



Swelling and electro-osmotic properties of cation-exchange membranes with different structures in methanol–water media

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ABSTRACT

Electro-osmosis experiments through three cation-exchange membranes with different morphology and similar electric properties have been performed using methanol–water solutions under different experimental conditions. The influence on the electro-osmotic transport of the percentage of methanol on solvent with two different electrolytes, NaCl and LiCl, has been studied. The experimental results show that the presence of methanol in the solutions affects strongly the electro-osmotic flow, and this influence is different depending on the membrane morphology. Correlations among electro-osmotic permeability, swelling behavior, and cell resistance are studied for these membrane systems at different percentages of methanol in solvent.

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1. Introduction

When an electric current circulates through the system

Anode|Solution|Ion-exchange Membrane|Solution|cathode (1)

a solvent flow associated with the transport of the corresponding ions takes place. Solvent is transported either by an association with the transported ion, such as hydration sphere, or by hydrodynamic pumping due to the movement of the ions and associated solvent molecules. This phenomenon is known as electro-osmosis and has been widely studied in the literature on aqueous media, especially within the framework of the thermodynamics of irreversible processes [1].

According to this theory, the relation between the total volume flow, J_V , and the electric current, I , passing through the membrane in the absence of a hydraulic pressure difference, $\Delta P=0$, is called apparent or measured electro-osmotic permeability, W [1,2]:

$$W = \left(\frac{J_V}{I} \right)_{\Delta P=0} \quad (2)$$

Knowledge of transport rates of ions and solvent in ion-exchange membranes is necessary for intelligent designs in various different systems. Particularly, electro-osmosis is significant in fuel cells

because it directly impacts water management. In the case of direct methanol fuel cells (DMFC), the electro-osmotic behavior is especially relevant since it is an important contribution to the methanol crossover from the anode to the cathode through the polymer membrane which causes fuel waste and polarization loss at the cathode [3,4]. DMFC currently uses Nafion membranes as a polymeric proton conducting membranes. These membranes offer high proton conductivity, good chemical and thermal properties, but they present a high methanol permeability [5,6]. For this reason, in recent years, there has been an intensive research effort for the development of alternative membranes, with potentially lower costs, to reduce methanol crossover. However, in most of the studies only the diffusion contribution is analyzed, probably due to the difficulty of measuring the electro-osmotic component to the crossover [7], and, in general, it has not been investigated to the same extent that other fuel cell relevant transport properties. Moreover, the study of the transport phenomena in non-aqueous media is fundamental in order to gain a better understanding of the crossover mechanism.

In this work, the swelling and the electro-osmotic behavior in different methanol–water electrolyte solutions of three commercial cation-exchange membranes with different structures have been studied. The aim is to study the influence of the membrane structure on the electro-osmotic behavior and to establish relations between the swelling and the electro-osmotic permeability as a function of the membrane structure. It would permit to obtain information about electro-osmotic behavior from the swelling studies of the membrane.

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Table 1
Membrane features provided by the manufacturer

Membrane	Thickness ($\times 10^{-3}$ m)	Water uptake (%)	Fixed charge (kmol m^{-3})	Capacity (mequiv g^{-1}) dry membrane
Nafion 117	0.183	35	1.13	0.94
MK40	0.480	40	1.84	2.6
CR67 HMR-412	0.570	46	1.6	2.1

