Chemical Engineering Science 72 (2012) 1–9

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

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

Water uptake and salt transport through Nafion cation-exchange membranes with different thicknesses

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A R T I C L E I N F O

Article history:
Received 4 August 2011
Received in revised form
23 December 2011
Accepted 24 December 2011
Available online 3 January 2012

Keywords:
Cation-exchange membrane
Diffusion
Salt
Monovalent cation
Transport number
Water uptake

A B S T R A C T

The water uptake of different aqueous salt solutions in different Nafion membranes, and the salt transport through those membranes under the driving force of a concentration gradient, have been studied. These experiments have been performed by using the following salts: lithium chloride, sodium chloride, potassium chloride and cesium chloride. Different homogeneous Nafion membranes, NF111, NF112, NF115 and NF117, have been used in this work, with the aim of studying the membrane thickness influence. It has been observed that the membrane water uptake increases with the membrane thickness and decreases with the size of the cation. The integral permeability coefficient has been determined from the time evolution of the salt concentration in the dilute solution. The results show that the integral permeability coefficient decreases with the membrane thickness. In general, the influence of the type of electrolyte on the integral permeability coefficient is not significant for the membranes with larger thickness (that is, NF115 and NF117). Average apparent cation transport number has been determined for the same salt solutions, and from that membrane apparent permselectivity has been estimated. In general, in membranes with large thickness, the average apparent cation transport number increases with the cation size. Finally, from fluxes and membrane potentials membrane negative ionic permeabilities have been determined finding also that they decrease with membrane thickness. Salt diffusion coefficient has been also determined from membrane negative ionic diffusion coefficient.

1. Introduction

Ion-exchange membranes find applications in many processes like electrodialysis, dialysis, reverse osmosis, membrane electrolysis, fuel cells, among other. The behavior of the membrane is of the greatest importance to the viability and performance of these processes.

Whenever two electrolyte solutions of the same nature at the same pressure and temperature, but of different concentrations are placed on both sides of a membrane, a salt flow through the membrane is observed. This transport phenomenon, which is called electrolyte permeation, has been widely studied by membrane researchers (Staverman, 1952; Hills et al., 1961; Delmotte and Chanu, 1973; Ibañez et al., 1980; Izquierdo-Gil et al., 2009). Electrolyte permeability belongs to the basic characteristics of membranes dedicated to dialysis or electrodyalisis techniques because of the knowledge of transport rates of electrolytes in ion-exchange membranes is necessary for designs in different systems. For this reason, a lot of work has been carried out on this subject (Koter and Zator, 2004; Cañas et al., 2002; Berezina et al., 2008; Filippov et al., 2008).

In an electrolyte permeation process, the salt flow through the membrane causes the concentration difference between both sides of the membrane to decrease with time, and as a consequence of that, the electrolyte permeation velocity also decreases. Therefore, the electrolyte permeation can be considered as a non-steady state process. Moreover, the higher the value of the permeability of the system, which is formed by the membrane and the two diffusion boundary layers flanking it, the former effect will be more pronounced. The determination of the corresponding transport coefficient (integral permeability coefficient) is very useful because its knowledge leads to obtain some internal characteristics of the membrane system.

At present, ion-exchange membranes are receiving considerable attention, because they are successfully applied for desalination of sea and brackish water, and for treating industrial effluents (Xu, 2005). In this paper, in order to get a better understanding of the influence of the membrane thickness on membrane electrolyte permeation features, the transport process of different aqueous solutions of chloride salts in several sulfonated cation-exchange membranes have been investigated. To this end, sorption and permeation properties have been studied for

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doi:10.1016/j.ces.2011.12.040

cation-exchange membranes with different thicknesses. In the case of electrolyte permeation, it was used an experimental method which allows the determination of the integral permeability coefficient directly from the fitting of the dilute chamber concentration experimental data as a function of the time. The influence of the membrane thickness and the type of electrolyte on the integral permeability coefficient has been analyzed. It is of particular interest, to investigate whether the membrane properties are influenced by the type of electrolyte in the solutions and to establish relations between the salt diffusion and the membrane thickness for different salt aqueous solutions. Average apparent cation transport number and water uptake have been determined for the different membranes and electrolytes. The membranes used were Nafion (perfluorinated polyethylene with pendant ether–linked side chains terminated with sulfonated groups). Nafion membranes are selected as being reference membrane for direct methanol fuel cell (Kauranen and Skou, 1996; Scott et al., 1998). The purpose is to investigate if for a charged membrane, acting as a barrier between two electrolyte solutions of different concentrations, the membrane thickness is the fundamental property or there are others.

2. Basic Equations

Two electrolyte solutions which are separated by a permeable or semipermeable membrane differ in their electrical potential. The electric potential difference is called membrane potential and can be measured by inserting suitable electrodes into the solutions. The existence of an electric potential difference between two electrolyte solutions in systems with or without a membrane is a consequence of the electroneutrality requirement. Conservation of electroneutrality prohibits the accumulation of net electric charge anywhere in the system. Membrane potential is given by (Helfferich, 1962; Lakshminarayanaiah, 1969):

$$\Delta E = \frac{RT}{F}(2\bar{t}_+ - 1)\ln\frac{c_1}{c_2} \tag{1}$$

where $\bar{t}_+$ is the called average apparent cation transport number in the membrane phase, R the gas constant, F the Faraday constant, T the temperature, and c_1 and c_2 the respective concentrations at both sides of membrane. Eq. (1) assumes constant ion mobility and negligible the osmotic flow between the two solutions. For this reason this equation has been used to calculate the called average apparent cation transport number in the membrane phase from membrane potential measurements. For low water transport numbers, the apparent ion transport number is very close to the real ion transport number. This average apparent cation transport number is an average value in the interval of concentrations between c_1 and c_2.

