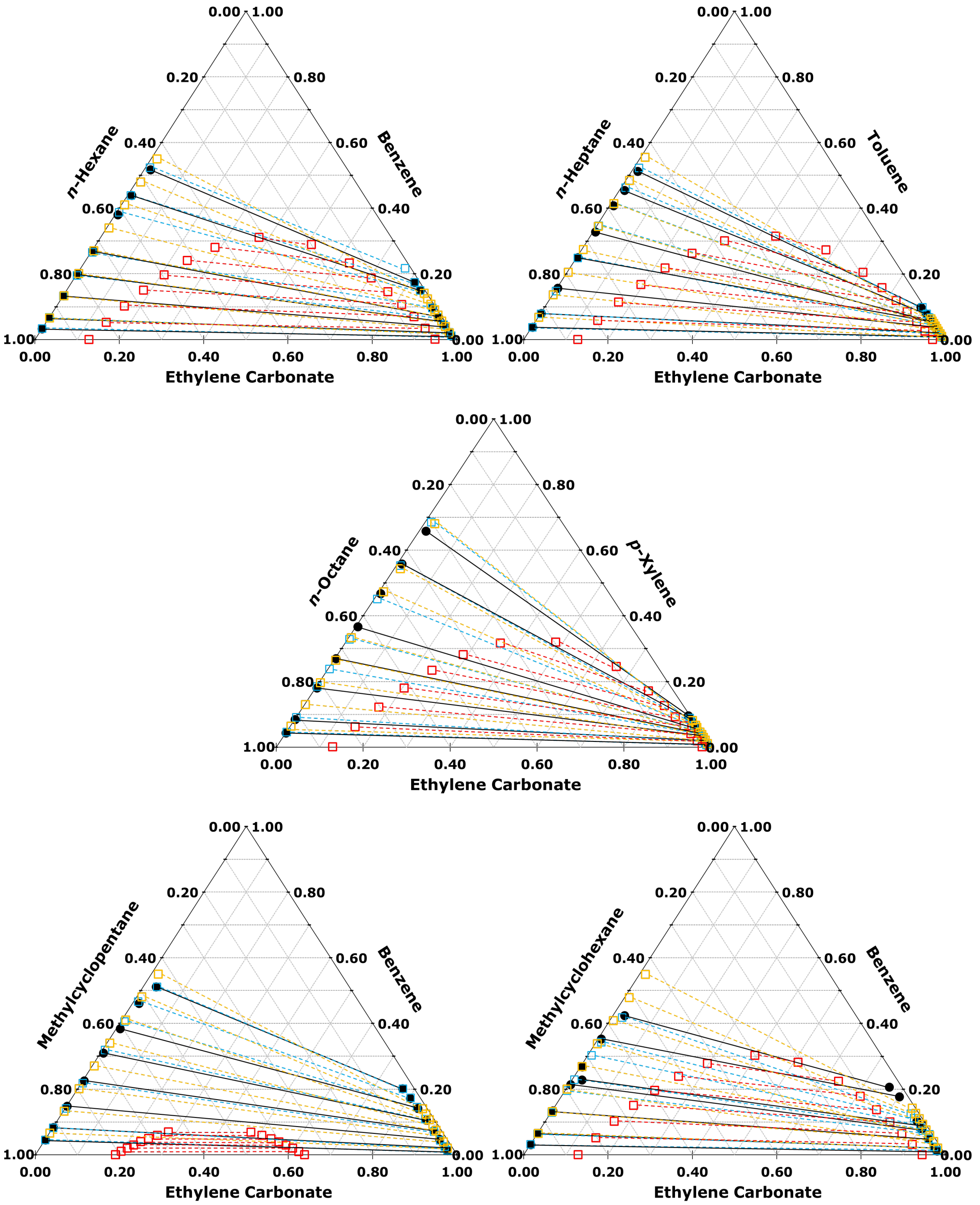


**Figure 8.** Liquid-liquid equilibria for the ternary systems {aliphatic/methylcycloalkane (1) + aromatic (2) + ethylene carbonate (3)} at $T = 313.2$ K and $P = 0.1$ MPa. Solid lines and full black points represent experimental tie-lines and points, whereas dashed lines and empty squares are the regressed data using the NRTL (blue), COSMO-SAC (yellow) and UNIFAC (red) models.