2. Experimental

2.1. Materials

Three different commercial cation-exchange membranes with similar electric properties but different morphology were tested in this work. The Nafion 117 membrane (NF117), with a nominal equivalent weight of $1100 \text{ g equiv}^{-1}$, is a homogeneous cation-exchange membrane consisted of a polytetrafluoroethylene backbone and long fluorovinyl ether pendant side chains regularly spaced, terminated by a sulfonate ionic group. There are no cross-links between the polymers. The MK-40 membrane (MK40), produced by NOP Plastmassy, Russia, is a sulphonic polystyrene divinylbenzene cation-exchange membrane of heterogeneous type prepared by the inclusion of a finely ground ion-exchange resin in a PE binder. The Ionics CR67 HMR-412 membrane (CR67) is a heterogeneous cross-linked sulfonated copolymer of vinyl compounds cast in homogeneous films on synthetic reinforced fabrics. The thickness, water content and ion-exchange capacity provided by the manufacturer for these membranes are given in Table 1. Fig. 1 shows the microscopic images of the membrane surfaces by using a scanning electronic microscope (SEM images) for the three membranes used in this work. The different structure of the three membranes can be observed in this figure.

The materials used in the experiments were solutions of water and methanol at different compositions. Sodium and lithium chlorides (NaCl and LiCl) were used as electrolytes to provide conductivity. These salts were selected due to the smallest size of the counterion, and with the aim of analyzing the influence of the ion nature. Pure pro-analysis grade chemicals and distilled pure water were used. Before measurements were carried out, the methanol–water solutions were degassed in order to prevent the bubbles formation during the measurement process.

2.2. Swelling measurements

In order to determine the total solvent uptake by the membranes, a swelling study was performed with water and methanol–water mixtures and with 0.01 M LiCl and NaCl solutions in mixtures of methanol and water with different methanol percentages, in order to analyze the effect of the electrolyte. Before the experiments the membrane samples were dried in an oven at 100°C for 24 h. After that, the samples were immersed in a closed bottle containing the corresponding solution and allowed to equilibrate at room temperature. After 48 h of immersion, the swollen membrane was taken out of the solutions, wiped carefully with filter paper and weighted. After each run, the membranes were dried in an oven at 100°C for 24 h and weighted again. The increase in weight was equal to the weight of the liquid sorbed by the membrane. The swelling ratio, S (%), was calculated from the weight of the swollen and the dry membrane samples according to the expression

$$S = \frac{m_w - m_d}{m_d} \times 100 \quad (3)$$

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.

2.3. Electro-osmotic permeability and voltage–current curve measurements

The experimental device used in this research was similar to one used in a previous work [8]. The main part of the experimental device was a cell, which basically consisted of two equal cylindrical glass chambers. The volume of each container was about $4 \times 10^{-4} \text{ m}^3$, which is large enough to ensure that the concentration changes in the solution during the measurements may be considered negligible. The membrane was mounted in a Teflon holder, which was positioned between the two chambers. O-rings were employed to ensure there were no liquid leaks in the whole assembly. The effective surface area of the membrane exposed to the flow was $5.7 \times 10^{-4} \text{ m}^2$.

Each chamber is provided with three communication orifices to the exterior. In order to measure the volume flow, two L-shaped capillary tubes were introduced in one of the orifices of each chamber, in such a way that the horizontal portions of the tubes were at the same height. A reversible Ag/AgCl electrode with a large surface was introduced in other of the orifices of each chamber on both sides of the membrane to inject an electric current. These electrodes consisted of a 14–15 turn spiral wire (1-mm diameter) prepared according to a method described in detailed elsewhere [9]. These electrodes could be used for a long time. The third orifice of each chamber stated closed during the measure of the electro-osmotic flow.

All the experiments were carried out under isothermal conditions at 298 K. Temperature requirements were achieved by immersing the cell in a water thermostated bath. In order to improve the uniformity of the temperatures and concentrations inside each chamber, the solutions were stirred by a magnetic stirrer assembly. The stirring rate in all the experiments was about 365 rpm. Under these conditions, the temperature was constant within ± 0.1 K.

Prior to each experiment, the membrane was immersed, for a minimum of 24 h, in the solution in order to achieve equilibrium. Once the membrane was positioned in the cell, both chambers were filled with the solution. When the system was stabilized at the selected temperature and stirring rate, a constant electric current was made to pass through the membrane. The volume change rate on both sides of the membrane, caused by the electric current, was determined by measuring the time displacement of the solution meniscus in the glass tubes connected to each chamber.

