Sorption and permeation of solutions of chloride salts, water and methanol in a Nafion membrane

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Abstract

The sorption of water–methanol mixtures containing a dissolved chloride salt in a Nafion 117 membrane, and their transport through the membrane under the driving force of a pressure gradient, have been studied. Both type of experiments was performed by using five different salts: lithium chloride, sodium chloride, cesium chloride, magnesium chloride and calcium chloride. It was observed that both the permeation flow through the membrane and the membrane swelling increase significantly with the methanol content of the solutions. These facts are attributed to the increase in wet membrane porosity, which brings about the increase of the mobility of solvents in the membrane, besides the increase of the mobility of the polymer pendant chains. In contrast, the influence of the type of electrolyte on the membrane porosity and permeability is not very important, with the exception of the CsCl solutions, which is probably due to the small hydration ability of the Cs⁺ ion.

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Keywords: Nafion membrane; Permeation; Sorption; Electrolyte water methanol mixtures

1. Introduction

The phenomena of transport across an ion-exchange membrane in aqueous electrolyte solutions have been widely studied by many authors [1–4]. However, the study and experimental data available for membrane systems using non-aqueous electrolyte are scarce, and the transport properties in these systems are not clear.

Recently, intensive interest has arisen in the study of transport phenomena in aqueous-organic electrolyte solutions due to the importance of their possible industrial and medical applications [5,6]. One of the non-aqueous systems that has generated more interest is the membrane system with methanol–water solution, mainly because of its importance in the development of direct methanol fuel cells [7,8]. These systems have shown to be one of the more attractive alternative systems to produce electric energy in mobile applications.

Amongst the ion-exchange membranes, Nafion perfluorosulfonic acid polymers are the most common membranes investigated in direct methanol fuel cell [9,10]. In order to account for the transport properties, various models of the Nafion structure have been proposed, e.g. the cluster-network model [11,12], the three-region model [13], and the uniform-pore model [14–16]. However, the behavior of this kind of membranes in organic media is not really well understood. This aspect is especially notable due to the problem of the methanol transfer through the membrane, better known as crossover, originated in direct methanol fuel cells.

The aim of this experimental study is to gain an insight into the behavior of a Nafion membrane in electrolyte methanol–water media. To this end, the membrane sorption and permeation properties have been studied for binary and ternary mixtures of chloride salts, water and methanol. It is of particular interest, to investigate whether the membrane properties are influenced not only by the composition of the solvent, but also by the type of electrolyte in the solutions.

2. Experimental

2.1. Membrane

A commercial cation-exchange membrane type Nafion 117 was used in this study. The dry thickness, maximum water uptake, ion-exchange capacity and nominal equivalent weight provided by the manufacturer for this membrane are...
by 1.83 × 10⁻⁴ m, 35%, 1.13 kmol/m³ and 1100 g/mol of fixed charge, respectively. This type of membrane consists of a polytetrafluoroethylene backbone and regularly spaced perfluorovinyl ether side chains terminated by sulfonate group [12,17]. The perfluorinated backbone is highly hydrophobic, whereas the sulfonic groups are very hydrophilic.

2.2. Materials

The materials used were analytical grade methanol, deionized bidistilled water, and five different chloride salts: lithium chloride (LiCl), sodium chloride (NaCl), cesium chloride (CsCl), magnesium chloride (MgCl₂) and calcium chloride (CaCl₂).

2.3. Swelling measurements

In order to determine the total solvent uptake by the membrane, a swelling study was performed by using binary and ternary mixtures of chloride salt, water and methanol. For binary solutions, the measurements were conducted with aqueous solutions with a salt concentration of 0.01 M. For ternary solutions, the concentration of salt was kept also at 0.01 M, whereas the solvent was mixtures of water and methanol with a methanol content of 25, 50 and 75 wt.%, respectively. Lithium chloride, sodium chloride, cesium chloride, magnesium chloride and calcium chloride were used as chloride salts. Before experiments, a membrane sample was dried in a vacuum oven at 100 °C for 24 h. After that, the sample was weighted and, then, immersed in a closed bottle containing the corresponding solution and allowed to equilibrate. The bottle was placed in an oven thermostatted at 25 °C. After 48 h of immersion, the swollen membrane was taken out of the solutions, wiped carefully with filter paper and weighted again. The increase in weight was equal to the weight of the liquid sorbed by the membrane. After each run, the membrane was dried in a vacuum oven at 100 °C for 24 h and weighed again. Finally, the overall solubility, S, was calculated from the weight of the swollen and the dry membrane sample according to the following expression:

\[ S = \frac{m_W - m_D}{m_D} \]  

where \( m_W \) and \( m_D \) are the masses of the swollen and dry membrane, respectively. The reproducibility of the measurements was checked in all cases.

