On the methanol–water electroosmotic transport in a Nafion membrane

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Abstract

Electroosmosis experiments through a Nafion membrane have been performed using methanol–water KCl solutions in different experimental situations. The influence on the electroosmotic transport of the percentage of methanol on solvent at different electrolyte concentrations has been studied. The experimental results show that the presence of methanol on the solutions affects strongly to the electroosmotic flow. From the current–voltage curves determined for this membrane system, the limiting currents were obtained at different volume percentages of methanol. The values obtained decrease with increasing the percentage of methanol and a minimum value seems to be reached at certain percentage of alcohol.

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1. Introduction

When an electric current circulates through the system

\[ \text{anode (solution)}(c_0) \text{membrane (solution)}(c_0) \text{cathode} \]  

a water flow associated to the transport of the corresponding ions takes place. This phenomenon is known as electroosmosis and has been widely studied in the literature in aqueous media, especially within the framework of the thermodynamics of irreversible processes [1].

According to this theory, the relation between the total volume flow, \( J \), 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 electroosmotic permeability, \( \mathcal{W} \):

\[ \mathcal{W} = \left( \frac{J}{I} \right)_{\Delta P = 0} \]  

It can practically be said that the electroosmosis phenomenon may exist in all kinds of membranes. It can be originated by the existence of charged groups caused by the adsorption of one or more ionic species of the solution on the walls of the membrane pores or by the existence of a fixed charge concentration in the own membrane structure, as is the case of the membrane used in this work.

The electroosmosic behavior of ion-exchange membranes in aqueous media has been widely studied in the literature [2–10]. This phenomenon depends on the nature of the system, the quantity of water transported by electroconvection, and some other relevant parameters such as temperature, electric current, and stirring rate of the solutions in contact with the membrane.

Special attention has been shown about the influence of the electric current and the concentration of the solutions at both sides of the membrane on the electroosmotic drag. All the measurements of the water electroosmotic transport show that it decreases when the external solution concentration increases and when the water content of the membrane decreases as well [3,7,8]. With reference to the influence of the electric current, the dependence observed is different depending on the electric current interval passing through the system. Thus, at sufficiently low values of the electric current, the electroosmotic permeability increase when the current density decreases. Although this increase, which is more appreciable when the solution concentration decreases, has been related with the water content of the membrane...
by some authors [11], its causes is not clear yet. At intermediate and high values of the electric current, the electroosmotic permeability is practically independent of the electric current. A third region is observed that the concentration changes in the solution during the measurement process may be considered negligible. The membrane specific conductivity was strongly influenced by the absorbed liquid within the membrane. They found that the size of the clusters was bigger for a methanol-swollen membrane than that for a water-swollen membrane. It was also observed that cations migrate along the restricted path through channels of hydrophilic domains, so the membrane specific conductivity was strongly influenced by the liquid content, as well as other transport properties [6].

In this paper, the electroosmotic behavior of a Nafion membrane in a methanol–water media has been studied in order to check how the presence of methanol affects to the electroosmotic transport. The understanding of the electroosmotic behavior in this media is very important from the point of view of the development of new materials more appropriate for using in methanol fuel cells.

### Table 1

<table>
<thead>
<tr>
<th>Thickness (10^{-3} m)</th>
<th>Water uptake (%)</th>
<th>Fixed charge (mol/m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.185</td>
<td>35</td>
<td>1.13 \times 10^{-7}</td>
</tr>
</tbody>
</table>

### 2. Experimental

#### 2.1. Materials

A commercial Nafion 117 membrane with a nominal equivalent weight of 1100 g/eq. was used in this study. The Nafion 117 is a cation-exchange membrane that can be considered as a pure cation conductor, with a transport number of K^+ of about unity for low concentration of KCl electrolyte. The polymer consisted of a polytetrafluoroethylene backbone and long fluorovinyl ether pendant side chains regularly spaced, terminated by a sulfonate ionic group. The thickness, water content and ion-exchange capacity provided by the manufacturer for this membrane are given in Table 1.

The materials used in the experiments were solutions of water and methanol at different compositions. Potassium chloride (KCl) was used as electrolyte. 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. Apparatus and procedures

In Fig. 1, a general sketch of the experimental device used in this research is given. 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 $4 \times 10^{-3}$ m³, 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 en-

![Fig. 1. Sketch of the experimental device used in the electroosmosis and permeability measurements.](image-url)
sure there were no liquid leaks in the whole assembly. The effective surface area of the membrane exposed to the flow was $5.7 \times 10^{-4}$ 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. An 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 [18]. After each measurement, an equal current was made to circulate under the same conditions, but alternating its sense, so that the electrodes stayed in good conditions. These electrodes could be used for a long time. The third orifice of each chamber stated closed during the measure of the electroosmotic 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, \( \Delta V_c \) and \( \Delta V_a \), respectively, are given by

\[
\Delta V_c = J + \frac{F}{F} (V_{Ag} - V_{AgCl}),
\]

(3)

\[
\Delta V_a = -J + \frac{F}{F} (V_{AgCl} - V_{Ag}),
\]

(4)

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

If one takes into account that \( \overline{V}_{AgCl} - \overline{V}_{Ag} = 15.5 \times 10^{-6} \) m\(^3\)/mol, the following relationship is obtained from Eqs. (2)–(4)

\[ W (\text{m}^3/\text{C}) = \left| \frac{\Delta V_c}{2J} + \left| \frac{\Delta V_a}{2J} \right| \right| + 1.6 \times 10^{-10} \]

(5)

This last expression may be used for the determination of the apparent or measured electroosmotic permeability.