The characteristic difference in membrane permeability for counter ions and coions is called permselectivity. Alternatively, the permselectivity of a cation-exchange membrane has been quantitatively defined as (Helfferich, 1962):

$$\Pi \equiv \frac{z_+(\bar{t}_+ - t_+)}{1 - z_+ t_+} \tag{2}$$

where Π is the permselectivity, z_+ is the valence, t_+ is the transference number of the counter ion and $\bar{t}_+$ has been defined previously. The permselectiviy is not a membrane constant, but depends on the nature of counter-ion and coion and on the concentration of the electrolyte solutions. If an apparent transport number is used in Eq. (2), an apparent permselectivity of the cation-exchange membrane is obtained.

On the other hand, the salt flux through the membrane (J) from a mass balance is given by:

$$J = \frac{V}{A}\frac{dc_1}{dt} = -\frac{V}{A}\frac{dc_2}{dt} \tag{3}$$

where c_1 and c_2 are the salt concentrations in chambers 1 and 2 (with $c_2 > c_1$), V is the volume of each chamber and A is the effective membrane area.

The integral permeability coefficient of the membrane system is defined by:

$$P_{\mathrm{ms}} = \frac{J}{c_2 - c_1} \tag{4}$$

where P_{ms} takes into account both the permeability of the membrane, $\bar{P}_{\mathrm{salt}}$ and the permeabilities of the diffusion layers, P_{layer}, originated by the concentration polarization effects.

From Eqs. (3) and (4), assuming that both volumes are equal and constant, the following equation can be obtained for c_1 (t) (concentration in the dilute chamber as a function of the time) (Barragán and Ruíz-Bauzá, 1999):

$$c_1(t) = \frac{c_1^0 + c_2^0}{2} - a\frac{\Delta c^0}{2}\exp\left(-\frac{2AP_{\mathrm{ms}}t}{V}\right) \tag{5}$$

where c_1^0 and c_2^0 are, respectively, the initial concentration in the dilute and concentrate chambers, Δc^0 is the initial concentration difference. The parameter a is introduced as a time origin correction, which considers the possibility that the diffusion process beginning time and the starting time of chronometer were not exactly the same. In general, the value of a will be very close to unity. Eq. (5) allows us to obtain P_{ms} directly from the fit of the experimental data of c_1 as a time function.

The flow of an ionic specie i, J_i through the membrane is given, in case of diluted solutions by the Nernst–Planck equation (Lakshminarayanaiah, 1969). If no electric field is applied and in case of 1-1 electrolytes, the following relation is found to obtain the called ionic permeability of the ion i in the membrane, $\bar{P}_i$, defined as $\bar{D}_i/d$, being d the membrane thickness and $\bar{D}_i$ the diffusion coefficient of the ion i in the membrane (Barragán and Ruíz-Bauzá, 1997):

$$\bar{P}_i = \frac{JRT}{z_iF\Delta E}\cdot\frac{\exp(-(z_iF\Delta E)/(RT)) - 1}{c_1 - c_2\exp(-(z_iF\Delta E)/(RT))} \tag{6}$$

where z_i is the ionic valence and the rest of parameters have been defined previously. This expression allows us to determine the membrane ionic permeability $\bar{P}_i$, between two given concentrations, if both flux J and membrane potential ΔE are known.

The "time lag" is the time which elapses until the diffusion of a species across a layer has attained the steady (or quasi-stationary) state. It is also defined the "breakthrough time", t_b, which characterizes ionic arrival on the permeate side of the membrane (Onuchukwu et al., 1994). t_b is related to membrane salt diffusion coefficient ($\bar{D}_{\mathrm{salt}}$) by the following equation:

$$t_b = \frac{0.758d^2}{\pi^2\bar{D}_{\mathrm{salt}}} \tag{7}$$

3. Material and methods

3.1. Material and methods

The membranes used in this work were four Nafion membranes, with analogous transport properties but different thicknesses. They are commercial cation-exchange membranes Nafion-111, Nafion-112, Nafion-115 and Nafion-117 (hereafter named NF111, NF112, NF115 and NF117, respectively), manufactured by DuPont Inc. This type of membrane consists of a polytetrafluoroethylene backbone (or matrix) and regularly spaced perfluorovinylether side chains

Table 1
Membrane thicknesses, density, ion-exchange capacity and IEC expressed by volume.

	NF111	NF112	NF115	NF117
Thickness[a] **(10^{-6} m)**	25	51	127	183
Hydrated thickness [b,c] **(10^{-6} m)**	27	58	161	208
Density[b] **(10^3 kg/m^3)**	2.39	2.05	2.00	1.98
IEC[a] **(meq/g)**	0.91	0.91	0.96	0.94
IEC (mol/l)	2.17	1.87	1.92	1.86

[a] Manufacturer values.
[b] Experimentally measured values.
[c] In pure water.

ending in sulfonic acid groups. According to the data provided by the manufacturer, this membrane has a nominal equivalent weight of 1100 g eq^{-1}. The maximum water uptake is 41%. The nominal thickness, hydrated thickness, the density, the ion-exchange capacity (IEC) and the IEC expressed by volume of the membranes are given in Table 1.