2.4. Permeation measurements

The permeation flux through the membrane was estimated by using an experimental set-up reported elsewhere [18]. Basically, the main part of the experimental device was a cell, which consisted of two equal cylindrical glass chambers. The membrane with an effective surface area of 5.7 cm² was mounted in a Teflon holder, which was positioned between the two chambers. The volume of each container was about 400 cm³, which is large enough to ensure that the concentration change in the solution during the measurements may be considered negligible. The right chamber was connected to an air reservoir and to a digital pressure gauge. The pressure in this chamber was varied over the atmospheric pressure, thus the reading of the pressure gauge gives the pressure difference between the two chambers. For each pressure difference, the measurement consisted of following the displacement of the liquid meniscus in a L-shaped capillary tube introduced into the left chamber, as a function of time. All the permeation experiments were carried out under isothermal conditions at 25 °C. Temperature requirements were achieved by immersing the whole cell in water that was maintained at the selected temperature. In order to improve the uniformity of the temperature and the concentration in the chambers, the solutions were stirred at a selected rotation velocity of 360 rpm.

Permeation experiments were performed with binary and ternary mixtures of chloride salt, water and methanol. In the case of binary solutions, the measurements were conducted with aqueous solutions with a salt concentration of 0.01 M. For the ternary solutions, the concentration of salt was kept also at 0.01 M, whereas the solvent was mixtures of water and methanol with a methanol content of 25, 50 and 75 wt.%, respectively. In order to analyze the influence of the type of cation on the membrane transport properties, five different chloride salts were used: lithium chloride, sodium chloride, cesium chloride, magnesium chloride and calcium chloride.

3. Results and discussion

3.1. Sorption

The overall swelling as a function of the wt.% of methanol in solvent for the different chloride salts used is shown in Table 1. When the membrane is immersed in the ternary solutions, 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 swelling of the membrane due to the water and methanol uptakes. Based on previous papers [19], the complete exchange of the H⁺ ions in the membrane by the cations of the salt was assumed in the present study.

As can be seen the solubility is little affected by the type of electrolyte because the differences are within the experimental

<table>
<thead>
<tr>
<th>Methanol (wt.%)</th>
<th>LiCl</th>
<th>NaCl</th>
<th>CsCl</th>
<th>MgCl₂</th>
<th>CaCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.26 ± 0.02</td>
<td>0.22 ± 0.02</td>
<td>0.14 ± 0.02</td>
<td>0.25 ± 0.02</td>
<td>0.23 ± 0.02</td>
</tr>
<tr>
<td>25</td>
<td>0.35 ± 0.03</td>
<td>0.32 ± 0.03</td>
<td>0.20 ± 0.02</td>
<td>0.32 ± 0.03</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td>50</td>
<td>0.37 ± 0.03</td>
<td>0.34 ± 0.03</td>
<td>0.19 ± 0.02</td>
<td>0.34 ± 0.03</td>
<td>0.30 ± 0.02</td>
</tr>
<tr>
<td>75</td>
<td>0.41 ± 0.03</td>
<td>0.37 ± 0.03</td>
<td>0.21 ± 0.02</td>
<td>0.31 ± 0.02</td>
<td>0.30 ± 0.02</td>
</tr>
</tbody>
</table>
error. Nevertheless, in the case of alkali metal chloride salts, for water sorption, the following sequence can be observed: $S(\text{LiCl}) > S(\text{NaCl}) > S(\text{CsCl})$ in order of decreasing water solubility. In the case of alkaline earth salt, $S(\text{MgCl}_2) > S(\text{CaCl}_2)$. The trend is similar for water–methanol solutions. Furthermore, the amount of solvent uptake increases, in general, with the methanol content of the solution. It is well known that the factors affecting the extent of solvent uptake by Nafion are temperature, ion-exchange capacity, pretreatment of the membrane, cationic forms of the membrane, and physical state of absorbing solvent [20,21]. From the trends observed, it can be stated that the swelling of the membrane decreases due to an increase in size of naked counterions from Li$^+$ to Cs$^+$, and from Mg$^{2+}$ to Ca$^{2+}$. This behavior is similar for aqueous and mixture solutions. In contrast, the effect of the increase in the valence of the cation is different if aqueous or water–methanol mixtures are used as solvent. For aqueous solutions, the comparison of the solubility data of LiCl and NaCl with the corresponding data of MgCl$_2$ and CaCl$_2$ indicates that, within experimental error, the solubility is independent of the valence of the cation. However, it is found that the solubility decreases with increasing valence of the cation for water–methanol solutions. This means that the presence of different ionic charges on these metal ions affects the amount of sorbed liquid. Water and methanol molecules may be inserted between metal ions and the anionic sulfonate groups leading a complete dissociation of all ion pair. In this case, the ion–sulfonate group interactions would be relatively weak.