Taking into account the volume change due to the electrochemical reactions at the Ag/AgCl electrodes, the volume change rates of the cathodic and anodic compartments, $\Delta \dot{V}_c$ and $\Delta \dot{V}_a$, respectively, are given by

$$\Delta \dot{V}_c = Jv + \frac{I}{F}(\bar{V}_{\text{Ag}} - \bar{V}_{\text{AgCl}}) \quad (4)$$

$$\Delta \dot{V}_a = -Jv + \frac{I}{F}(\bar{V}_{\text{AgCl}} - \bar{V}_{\text{Ag}}) \quad (5)$$

where I is the electric current flowing through the membrane, F is the Faraday constant, and \bar{V}_{Ag} and \bar{V}_{AgCl} are the partial molar volumes of Ag and AgCl, respectively.

If one takes into account that $\bar{V}_{\text{AgCl}} - \bar{V}_{\text{Ag}} = 15.5 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, the following relationship is obtained from

Eqs. (2), (4) and (5):

$$W(\text{m}^3/\text{C}) = \left(\frac{J_V}{I} \right) + 1.6 \times 10^{-10} \quad (6)$$

where J_V is the mean volume change per unit time, given by

$$J_V = \frac{|\Delta \dot{V}_a| + |\Delta \dot{V}_c|}{2} \quad (7)$$

Eq. (6) may be used for the determination of the apparent or measured electro-osmotic permeability.

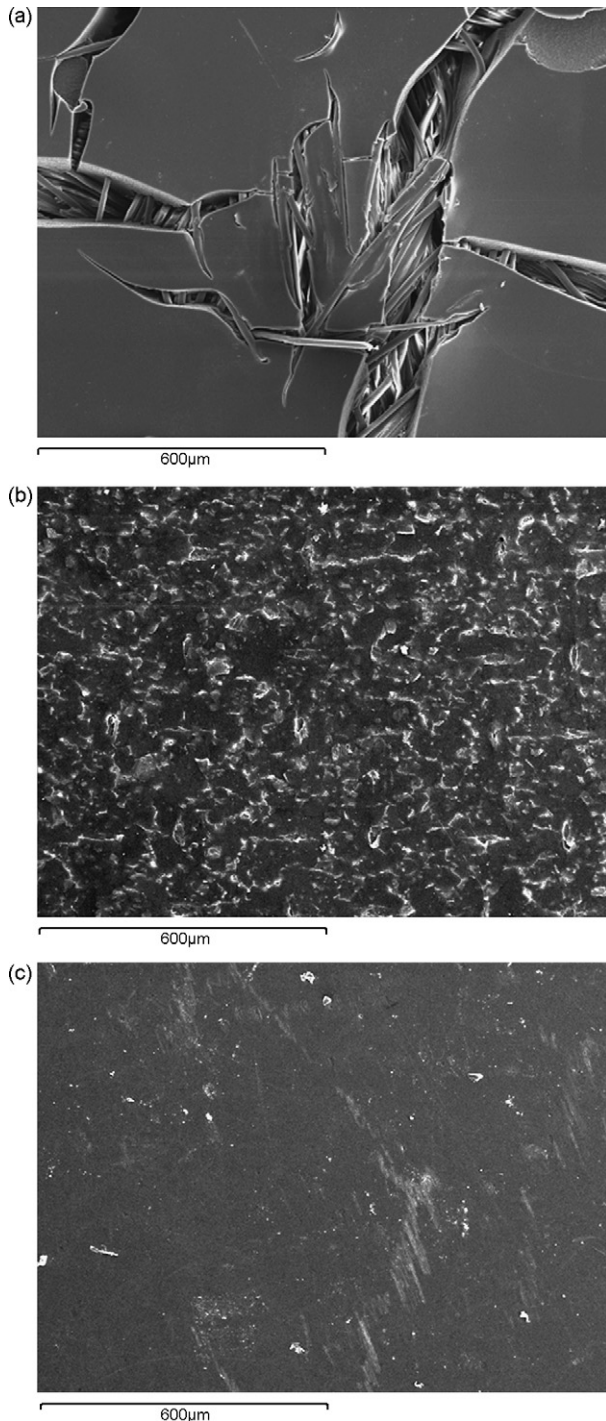


Fig. 1. SEM images of the membrane surface of the three membranes used in this work: (a) CR67; (b) MK40; and (c) NF117.