Pro-analysis LiCl, NaCl, KCl and CsCl (Merck) and bidistilled pure water were used in this study.

3.2. *Water uptake measurements*

In order to determine the total solvent uptake by the membrane, a water uptake study was performed by using binary salt aqueous solutions. The salt concentration used was 0.005 M (the same average concentration value was used for permeability and transport number measurements). Lithium chloride, sodium chloride, potassium chloride and cesium chloride aqueous solutions were used. The membrane sample was immersed in a close bottle containing the corresponding solution and allowed to equilibrate. The bottle was placed in an oven thermostated at 298 K. After 48 h of immersion, the swollen membrane was taken out of the solutions, wiped carefully with filter paper and weighted. After that the membrane sample was dried in a vacuum oven at 373 K for 24 h and was weighted again. The decrease in weight was equal to the weight of the liquid sorbed by the membrane. Finally, the water uptake, *S*, was calculated from the weight of the swollen and the dry membrane sample according to the following expression:

$$S=\frac{m_w-m_d}{m_d} \tag{8}$$

where m_w and m_d are the masses of the swollen and dry membrane, respectively. The reproducibility of measurements was checked in all cases.

3.3. *Average apparent cation transport number measurements*

The average apparent cation transport number was measured using the experimental setup shown in Fig. 1. The membrane was positioned between two equal glass chambers by means of a telescopic joint. Each chamber was provided with four orifices communicating to the exterior. Two of them were used as solution inlet and outlet, respectively. In the other two orifices a reversible Ag/AgCl electrode and a temperature probe, respectively, were introduced. The membrane surface area was 2.06×10^{-4} m^2. The temperature was kept constant at 298 K. The reservoirs had a glass made jacket where water was recirculated by means of a Techne TU-16D thermostat with a refrigerated bath RB-5. Water was recirculated in order to maintain constant the solution temperature. In order to reduce the concentration polarization effects in the membrane system the solutions were recirculated by means of both peristaltic pumps, Velp Scientifica SP311. Prior to each experiment the membrane to be used was immersed for a minimum of 24 h in the solution of lower concentration in order to achieve equilibrium. The potential through the system was measured by means of the electrodes. The concentration of electrolyte was kept constant at $c_1^0=10^{-4}$ M in one of the chambers, and it was changed in the other chamber (c_2) from that value to 10^{-2} M. The membrane potential was measured when it reached a stationary value (for $c_1^0=10^{-4}$ M. and $c_2^0=10^{-2}$ M). The contribution of the Ag/AgCl electrodes to the electric potential difference must be taken into account (Janz and Ives, 1961). Average apparent transport number was estimated from membrane potential by using Eq. (1) (Helfferich, 1962; Lakshminarayanaiah, 1969). Using these data, the membrane apparent permselectivity was estimated by Eq. (2).

3.4. *Permeability measurements*

The experimental device used for the permeability measurements is similar to one used in previous works (Barragán et al., 2004; Villaluenga et al., 2006; Godino et al., 2006). The membrane cell had two PTFE independent chambers of an approximate volume of 5.64×10^{-5} m^3 separated by the membrane. The effective membrane area was 2.5×10^{-3} m^2. Each chamber had four orifices communicating to the exterior, two of them were used as solution inlet and the other two as solution outlet.

Two glass reservoirs were used to contain the circulating solution in both chambers. Each reservoir was provided with three orifices. Two of them were used as solution inlet and outlet. In the third one, a conductivity and temperature probe was introduced in order to measure the solution concentration. For this purpose an electronic device (Oakton PH/CON 510 series) with an accuracy of ±0.1 K was used. The reservoirs had a glass made jacket where water was recirculated by means of a Techne TU-16D thermostat. This water was recirculated in order to maintain constant the solution temperature. The solutions were circulated between the cell and the reservoirs by means of a peristaltic pump (Heidolph Typ 52100).

Prior to each experiment, the membrane sample was immersed, for a minimum of 24 h, in the solution in order to achieve the equilibrium. The membranes were washed with deionized bidestilled water, and dried the superficial water with filter paper. Once the membrane was positioned in the cell, both tanks were filled with water in one side of the membrane and the salt solution in the other side, with an initial concentration 0.01 M. The concentration of the solutions was measured in both containers just before beginning the experiment. The solution volumes used were 0.35×10^{-3} m^3. When both solutions were thermostatized at 298 K, they began to be pumped through the system. The evolution of conductivity, more exactly, of concentration in the dilute reservoir with time was studied. Using the time variation of the concentration, the integral permeability coefficient, P_{ms}, was determined following the method described above.

4. Results and discussion

4.1. *Water uptake measurements*

When a membrane is immersed in an aqueous salt solution two phenomena are expected to occur simultaneously: the exchange of the H$^+$ ions associated to the sulfonate fixed groups by the cations of the salt, and the water uptake of the membrane due to the water uptake. The water uptake of the membrane depends on the polymeric structure of the membrane (e.g. number of cross-links, ion-exchange capacity), the