On the other hand, a decreased solvent content would be expected to cause stronger interaction between metal cations and the anionic groups in the membrane [22]. One possible explanation might be that cations of higher atomic number have higher affinity to the membrane than those of lower atomic numbers. Thus, it is expected that membrane exchanged with cations of higher affinity shows lower solvent content [23]. Finally, it is worth mentioning here that the behavior observed when using aqueous solutions 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 counter ion [19,24,25]. With regard to the solubility values, it is found that, in spite of the different pretreatments of the membrane used, the swelling data obtained in the present study when using aqueous solutions are in agreement with the literature values [22,25,26].

It is well known that the cations from solution interact with the 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. For alkali metal and alkaline earth ions, it seems that these cations do not have a strong preference for either solvent molecule in water–methanol mixtures, i.e. the composition of the primary solvation sheath of the cations does not differ appreciably from the stoichiometric composition of the mixed solvent [27].

With regard to the effect of methanol in the sorption properties of the membrane, several researchers found that the water uptake in the membrane remains the same as that of pure water and only the methanol uptake increases with the increase in concentration of methanol [28–31]. Moreover, the water resides completely in the hydrophilic domains of the polymer, whereas the methanol is also soluble to a certain extent in the hydrophobic fluorocarbon backbone.

According to the Gierke model [12] and to the network model developed by Eikerling et al. [32,33], highly phase separated ionomer membranes like Nafion can be interpreted as porous media consisting of the sponge-like hydrophobic polymer backbone which surrounds the well-connected hydrophilic domains allowing for species transport. Thus, it is reasonable to think that salt water–methanol solutions may create pores of different sizes upon the hydration/solvation of sulfonic groups in the membrane, so it may be interesting to estimate the membrane porosity. The wet membrane porosity can be defined as the volume of the solution within the membrane per unit volume of the wet membrane [19,34]:

$$
\varepsilon = \frac{(m_W - m_D) \rho_m}{(m_W - m_D) \rho_m + m_D \rho_S}
$$

where $\rho_m$ and $\rho_S$ are the density of the dry membrane and the density of the ternary solution that enters into the membrane.

The masses of the swollen, $m_W$, and dry membrane, $m_D$, were determined experimentally. The density of the dry Nafion membrane is taken as 1.98 × 10$^3$ kg/m$^3$ [19]. Literature values were used to calculate the density of the ternary solutions within the membrane [35,36]. This is an approximation since the density of the sorbed solution may not be equal to its bulk value. Finally, membrane porosities calculated for Nafion 117 membrane are summarized in Table 2 as a function of the external solvent composition. The analysis of the data shows that the composition of the solvent has a significant impact on the wet membrane porosity, with an increase with methanol that can reach 50%.