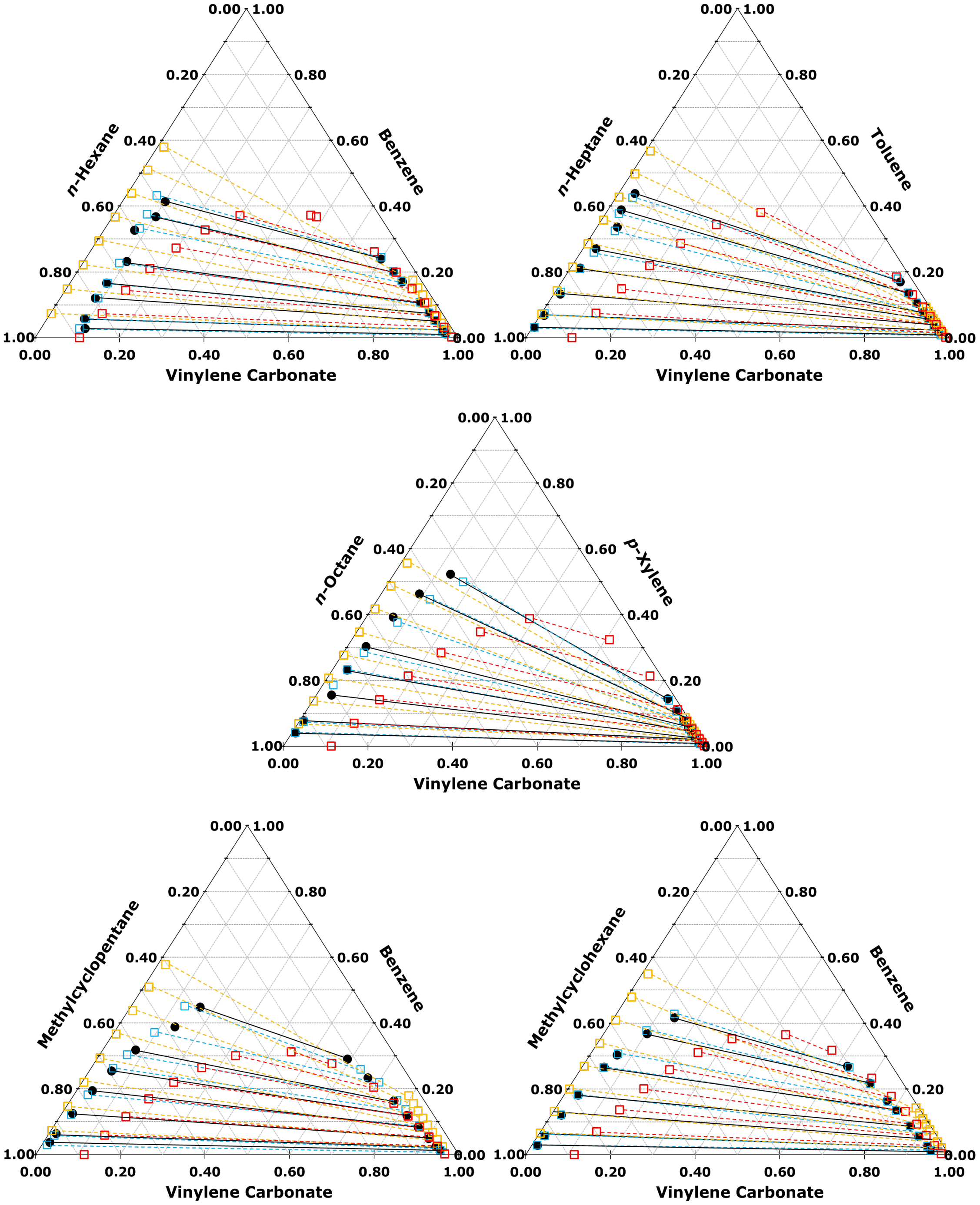


**Figure 9.** Liquid-liquid equilibria for the ternary systems {aliphatic/methylcycloalkane (1) + aromatic (2) + vinylene carbonate (3)} at $T = 313.2$ K and $P = 0.1$ MPa. Solid lines and full black points represent experimental tie-lines and points, whereas dashed lines and empty squares are the regressed data using the NRTL (blue), COSMO-SAC (yellow) and UNIFAC (red) models.