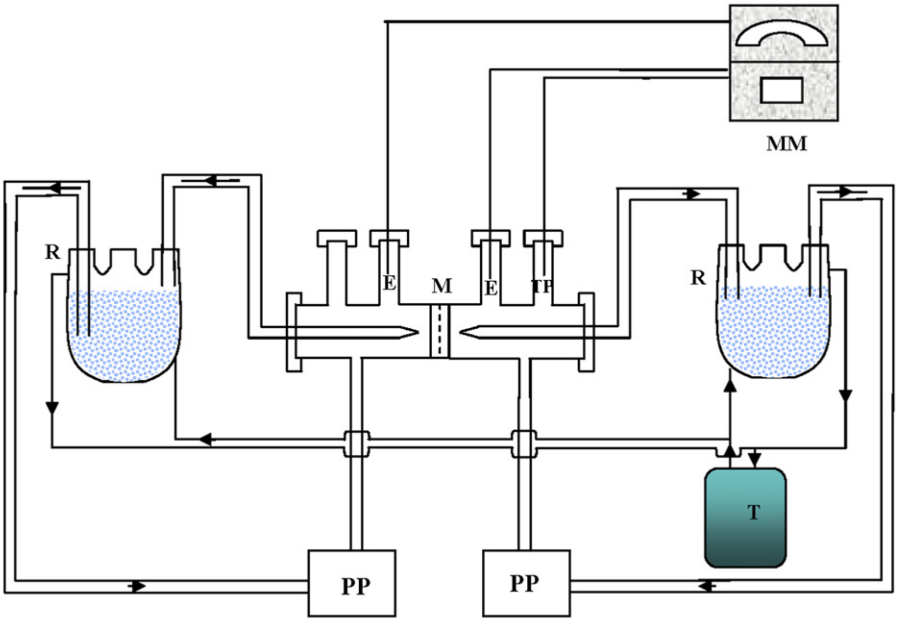

Fig. 1. Experimental setup used in the measurement of the average cation transport number. M: membrane; E: electrode; TP: temperature probe; PP: peristaltic pump; MM: multimeter; R: reservoir; T: thermostat.

Table 2
Overall water uptake for the different membranes and electrolytes. Concentration: 0.005 M.

Electrolyte	NF111	NF112	NF115	NF117
LiCl	0.15	0.18	0.21	0.23
NaCl	0.11	0.14	0.17	0.20
KCl	0.05	0.08	0.09	0.12
CsCl	0.03	0.07	0.07	0.08

total electrolyte solutions concentration, as well as the type of cations in solution (Pourcelly et al., 1990; Dalla Costa et al., 2003). The membranes used in this work are similar in composition and structure, except little differences in their IEC and density, but with different thicknesses. The water uptake values of the different membranes are shown in Table 2. It is observed that the water uptake values of the different membranes follow the sequence: $S(\mathrm{NF111}) < S(\mathrm{NF112}) < S(\mathrm{NF115}) < S(\mathrm{NF117})$. At first one would expect that the water uptake does not depend on the membrane thickness, due to definition, it is a relative value. However, a trend has been found, that the membrane water uptake increases with membrane thickness, probably due to the IEC increase and the density decrease with the membrane thickness. It has been also found that the water uptake decreases with the size of the cation increasing. This behavior is in accordance with that reported elsewhere, since it was found that the solvent uptake by Nafion membrane rises with increasing hydration ability of the counterion (Cabasso et al., 1986; Suresh et al., 2005; Villaluenga et al., 2006). It is well known that the nature of the counterion can influence membrane water uptake (Pourcelly et al., 1990) and water uptake naturally rises with increasing hydrative capacity of the counterion. The cations from solution interact with solvent and, consequently, a different number of solvent molecules surround each cation. This number is directly proportional to the charge and inversely proportional to the size of the ion. The real radius of a cation is the one that considers the solvent molecules around it, i.e., the hydrated radius. It may be stated that the water uptake of the membrane decreases due to an increase in size of naked counterions from Li^+ to Cs^+, as it can be seen in Fig. 2 where the overall water uptake has been plotted versus the hydrated radius (Xie and Okada, 1996). Cations of higher atomic number have higher affinity to the membrane than those of lower atomic numbers. Thus, it is expected that membranes exchanged with cations of higher affinity show lower water content (Okada et al., 2002). With regard to the solubility values, it is found that, in spite of the different pretreatments of the membrane used, the water uptake data obtained in the present study are in agreement with the literature values (Suresh et al., 2005; Goswami et al., 2001; Xue et al., 1991).

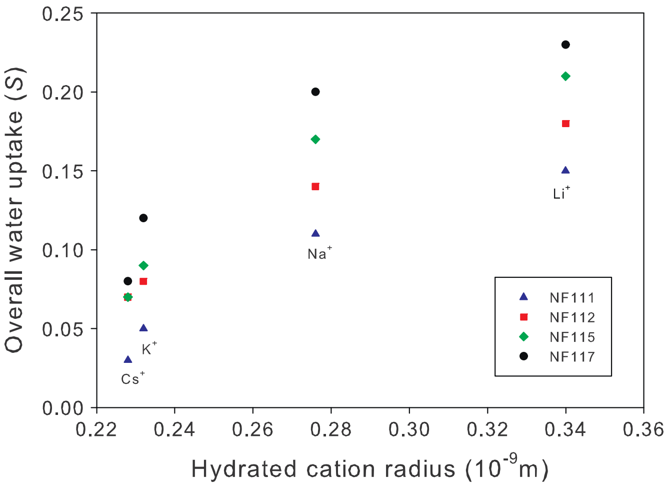

Fig. 2. Overall water uptake of NAFION membranes versus the hydrated radius for the different aqueous electrolyte solutions.