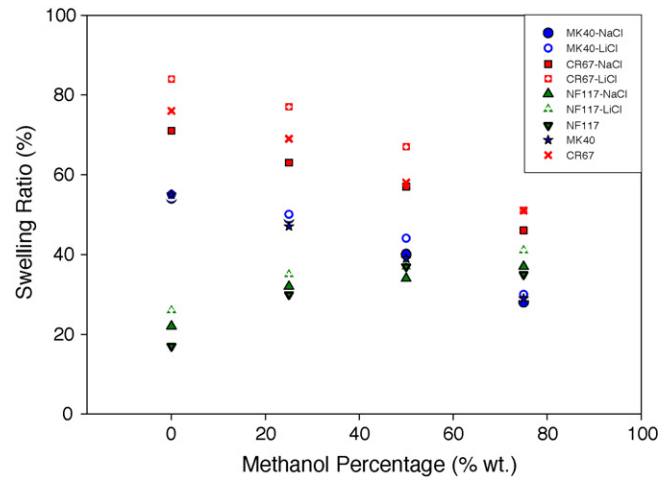


Fig. 2. Swelling ratio as a function of the methanol percentage on solvent for the three membranes.

The experimental device was designed to make possible the measure of the voltage–current curves under each experimental condition using the four-electrode configuration. To this end, a reversible Ag/AgCl electrode was introduced in the third orifice of the each chamber to measure the electric potential difference. These electrodes consisted of two linear Ag wires of approximately 4-mm longitude and 0.5-mm diameter and they were also prepared by the usual method [9].

3. Results and discussion

3.1. Swelling ratio

In order to determine the total solvent uptake by the membranes, a swelling study was performed by using different solutions. Water and mixtures of water and methanol with a methanol content of 25, 50 and 75 wt.% were used, whereas in presence of electrolyte, the concentration of salt was kept at 0.01 M. The results obtained are shown in Fig. 2. In the case of water and aqueous electrolyte solutions, the swelling follows the sequence: CR67 > MK40 > NF117. However, the influence of the methanol percentage on solution is different for the three membranes. For the reinforced CR67 and MK40 membranes, the swelling ratio decreases with an increase of the methanol content, while the opposite behavior is observed for the NF117 membrane. This result is similar in presence and in absence of electrolyte. The results also showed that the influence of the ionic form of the membrane is, in general, similar for the three membranes, and the higher the cation size, the lower the swelling. However, the influence of the electrolyte nature is stronger for the CR67 membrane. Moreover, this membrane is less influenced by the nature of the electrolyte as methanol concentration increases. The influence of this parameter is small, and practically independent on the methanol content, for the NF117 membrane. For the MK40 membrane, the swelling properties are virtually independent of the ionic form of the membrane for either of the electrolytes. The general trend of the swelling ratio with the methanol percentage is not affected by the presence or nature of the electrolyte.