This indicates that the dimensions of channels connecting the swollen ionic clusters increases systematically for membrane with increasing the methanol content. Nandan et al. [37] found that the size of the clusters was bigger for a methanol-swollen membrane than that for a water-swollen membrane. On the other hand, the influence of the type of salt in the membrane porosity is small because the variation is less than 15%, with the excep-

Table 2
Membrane void porosity $\varepsilon$ as a function of the wt.% of methanol on solvent for different chloride salts

<table>
<thead>
<tr>
<th>Methanol (wt.%)</th>
<th>LiCl</th>
<th>NaCl</th>
<th>CsCl</th>
<th>MgCl$_2$</th>
<th>CaCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.34 ± 0.03</td>
<td>0.30 ± 0.03</td>
<td>0.21 ± 0.03</td>
<td>0.34 ± 0.03</td>
<td>0.31 ± 0.03</td>
</tr>
<tr>
<td>25</td>
<td>0.42 ± 0.04</td>
<td>0.40 ± 0.04</td>
<td>0.29 ± 0.04</td>
<td>0.40 ± 0.04</td>
<td>0.38 ± 0.04</td>
</tr>
<tr>
<td>50</td>
<td>0.45 ± 0.04</td>
<td>0.42 ± 0.04</td>
<td>0.30 ± 0.03</td>
<td>0.42 ± 0.04</td>
<td>0.40 ± 0.04</td>
</tr>
<tr>
<td>75</td>
<td>0.48 ± 0.04</td>
<td>0.46 ± 0.04</td>
<td>0.32 ± 0.03</td>
<td>0.42 ± 0.04</td>
<td>0.41 ± 0.04</td>
</tr>
</tbody>
</table>
tion of the CsCl solutions. This could be explained by the small hydration ability of the Cs⁺ ion. Since there is no extensive solvation shell on this cation, it can approach the membrane sulfonate groups more closely, leading to stronger cation–anion interaction, which causes a smaller swelling and, consequently, a lower value for the membrane porosity. Furthermore, the results are in agreement with those reported by others [19,25] when using binary salt-water solutions.

3.2. Permeation

The measurement of the flux through the membrane was performed as described in Section 2. An illustrative curve depicting the time evolution of the volume change in the left chamber, \(v(t)\), is shown in Fig. 1. The curve has at short times a transitory followed at longer times by a steady state region, in which the volume change is a linear function of time. In general, stationary flows through the membrane were attained after 1 h. The volume flow through the membrane was estimated from the slope of the permeation curve, in the steady state region, by using the following expression:

\[
J_V = \frac{1}{A} \frac{dv}{dt} \tag{3}
\]

where \(A\) is the effective surface area of the membrane. The regression analysis of the data gives correlation coefficients of at least 0.99. Mean deviation in determining the volume flow was 5%. The overall volume flow values obtained are shown in Figs. 2–4 as a function of pressure difference across the membrane. In the case of electrolyte aqueous solutions (Fig. 2a and b), the overall flux varies significantly depending on the type of cation in solution. As an example, for alkali metal cations, the permeation fluxes (in \(m^3/m^2s\)) measured for a pressure difference of 22 kPa are \(1.75 \times 10^{-8}\), \(1.07 \times 10^{-8}\) and \(0.55 \times 10^{-8}\) for LiCl, NaCl and CsCl aqueous solutions, respectively. So, the following sequence is observed: LiCl > NaCl > CsCl. In the case of alkaline earth cations, although the differences are relatively small, it seems that the flux of the solutions with MgCl₂ is higher than that contains CaCl₂. For example, for a pressure difference of 27 kPa, the volume fluxes (in \(m^3/m^2s\)) are \(0.98 \times 10^{-8}\), \(0.96 \times 10^{-8}\) for MgCl₂ and CaCl₂ solutions, respectively. These results indicate that not only the size of the cation is a factor in determining the permeation through the membrane, but also the valence of the cation can be important. On the other hand, in the case of ternary solutions (Figs. 3–5), the trend is the same as found for aqueous solutions, but the permeation flow increases with the methanol content of the solutions. The influence of the solvent composition on the transport properties of the membrane was reported and discussed in our previous work [18].

The comparison of sorption and permeation results shows that the solubility of the ternary solutions follows the same sequence with the type of ion and the solvent composition as that obtained for the volume flow through the membrane. This fact indicates that the degree of liquid sorption by the membrane plays an important role in determining the membrane transport properties. One possible explanation might be that, when the level of membrane sorption rises, the solvent influences the ionomer structure, leading to an increase of the cluster
and channel size, which brings about an increase of the mobility of water, methanol and solvated ions in the membrane. This fact may explain the enhancement of the permeation flow through the membrane with both the methanol content and the ion type. We think that it is likely that the structure of the swollen membrane involves broader solvent filled channels, according to Gierke model, which brings about the variation of the membrane porosity observed in Table 2. This fact facilitates the liquid and ion transport through the complex structure of cross-linked channels, consequently, a higher flux through the Nafion membrane is expected. The relation between both the permeability and the solvent content in polymer electrolyte membranes and the size of their hydrophilic pores has also been shown in a number of papers [17,38,39].