### 3.3. Simulation of the liquid-liquid extraction process to separate BTX from reformer gasoline with a cyclic carbonate as solvent.

Firstly, the liquid-liquid extraction column to separate the BTX from reformer gasoline with propylene, ethylene, and vinylene carbonates has been simulated in Aspen Plus v.12 using the NRTL and COSMO-SAC models. A temperature of 313.2 K was established in the column and the performance of propylene, ethylene, and vinylene carbonates was analyzed by several sensitivity analyses.

In Figure 10, the aromatic and aliphatic recoveries in the raffinate and extract streams as a function of with the solvent-to-feed ratio have been depicted for a liquid-liquid extraction column with 15 equilibrium stages. As can be seen, both NRTL and COSMO-SAC models provided similar results. Quantitatively speaking, COSMO-SAC slightly underestimated the aromatic recovery in the extract stream while the recovery of aliphatics in the raffinate stream was slightly overestimated.

As can be noted in Figure 10, it is needed a non-realistic solvent-to-feed ratio of 8 to completely recover the aromatics with ethylene carbonate. Although propylene and vinylene carbonate show quite similar results with the NRTL model, being necessary a solvent-to-feed ratio of only 2 and 3, respectively, to achieve complete recovery of aromatics in the extract stream, this value increased up to 5 with the COSMO-SAC model for vinylene carbonate. In any case, the solvent and energy requirements of the process would be higher with vinylene carbonate than with propylene carbonate. In addition, vinylene carbonate's boiling point is 451 K being more volatile than propylene carbonate ($T_{eb}$ = 515 K), which would lead to an increase of solvent losses in distillate, lowering the aromatic purity for the same operating conditions. That is, propylene carbonate is the solvent that offers the highest aromatic recovery with the lowest solvent consumption among the three carbonates studied here, both with NRTL and COSMO-SAC calculations. Therefore, propylene carbonate has been selected to simulate the whole process of liquid-liquid extraction of the BTX fraction from reformer gasoline and compare its performance and energy consumption with those obtained with sulfolane, the benchmark solvent for this process.

The COSMO-SAC model has been used for this simulation given the lack of suitable NRTL binary interaction parameters to correctly describe the vapor-liquid equilibria for the systems {aliphatics + aromatics + cyclic carbonate}. In Table 3, the main results of the liquid-liquid extraction process of BTX from reformer gasoline with propylene carbonate and sulfolane have been summarized. A solvent-to-feed ratio of 2 was kept for both processes, as well as 15 equilibrium stages in the extractor, and the stripping and distillation columns. As can be seen, the energy consumption is reduced by 6 % with propylene carbonate in comparison with sulfolane. Although the solvent losses in the raffinate are higher with the propylene carbonate, the solvent expenditure would be clearly reduced since propylene carbonate presents a much lower price than sulfolane (around 1-3 $/kg vs 30 $/kg). Additionally, propylene carbonate is a more compatible compound in this petrochemical cut since cyclic carbonates are well-known additives to enhance octane number [60] and it can be synthesized by $CO_2$ which is an environmental step-forward [13,61]. Therefore, from the obtained results, it can be concluded that propylene carbonate is a promising alternative to sulfolane regarding the liquid-liquid extraction of aromatics from refinery streams at process scale.