3.2. Voltage–current curves

The voltage–current (V – I) curves for the studied system (membrane plus solutions) were determined under different experimental conditions in order to make sure that the electric current

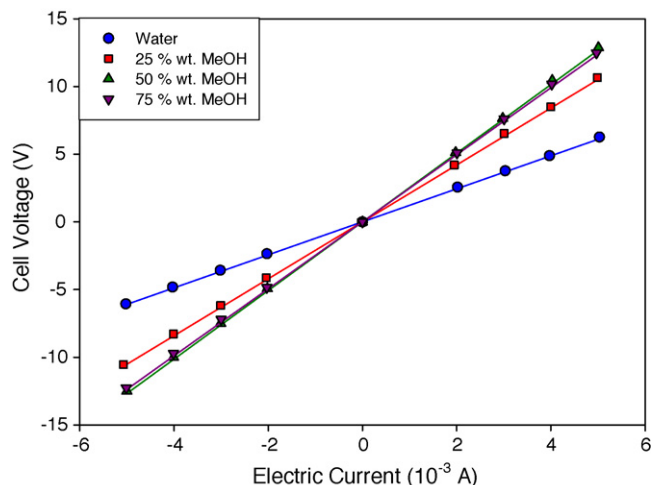


Fig. 3. Current–voltage curves for membrane Nafion 117 with LiCl 0.01 M at different methanol percentages on solvent.

used was in the ohmic region and the concentration polarization effect on the electro-osmotic permeability could be neglected [10]. Fig. 3 shows, as an example, the curves $V-I$ obtained for membrane NF117 with LiCl at different methanol percentages on solution. In all cases, a linear behavior between current and voltage was observed. From these voltage–current curves, it was possible to estimate, using the Ohm law, the value of the ohmic resistance of the cell. The results are shown in Fig. 4 for the three membranes as a function of the methanol percentage on solution. The specific conductivities in 0.1 M NaCl are 3.43, 5.14 and 11 mS cm^{-1} for MK40, CR67 and NF117 membranes, respectively [11,12]. As can be expected, the higher the conductivity of the membrane, the lower the cell resistance at the same solution conditions.

For all the membranes, the classification order of the cell conductivity remains independent on the membrane type: $k(\text{Na}^+) > k(\text{Li}^+)$. In accordance with theoretical previsions and whatever the membrane model this order varies in the same direction that the equivalent limiting conductivity of the counterion in aqueous solutions [13], or its hydration number in the membrane. This is in agreement with the results in [14], where the transport numbers of Na^+ and Li^+ were determined in MeOH/water media, and a higher value was found for Na^+ .

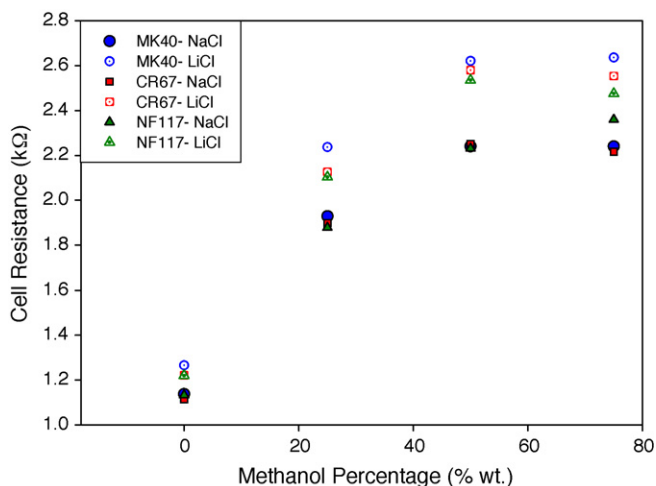


Fig. 4. Ohmic resistance of the cell as a function of the weight methanol percentage on solvent for the three membranes.

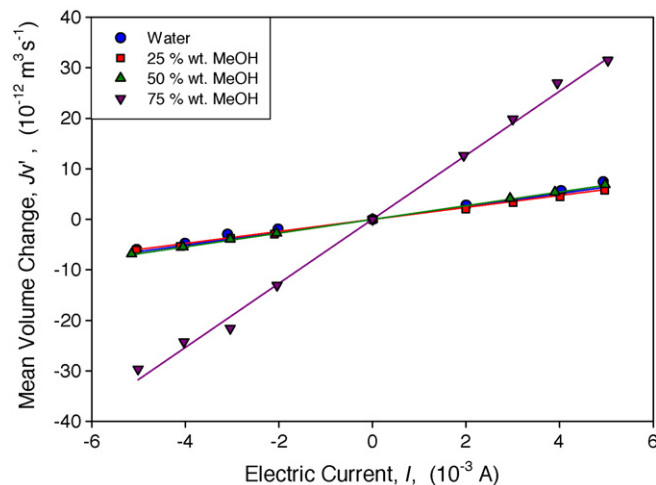


Fig. 5. Volume change rate, J_v , vs. electric current at different methanol percentages. The data correspond to the MK40 membrane and a NaCl 0.01 M solution.