As it was mentioned above, the volume flow measured is a combination of the transport of mixed solvent and solvated ion. Taking into account that the concentration of ions within the membrane is much less than that of solvents, because of the very low concentration of salt in the external solution, the diffusive flux of ions in the membrane can be neglected compared to the solvent flux, under the experimental conditions given in the measurements. Then, the transport through the membrane driven by a pressure gradient is described by the following equation [33,40]:

$$J_V = \frac{k c_S \Delta p}{\mu l}$$  \hspace{1cm} (4)

where $k$ is the solvent permeability in the membrane, $c_S$ the concentration of solvent in the membrane, $\mu$ the viscosity coefficient of the solvent, $l$ the membrane thickness, and $\Delta p$ is the pressure difference across the membrane. Eq. (4) implies that the change in the flux through the membrane reflects the changes in the viscosity solution, membrane permeability and the solvent content of the membrane.

The analysis of the data in Figs. 2–5 shows a linear dependence between the volume flux and the pressure difference as predicted by Eq. (4). Nevertheless, in some cases, it is observed a positive deviation from a linear behavior at high $\Delta p$ values, especially for high-methanol content solutions. This behavior can be also observed in other organic aqueous electrolyte systems when a Nafion membrane is used [18]. On the other hand, Eq. (4) allows estimating the permeability as a property influenced by the microstructure of the membrane, in contrast to other studies in which the permeability depends also on the solvent
content of the membrane [18,33,39]. Thus, by complying with the requirements of linearity of Eq. (4), the slope \( \frac{dJ}{dp} \) was calculated using the experimental results. By using these data in convenient units, if the viscosity of the solution and the solvent content of the membrane are considered to be known, the permeability can be calculated by using Eq. (4). The viscosity coefficient of the internal solution is taken as the viscosity of the external solution. The viscosity of the salt–water–methanol solutions were calculated by using the mixing rules developed by Wang et al. [41]. To calculate the liquid content of the membrane, it is assumed that the solvent sorbed by the membrane has the same composition as the solution outside the membrane. This assumption is supported by different studies, which have been shown that there is no selective sorption by a Nafion membrane when using water–methanol mixtures [42,43]. Finally, the estimated permeability coefficients are summarized in Table 3 as a function of the methanol content of the solution. It is worth mentioning that our estimated values of the permeability are of the same order of magnitude as that reported by Verbrugge and Hill [14–16], they measured a value of \( 1.16 \times 10^{-19} \) m\(^2\) for water permeability in a Nafion 117 membrane in H\(^+\) form.

With regard to the influence of the solvent composition on the membrane permeability, it is found that the permeability increases with the methanol content of the mixtures, regardless the dissolved salt. As the methanol concentration increases, the cluster and channel size in the membrane are increased, which brings about an increase of the mobility of solvents in the membrane. Moreover, as the methanol experiences stronger interaction with the Nafion internal structure than water, the polymer can be plasticized, thus increasing the mobility of the pendant chains [44]. In addition, the membrane swelling (i.e. porosity) increases with methanol, as can be observed in the data of Table 2. All these facts determine the increase of the apparent permeability coefficient with the methanol content of the solutions [45].

The influence of the salt type in the membrane permeability is not straightforward because the variation in the permeability coefficient is within the experimental error. In the case of alkali metal chloride salts, it may be stated that the permeability coefficient follows the trend \( k(\text{LiCl}) > k(\text{CsCl}) > k(\text{NaCl}) \), with the exception of the solution with 75 wt.% methanol content. In the case of alkaline earth salts, the permeability coefficient for \( \text{MgCl}_2 \) and \( \text{CaCl}_2 \) solutions is nearly the same, for a given solvent composition. On the other hand, values of \( k \) for \( \text{NaCl} \) and \( \text{CaCl}_2 \) are practically the same, suggesting that the valence has a negligible influence on the membrane permeability. The comparison of data in Tables 2 and 3 reveals that the variation in membrane swelling is not closely related with the membrane permeability variation. For example, for alkali metal chloride salts, the membrane swelling follows the trend \( \text{LiCl} > \text{NaCl} > \text{CsCl} \), while the permeability follows the trend \( \text{LiCl} > \text{CsCl} > \text{NaCl} \). In order to clarify the effect of salt type on the membrane permeability, the permeability coefficient is plotted as a function of the membrane porosity for the different electrolytes in Fig. 6. In general, it is observed an increase of solvent permeability with membrane porosity. Moreover, the differences between the data obtained with different electrolytes are not physically relevant, with the exception of Cs\(^+\) electrolyte. In this case, the lowest membrane porosity is associated with the highest membrane permeability. It is known that the lower swelling favors the interaction between counterion and the sulfonate groups in the polymer, and so, a decrease of the effective fixed charge of the membrane. It could be speculated that the decrease in the sul-