The sorption of a liquid not only depends on the specific chemical affinity between the liquid molecules and the polymer matrix, but also on free volume or extent of amorphous regions available in the membrane, and the size of the penetrate. Water sorbed by the membrane is formed as water forming the structure of the hydration shell of the ions, and free water filling the interstitial holes of the membrane. Modeling of the solubility of a liquid in a membrane polymer can be made by the Flory–Huggins (FH) theory (Jonquieres et al., 1998a,b). This model is a general method for describing sorption in polymer materials. Nafion membranes, as has been said above, present a polytetrafluoroethylene backbone highly hydrophobic, whereas the sulfonic groups are very hydrophilic, therefore the water molecules reside only in the hydrophilic domains of the polymer, so Nafion membranes sorption with aqueous solutions is lower than with other solvents as methanol (Villaluenga et al., 2006). For denser membranes the ion nature has a lower influence since the ions have less possibility for enlarging the internal channels. The influence of the membrane thickness is higher for the cations with higher hydrated radius.

The water uptake properties of the membrane are very important because in Nafion membrane systems, the transport behavior is closely dependent on the amount of water absorbed. Water molecules may be inserted between ions and the anionic sulfonate groups leading to a complete dissociation of all ion pairs. In this case, the ion-sulfonate group interactions would be relatively weak. On the other hand, a decreased water content would be expected to cause stronger interaction between cations and the anionic groups in the membrane. In this case, the membrane effective fixed charge concentration is lower (Matsumoto et al., 2005; Barragán and Pérez-Haro, 2011) and hence the membrane possesses present a lower capacity for excluding coions, affecting to its permeability.

The concentration of fixed ionogenic groups (associated groups included) in a membrane which is in an arbitrary ionic form and contains arbitrary amounts of sorbed solutes is related to the ion-exchange capacity by (Helfferich, 1962):

$$\overline{X} = \rho \frac{100-S}{100(1+\sum_i Q_i - M_{\mathrm{ref}} 10^{-3} IEC)} IEC \qquad (9)$$

where $\overline{X}$ is the molarity of fixed groups in equivalents per cubic decimeter; ρ is the density of the membrane in grams per cubic centimeter; S is the solvent content of the membrane in weight per cent; Q_i is a dimensionless variable which expresses the amount of species i in the “specific amount” of membrane, M_{ref} is the atomic weight of the reference ion (1 for cation exchangers, 35.5 for anion exchangers); the summation is carried out over counter ions and sorbed solutes, if any. This fixed charge concentration depends on the water uptake properties, and thus it will be different for different membranes. The values obtained for concentration of the fixed charge in the membrane are shown in Table 3. They seem to decrease with membrane thickness, and for the same membrane they increase with size of the cation, with the exception of CsCl.

According to the Teorell–Meyer–Sievers theory in charged membranes (Lakshminarayanaiah, 1969) the concentration of coions in the membrane has been estimated from the concentration of the fixed charge in the membrane, $\overline{X}$, as follows:

$$\overline{C}_{-} = -\frac{\overline{X}}{2} + \left[\left(\frac{\overline{X}}{2} \right)^2 + C_0^2 \right]^{1/2} \qquad (10)$$

where C_0 is the bulk electrolyte concentration. Obviously, the more the fixed charge concentration, the lower the coion concentration due to the high capacity of excluding coions. To determine the values of the membrane theoretical concentration of coions shown in Table 4, a mean value of the concentration, 0.005 M, in the operating interval was considered for C_0. As can be seen in Table 4, the concentration of coions in the membrane seems to increase with membrane thickness, but for the same membrane they decrease with size of the cation, neglecting CsCl.

Table 3
Concentration (M) of the fixed charge in the membrane. Concentration: 0.005 M.

Electrolyte	NF111	NF112	NF115	NF117
LiCl	1.84	1.52	1.51	1.43
NaCl	1.90	1.57	1.56	1.46
KCl	2.00	1.66	1.68	1.58
CsCl	1.88	1.55	1.58	1.52

Table 4
Theoretical concentration (10^{-5} M) of coions (anion Cl^-) in the membrane. Bulk concentration: 0.005 M.

Electrolyte	NF111	NF112	NF115	NF117
LiCl	1.36	1.65	1.66	1.75
NaCl	1.32	1.59	1.60	1.71
KCl	1.25	1.51	1.49	1.58
CsCl	1.33	1.61	1.58	1.65

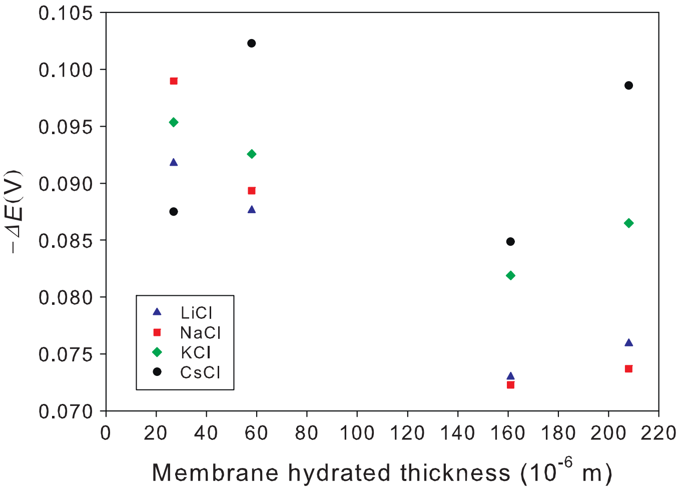

Fig. 3. Membrane potential versus the membrane hydrated thickness of NAFION membranes for the different aqueous electrolyte solutions.