In addition, the cell resistance increases when the methanol percentage increases, with a similar behavior for the two electrolytes. The rate of the increase is higher at methanol percentage lower than approximately 50%. At higher percentages of methanol the slope decreases. This behavior may be due to the dependence of the conductivity of the solution on the methanol percentage, where is observed that a minimum is presented at percentages around 50% [15], and it is in agreement with previous results [8,16]. This observed decrease in specific conductivity is due to the decrease in the dielectric constant of the solvent with increasing methanol content and, so, to the decrease in the ability of the solvent to dissolve the electrolyte [17]. Taking into account that the membrane resistance depends on the conductivity of the solutions in contact with it [18], it is expected a similar dependence of the membrane specific conductivity on the percentage of methanol. These results show that the influence of the methanol content of the solutions in the cell resistance, and thus in the membrane conductivity, does not depend on its morphology.

3.3. Electro-osmotic permeability

The volume changes in the cathodic and anodic compartments were measured when the steady state was reached. The steady state was considered reached when, in the same time interval, the same displacement of the meniscus in the capillary tubes connected to each compartment was obtained. The time necessary to reach the steady state depended on the experimental conditions, and it varied from a few minutes until more than 1 h. In all the cases a linear dependence was observed in the steady state. The volume change rates were calculated from the slope of the straight lines obtained from the linear fits of the experimental data. In all the cases, the reproducibility of the measurement was checked.

The volume change rates at different electric currents have been measured with 10^{-2} M LiCl and NaCl and different methanol percentages. As an example, the experimental values obtained for the MK40 membrane with pure water, 25, 50 and 75 wt.% methanol and NaCl have been shown in Fig. 5. In general, the electro-osmotic flux through the membrane, which is composed by a mixture of methanol, water and ions, will depend on the composition of the external solution. Our experimental method does not allow to determine accurately the individual flux of each solvent. However, in agreement with the results obtained for other authors [19], the difference in transport behavior for water

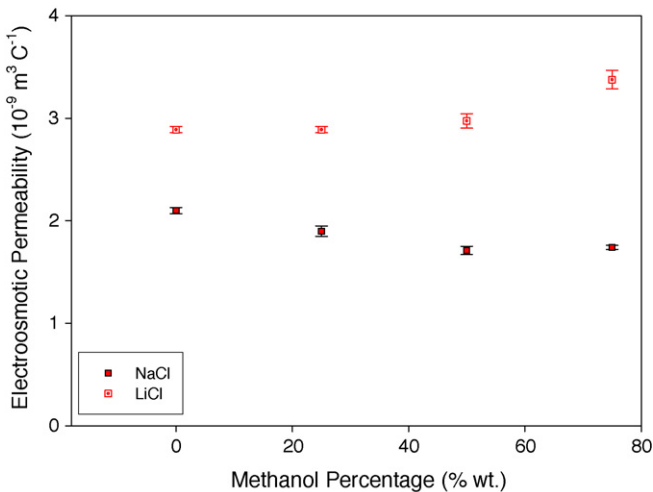


Fig. 6. Electro-osmotic permeability as a function of the methanol percentage on solvent for membrane Ionics CR67.

and methanol should be relatively low, due to the similarity of molecules.