### Table 3
Membrane permeability \( k \left(10^{-19} \text{ m}^2\right) \) as a function of the wt.% of methanol on solvent for different chloride salts

<table>
<thead>
<tr>
<th>Methanol (wt.%)</th>
<th>LiCl</th>
<th>NaCl</th>
<th>CsCl</th>
<th>MgCl(_2)</th>
<th>CaCl(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.44 ± 0.05</td>
<td>0.38 ± 0.04</td>
<td>0.42 ± 0.05</td>
<td>0.39 ± 0.04</td>
<td>0.36 ± 0.04</td>
</tr>
<tr>
<td>25</td>
<td>2.1 ± 0.2</td>
<td>1.6 ± 0.2</td>
<td>2.0 ± 0.2</td>
<td>1.6 ± 0.2</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td>50</td>
<td>5.0 ± 0.5</td>
<td>3.8 ± 0.4</td>
<td>4.1 ± 0.4</td>
<td>3.9 ± 0.4</td>
<td>3.8 ± 0.4</td>
</tr>
<tr>
<td>75</td>
<td>5.1 ± 0.5</td>
<td>4.7 ± 0.5</td>
<td>4.4 ± 0.5</td>
<td>4.9 ± 0.5</td>
<td>4.7 ± 0.5</td>
</tr>
</tbody>
</table>
the exception of the CsCl solutions, which is due to the small
of the type of salt in the membrane porosity is not relevant, with
increases with the methanol content. In contrast, the influence
channels connecting the swollen ionic clusters in the membrane
content of the solutions. This indicates that the dimensions of
the solubility is independent of the valence of the cation.
to Ca2+, regardless the composition of the solvent. Moreover,
the size of naked counterions from Li+ to Cs+, and from Mg2+
observed that the membrane swelling decreases with increasing
the methanol content of the mixtures, regardless the dissolved salt.

Fig. 6. Solvent permeability coefficient vs. membrane porosity for solutions
with different chloride salts.
fonate group density of the membrane may affect the membrane
permeability. However, to achieve a better understanding of the
influence of the type of electrolyte on the membrane permeabil-
ity coefficient, more information about the interaction between
cations and the fixed charge groups in the membrane is needed.

4. Conclusions

The amount of solvent uptake increases significantly with
the methanol content of the solution. In contrast, the membrane
swelling is little influenced by the type of electrolyte. It was also
observed that the membrane swelling decreases with increasing
the size of naked counterions from Li+ to Cs+, and from Mg2+
to Ca2+, regardless the composition of the solvent. Moreover,
the solubility is independent of the valence of the cation.
The wet membrane porosity increases with the methanol
content of the solutions. This indicates that the dimensions of
channels connecting the swollen ionic clusters in the membrane
increases with the methanol content. In contrast, the influence
of the type of salt in the membrane porosity is not relevant, with
the exception of the CsCl solutions, which is due to the small
hydration ability of the Cs+ ion.
The permeation fluxes through the membrane depend not
only on the size of the cation but also on the valence of the cation.
Moreover, the permeation flow increases with the methanol con-
tent of the solutions.
The membrane permeability coefficient increases with the
methanol content of the mixtures, regardless the dissolved salt.
This is attributed to both the increase of the mobility of solvents
in the membrane and the increase of the mobility of the polymer
pendant chains. In contrast, the influence of the salt type in
the membrane permeability is not straightforward. Nevertheless, it
seems that the membrane permeability is little affected by the
type of electrolyte.

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