4.2. *Average apparent cation transport number and apparent permselectivity*

Membrane potential values have been plotted in Fig. 3 for each electrolyte and membrane. In general, it seems that the electrolyte influence is relatively significant in membranes with larger thickness, with an increase of the membrane potential with the size of the cation involved. These results are in agreement with reported data in the literature (Barragán and Ruíz-Bauzá, 1997). An exception is observed, however, for NF111 for which the lowest membrane potential value is observed with Cesium. The reproducibility of the measurements was checked in all the cases, specially the value corresponding to cesium and NF111. From these data, the average apparent cation transport number can be determined by using Eq. (1). A general trend has been found in the average apparent cation transport number for all the electrolytes, it shows a soft minimum value for NF115 membrane and from that transport number increases with membrane thickness, except for CsCl, where an anomalous behavior is found for NF111 membrane. For larger thicknesses it seems that transport number increases with the size of the cation. For NF111 with CsCl the transport number seems to decrease instead of increasing as the other electrolytes do. In general, the average apparent cation transport numbers found are in agreement with those found in the literature (Lehmani et al., 1997; Lindheimer et al., 1987; Stenina et al., 2004) for similar membranes. For an electrolyte, the decrease observed in the membrane potential when the membrane thickness increases may be due to the increase of the water transport. Larchet et al. (2004) studied the correlation between

Table 5
Apparent permselectivity and average apparent cation transport number for the different membranes and electrolytes. Bulk concentration: 0.005 M.

Electrolyte	NF111		NF112		NF115		NF117	
	Π	$\bar{t}_+$	Π	$\bar{t}_+$	Π	$\bar{t}_+$	Π	$\bar{t}_+$
LiCl	0.83	0.89	0.80	0.87	0.71	0.81	0.73	0.82
NaCl	0.87	0.92	0.82	0.88	0.68	0.81	0.69	0.81
KCl	0.81	0.90	0.78	0.89	0.70	0.85	0.75	0.87
CsCl	0.74	0.87	0.86	0.93	0.72	0.86	0.83	0.92

the membrane potential and the water transport number of cation-exchange membranes, finding that in most cases the water transport through a membrane increases with increasing membrane water uptake. In this approach, more water uptake, more water transfer and lower average apparent cation transport number. This behavior would be in agreement with the data found for the water uptake of the studied membranes. For a given electrolyte, at higher membrane thickness, higher water uptake and lower membrane potential. On the other hand, the water transport number increases with the hydration number of the cation increasing (Larchet et al., 2004; Barragán et al., 1995), a more hydrated ion transports not only more water molecules in this hydration shell, but the amount of dragged water is higher also due to a greater size of the hydrated ion. For a given membrane, the membrane potential is higher for the less hydrated cations. However, it fails for the thinnest membrane NF111, for which the correlation between membrane potential and water uptake is not observed. The increase observed for the thickest membrane, with higher water content, could not be explained either according this argument.

The membrane apparent permeselectivity and the average apparent cation transport number are shown in Table 5 for each membrane and electrolyte. The corresponding values of t_+ used in Eq. (2) have been taken from the literature (Lobo and Quaresma, 1989; Robinson and Stokes, 2003). Comparing data in Tables 4 and 5, a correlation is found between data as may be expected. When concentration of coions in the membrane increases the membrane apparent permselectivity decreases. Thus, in general, membranes with larger thickness would be less selective due to a higher concentration of coions inside them. This trend, however, is not so clear for the larger size cations or for membrane NF111. It may be speculated that this behavior may be related to the low water content of this membrane. At low water contents, interactions between cations and the fixed group of membrane could cause the effective fixed charge concentration could be lower than the theoretical value shown in Table 3 (Barragán and Pérez-Haro, 2011). In this case, the coions concentration inside the membrane could be different to the values shown in Table 4. Membrane NF111 and CsCl electrolyte present the lowest water uptakes.

4.3. Permeability measurements

The integral permeability coefficient, P_{ms}, was determined by using Eq. (5) if the time variation of the concentration in the dilute chamber is known. Fig. 4 shows, as an example, the concentration data measured when the NF111 membrane and aqueous KCl solution were used. It has been found from the fit results to Eq. (5) that the parameter a is very close to unity. This is the general behavior, as may be expected, because the first measurement was taken when the conductivity began to change, that is, when the diffusion process began to take place.

The values obtained for the integral permeability coefficient are of the order of magnitude of 10^{-9} m s^{-1}. These low values of the integral permeability coefficient confirm that a high capacity ion-exchanger membrane between dilute solutions acts as a barrier which prevents electrolyte diffusion almost completely (Helfferich, 1962). The inverse of the integral permeability coefficient is shown as a function of the hydrated membrane thickness, d, in Fig. 5. As can be observed, a non linear behavior of $1/P_{ms}$ with d was found. This result seems to indicate that the salt diffusion coefficient in the membrane, $\overline{D}_{salt} = \overline{P}_{salt}\, d$, would be dependent on the membrane thickness.