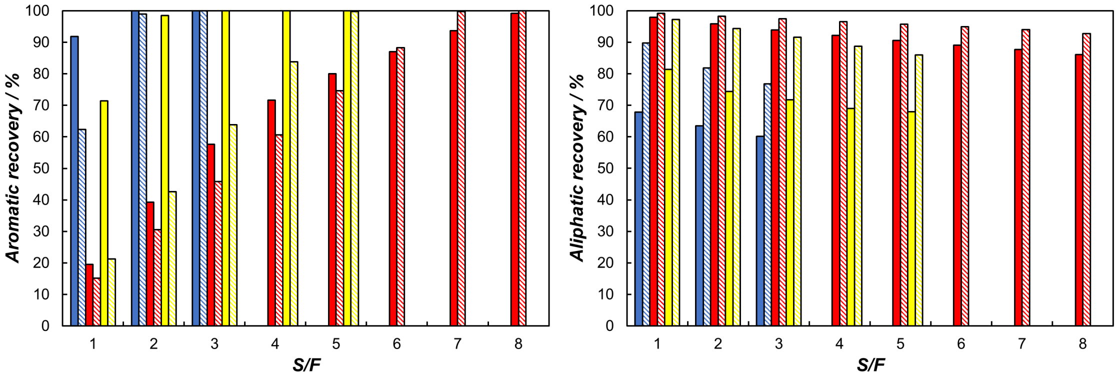


**Figure 10.** Mass-based aromatic and aliphatic recoveries in extract and raffinate streams, obtained in a liquid-liquid extraction column with 15 equilibrium stages, as a function of solvent-to-feed ratio employing propylene carbonate (blue), ethylene carbonate (red), and vinylene carbonate (yellow) as solvents at 313.2 K. The NRTL results are represented by full columns and the COSMO-SAC ones by stripped columns.

**Table 3.** Results of the simulation of the liquid-liquid extraction process of BTX from reformer gasoline. Comparison between propylene carbonate and sulfolane as solvents.

| **Solvent** | **Solvent losses (wt%)** | **Energy consumption (kJ/kg)** | **BTX purity (wt. %)** | **Aliphatics purity (wt. %)** | **BTX recovery (wt.%)** |
|---|---|---|---|---|---|
| Propylene carbonate | 0.160 | 430.5 | 99.9 | 99.1 | 99.6 |
| Sulfolane | 0.044 | 455.1 | 99.9 | 99.3 | 99.6 |

## 4. CONCLUSIONS

This work involves an experimental study of the liquid-liquid equilibria of several ternary systems {aliphatic/methylcycloalkane + aromatic + cyclic carbonate} at 303.2, 313.2, and

323.2 K and atmospheric pressure. The extractive properties of five cyclic organic solvents namely, propylene, vinylethylene, glycerol, ethylene, and vinylene carbonates, were determined. From the obtained results, the higher polarity of the carbonate the higher aromatic selectivity and the lower aromatic distribution ratio. However, experimental data are needed to check the steric hindrance caused by side chains in the solvent and additional functional groups. In quantitative terms, propylene carbonate was the solvent with the highest aromatic distribution ratio, ethylene carbonate reported the highest aromatic selectivity, and vinylene carbonate was also selected because of its balanced extractive properties.

The experimental data was accurately fitted with the NRTL model, obtaining the correspondent binary interaction parameters. In addition, the liquid-liquid equilibria for the ternary systems were predicted by the COSMO-SAC and UNIFAC models. The UNIFAC model was unable to correctly predict the experimental data, obtaining even no liquid-liquid splitting through the entire composition range for some cases. The COSMO-SAC's ability to qualitatively predict the liquid-liquid equilibrium of systems composed of aromatics, aliphatics, and polar solvents was confirmed, also showing a comparable accuracy in quantitative terms with the classic fitting approach with the NRTL model. Therefore, the NRTL and COSMO-SAC models were selected to simulate in Aspen Plus a liquid-liquid extraction column to separate the BTX fraction from reformer gasoline with propylene, ethylene, and vinylene carbonates. Both models provided similar results: ethylene carbonate was not able to separate the aliphatics and aromatics with a reasonable solvent-to-feed ratio, with propylene carbonate providing the best results in terms of solvent necessities. The whole process of BTX extraction from reformer gasoline process was simulated with propylene carbonate and sulfolane. The lower energy consumption of the propylene carbonate-based process and the quite lower price of propylene carbonate against sulfolane confirm this cyclic carbonate as a suitable, cheaper, and environmentally friendly alternative to conventional solvents to separate aromatics from refinery streams.

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