Under all the experimental conditions, a linear dependence is found between the volume change rate and the applied electric current, as it would be expected in a region where the electro-osmotic permeability was constant. In this linear region, we can express:

$$J_V (\text{ml/s}) = \vartheta I \quad (8)$$

and from Eq. (6), the parameter ϑ is related to the mean electro-osmotic permeability W as follows:

$$\vartheta = W (\text{in } \text{m}^3 \text{ C}^{-1}) - 1.6 \times 10^{-10} \quad (9)$$

Eq. (9) permits to determine a mean value of the measured W for each electrolyte and percentage of methanol for the three membranes used. The obtained results are presented in Figs. 6–8, where W is shown vs. methanol percentage for the three membranes, CR67, MK40 and NF117, respectively, with LiCl and NaCl.

In general, the influence of the electrolyte nature is similar for the three membranes. At a given methanol percentage, the electro-osmotic permeability is higher for the electrolyte of lower cation size, in agreement with the results found in literature [14,20]. An exception is observed in the case of the membrane MK40 with

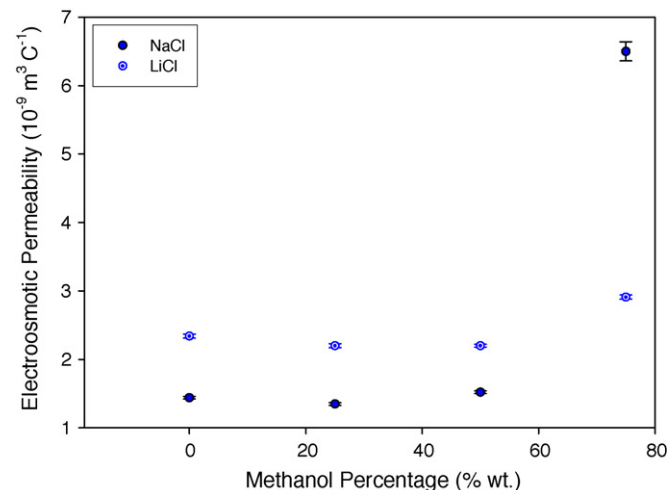


Fig. 7. Electro-osmotic permeability as a function of the methanol percentage on solvent for membrane MK40.

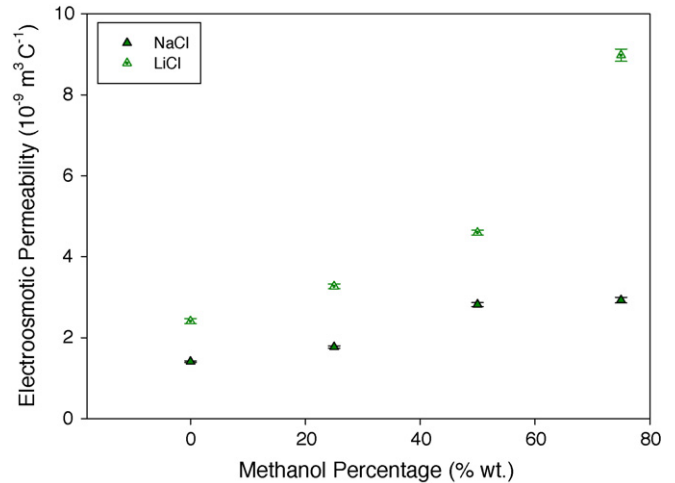


Fig. 8. Electro-osmotic permeability as a function of the methanol percentage on solvent for membrane NF117.

NaCl, where a higher value of the electro-osmotic permeability is obtained for NaCl at 75% of methanol. In general, a higher influence of the electrolyte nature is observed at the higher methanol percentages.

The influence of the solution methanol percentage is different for the three membranes and also depends on the electrolyte solution nature. In the case of LiCl solutions, the behavior is similar for the heterogeneous reinforced membranes CR67 and MK40. For these membranes, the electro-osmotic coefficient decreases when the methanol percentage increases up to around 50%, and the opposite trend is found at higher percentages, observing a minimum value at certain methanol percentage. For NaCl solutions, the behavior at lower methanol percentages is qualitatively similar for the heterogeneous membranes. At higher percentages, however, a strong increase is observed for MK40 membrane, as it was previously said.