The integral permeability coefficient takes into account the two adjoining layers permeability due to the concentration polarization effects. However, as the salt flux along all the system, layers plus membrane, must be the same, it allows us to estimate it from the P_{ms} values. The flux values obtained have been shown

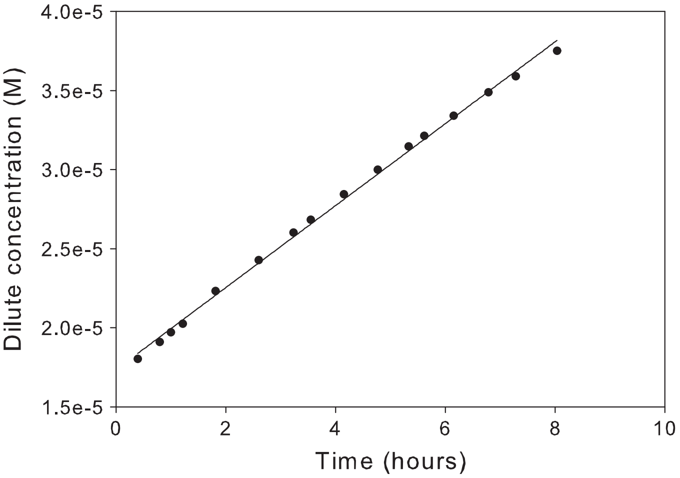

Fig. 4. Dilute concentration versus time for NF111 membrane with KCl aqueous solutions.

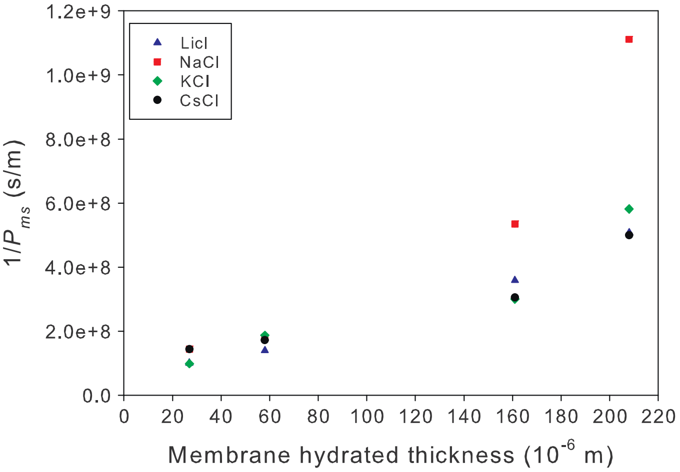

Fig. 5. Inverse of integral permeability coefficient versus membrane hydrated thickness of NAFION membranes for different aqueous electrolyte solutions.

in Table 6 for the different membranes and electrolytes, finding higher fluxes values for thinner membranes, as might be expected.

From the flux and membrane potential values, the membrane negative ionic permeability can be determined by using Eq. (6). The values obtained are shown in Fig. 6 as a function of the hydrated membrane thickness. With the exception of cesium and membrane NF111, the trend observed is the expected, with a decrease of the membrane negative ionic permeability with the increase of the membrane thickness. With respect to the influence of the electrolyte nature, as a general trend, the membrane negative ionic permeability seems to increase with the size of the cation, in agreement with other results reported in the literature (Barragán and Ruíz-Bauzá, 1997; Stenina et al., 2004). However an exception is observed when using aqueous CsCl solution in NF111 membrane and for LiCl solutions. This anomalous result found for CsCl and NF111 could be a consequence of the low membrane potential observed. From this membrane ionic permeability the diffusion coefficient for the anion may be estimated directly. As the solution is very dilute, the membrane is very selective and therefore the diffusion penetrability is defined by the magnitude of the diffusion coefficient for the anion, $\overline{D}_{\text{salt}} \sim 2\overline{D}_{i-}$ (Novikova et al., 2005). Thus, in these conditions, from the diffusion coefficient for the coions it is possible to estimate the membrane salt diffusion coefficient. The results are shown in Fig. 7, where it has been plotted versus the membrane hydrated thickness for the different electrolytes (Xie and Okada, 1996). As can be observed, the membrane salt diffusion coefficient, $\overline{D}_{\text{salt}}$, depends both on the membrane and on the electrolyte, which was an expected result from the behavior shown in Fig. 5 for the inverse of the membrane system permeability (integral permeability coefficient). With a given electrolyte and for similar membranes, only different in their thickness, a salt diffusion coefficient independent on the membrane would be expected. Thus, the observed differences must be due to the different membrane properties. As the chemical structure and IEC values are similar for all the used Nafion membranes, the differences may be due to their different density which leads to different water uptakes and hence to different size of the internal membrane channels and different effective fixed charge concentrations. This last parameter controls the concentration of coions inside the membrane and thus the permeselectivity and the diffusion process through it. The results shown in Fig. 7 indicate that, for the less dense membranes and the larger size cations, the salt diffusion inside the membrane has the same general trend that in free solution, decreases with the cation size decreasing. The NF111 membrane, with the highest density, shows an anomalous behavior with Cs.

Table 6
Flux values (10^{-8} mol/m^2 s) for the different membranes and electrolytes. Solutions concentrations: 0.01 M and 0.0001 M.

Electrolyte	NF111	NF112	NF115	NF117
LiCl	9.86	7.11	2.76	1.95
NaCl	6.88	5.54	1.85	0.89
KCl	10.04	5.29	3.27	1.70
CsCl	6.70	5.98	3.06	1.94

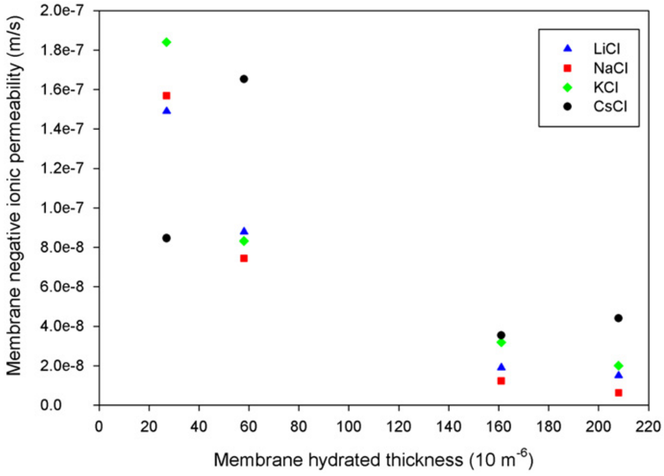

Fig. 6. Membrane negative ionic permeability versus membrane hydrated thickness of NAFION membranes for different aqueous electrolyte solutions.