For the homogeneous NF117 membrane, the electro-osmotic permeability increases with the increase of the alcohol content, independently of the electrolyte type. A different behavior with LiCl or NaCl is observed, however, at the highest methanol percentages. In the case of LiCl, the slope increases with the methanol percentage. With NaCl, although an increase of the electro-osmotic permeability is also observed, this increase becomes less pronounced at the highest methanol percentages.

The differences observed in the electro-osmotic behavior of the three membranes with the methanol percentage in solution may be due to their morphological differences, since the electrical properties are similar as it is evidenced from Fig. 4. This is in agreement with the results in [14], where the authors observed differences which attributed to chemical and structural effect of the membranes, and demonstrated the utility of electro-osmotic drag coefficients as a probe for polymer microstructure [7,21].

For NF117 membrane there is a strong relation between electro-osmotic transfer and swelling, in that the higher the swelling, the higher the electro-osmotic transport. This influence is higher for the electrolyte with the lowest cation size. According to the literature, in these membranes, the water swelling is much lower than that of alcohol, but the methanol besides the hydrophilic sulfonic groups has a certain solubility in the hydrophobic perfluorinated domains. The convective contribution to the solvent transport in the membrane should be considered. These results are in agreement with other authors [22]. The increase of the electro-osmotic coefficient with rising methanol concentrations may be because

higher methanol concentrations lead to an increase of the channel diameters in the membranes, and the ions can be carried along in the solvating envelope more easily. These results are in agreement with other found in the literature [19].

For CR67 and MK40 membranes, the relation between electro-osmosis and swelling is, in general, little significant. For these membranes, a decrease of the swelling with the methanol content is observed, and thus, the increase of the channels diameters in the membrane would not happen. In this case, the influence of the methanol content on the electro-osmotic transport may be mainly due to the influence of the methanol presence on the electrical properties of the membrane. These results are in agreement with the dependence observed for the effective membrane charge density and the cation-to-anion mobility ratio in the membrane [23], and for the limiting current [15] with the methanol percentage of the solutions; this behavior being attributed to the diminution in the specific conductivity due to the decrease in the dielectric constant of the solvent with increasing methanol, and so, to the decrease in the ability of the solvent to dissolve the electrolyte [17]. We have not any satisfactory explanation for the behavior observed for the MK40 membrane at 75% methanol percentage, where a decrease of the solubility is observed together a high increase of the electro-osmotic permeability. It would be probably due to chemical interactions with the membrane structure.

These results indicate that the degree of swelling seems to have less influence in the electro-osmotic behavior of highly cross-linked membranes. For non-cross-linked membrane, an increase of the swelling leads to a higher electro-osmotic drag.

4. Conclusions

Differences have been observed in the swelling and electro-osmotic behaviors of three commercial cation-exchange membranes of different morphology. No significant influence of the membrane structure has been found in the cell voltage.

The electro-osmotic behavior of three cation-exchange membranes has been studied under different experimental conditions. The electro-osmotic permeability depends on the solution methanol content, but this dependence is function of the membrane structure. For the reinforced membranes, the membrane swelling has a small influence on the electro-osmotic permeability, which showed a minimum at a certain percentage of methanol. For non-cross-linked membrane, higher the swelling, higher the electro-osmotic transfer, and an increase of the electro-osmotic permeability with the methanol percentage on solvent was observed.

The influence of the ionic form of the membrane is, in general, similar for the three membranes, and higher the cation size, lower the swelling, the cell resistance, and the electro-osmotic permeability, independently of the membrane morphology.

The ionic form of the membrane affects, however, the dependence of the electro-osmotic permeability on the methanol percentage of the solutions, this dependence being higher at higher methanol concentrations and different depending on the membrane structure.

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