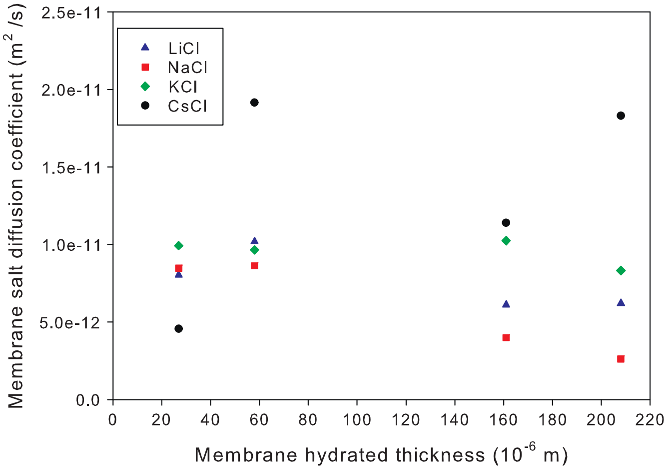

Fig. 7. Membrane salt diffusion coefficient versus membrane hydrated thickness of NAFION membranes for different aqueous electrolyte solutions.

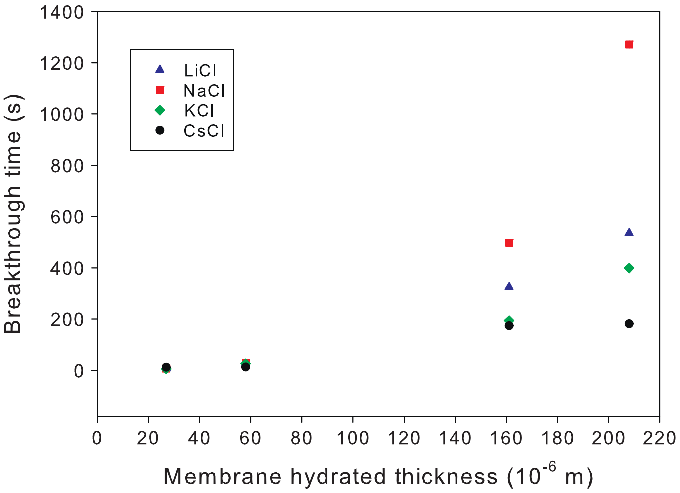

Fig. 8. "Breakthrough time" versus membrane hydrated thickness for NAFION membranes with different aqueous electrolyte solutions.

The "breakthrough times" plotted in Fig. 8 were evaluated by Eq. (7). It is observed that the "breakthrough time" increases with membrane thickness, as might be expected. However, the influence of the membrane decreases when the cation size increases. An exception is observed with NaCl, which presents the highest breakthrough times for all the membranes. Moreover the influence of the membrane thickness is greater than for the other cations. This fact is in relative agreement with that observed during the experimental run, in those cases, the diffusion process took a long time to begin to occur. The first experimental data were considered just when the diffusion process began to take place. In general, for thinner membranes the “breakthrough times” seem to be independent of the electrolyte, however, for thicker membranes it seems to show a certain dependence on the type of electrolyte.

5. Conclusions

A membrane water uptake study for the different membranes and electrolytes was made resulting that S increases with membrane thickness and decreases with the size of the cation. It may be concluded that the membrane overall water uptake increases with decreasing membrane density and with increasing hydration ability of the counterion.

Average apparent cation transport numbers were measured for the different membranes and electrolytes, and from those values the membrane apparent permselectivity was determined. For larger thicknesses it seems that it increases with the size of the cation, neglecting LiCl. A clear trend has been observed for the integral permeability coefficient, it decreases with membrane thickness, as might be expected. However no clear tendency has been found about the type of electrolyte. It seems that the differences are less significant for larger membrane thicknesses. As a general trend, at larger membrane thicknesses, that is, NF115 and NF117 the integral permeability coefficient is larger for larger sizes of cation, however for smaller membrane thicknesses, that is, NF111 and NF112 membranes, the behavior is just the opposite, the integral permeability coefficient is smaller for the largest size of the cation. Membrane negative ionic permeabilities were also determined finding a similar behavior. From this membrane ionic permeability, the diffusion coefficient for the anion was estimated directly. As the solution is very dilute, the membrane is very selective and therefore the diffusion penetrability is defined by the magnitude of the diffusion coefficient for the anion. The found results show that the membrane salt diffusion coefficient, $\overline{D}_{\text{salt}}$, depends both on the membrane and on the electrolyte. As a general trend, it increases when the cation size increases with the exception of the thinnest membrane and the smallest cation.

The results found, that is, the low diffusion coefficients values obtained, confirm that a high capacity ion-exchanger membrane between dilute solutions acts as a barrier which prevents electrolyte diffusion almost completely.

Acknowledgements

Financial support from Banco de Santander and Universidad Complutense de Madrid under Project GR35/10–910358 is gratefully acknowledged.

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