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 [18].

3. Results and discussion

3.1. Current–voltage curves

The voltage–current curves for the studied system (membrane plus solutions) were determined under different experimental conditions. In all cases, they showed the three usual characteristic regions in this kind of membranes. From these voltage–current curves, it was possible to estimate, using a method describe in [19], the value of the limiting current, \( I_L \), under every experimental conditions, as well as the ohmic resistance of the cell. The results are shown in Figs. 2 and 3.

![Fig. 3. Limiting current as a function of methanol percentage on solvent at different KCl concentrations: (■) 2.5 mol/l; (□) 5 mol/l; (■) 7.5 mol/l; (○) 10 mol/l.](image-url)
Fig. 2 shows the cell resistance as a function of the methanol percentages at different KCl concentrations. This resistance is the sum of two terms, the resistance of the membrane and the resistance of the bulk solutions at both sides of it. It is well known that, in the absence of methanol in solvent, the cell resistance decreases with increasing the electrolyte concentration. Fig. 2 shows that this same trend is observed in the presence of alcohol. In addition, at a given electrolyte concentration, the cell resistance increases when the methanol percentage increases, with a similar behavior at all the electrolyte concentrations. The rate of the increase is higher at methanol percentage lower than approximately 50%. At higher percentages of methanol the slope decreases. Moreover, the influence on the cell resistance of the presence of methanol on solvent is higher at lower electrolyte concentration, for which the cited slope change is more appreciable. 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% [19]. This observed diminution in specific conductivity is due to the decrease in the dielectric constant of the solvent with increasing proportion of methanol and, so, to the decrease in the ability of the solvent to dissolve the electrolyte [20].

Taking into account that the membrane resistance depends on the conductivity of the solutions in contact with it [21], it is expected a similar dependence of the membrane specific conductivity on the percentage of methanol.

Fig. 3 shows the limiting current value as a function of the methanol percentages at different electrolyte concentrations. As can be observed, the limiting current depends on the methanol content with all the electrolyte concentrations in a similar way. The values of \( I_L \) obtained decrease with increasing alcohol content and seem to reach a minimum at a certain methanol percentage. It can be due to the dependence observed in the specific conductivity on the methanol content, because it can be speculate that at low methanol concentrations, the water content in the membrane is little affected by the uptake of methanol, i.e., the methanol is taken up in addition to the water already present. At higher methanol concentrations, water starts to become excluded [22]. In addition, these results are in agreement with the results found in a previous work with an ionic membrane with 10 mol/m^2 methanol–water KCl solutions, for which a min-

![Graph](image.png)
imum was observed at about 60–80% alcohol. With respect to the dependence of the limiting current on the electrolyte concentration, it is similar at all the methanol percentages, and an increase of the limiting current is observed with increasing the electrolyte concentration, in agreement with the results obtained in other works [19].

3.2. Electroosmotic 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. Fig. 4 shows an example of the meniscus displacement in both capillaries in two experimental situations. In all the cases, the reproducibility of the measurement was checked.

The volume change rates at different electric currents, in the (1–5) × 10⁻³ A interval, has been measured with various KCl concentrations and different methanol percentages. The experimental values obtained for pure water, 25, 50 and 75 vol.% methanol at the different concentrations of KCl have been shown in Figs. 5–8. In general, the electroosmotic 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.

The accuracy of our measurements can be checked by comparing our data for KCl–water solutions with data published by others. For instance, Okada et al. [6], in their study about the transport of aqueous solutions through Nafion membranes, reported a mass transfer coefficient of about 5 for a membrane in a solution containing 0.03 mol/l of KCl electrolyte. By using our data, we calculated a value of 3.9 for the water transport number or a KCl–water solution with 0.025 mol/l of KCl electrolyte. The agreement between

Fig. 5. Volume change rate, \( J'_V \) vs. electric current at different KCl concentrations (●) 2.5 mol/l; (○) 5 mol/l; (■) 7.5 mol/l; (□) 10 mol/l. The data correspond to a pure water solvent.
the two data, although the effect of polarization concentration is not considered, is deemed acceptable.

As it can be observed, 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 electroosmotic permeability was constant. An exception is observed in the case of pure water solvent for the lower electric current applied, $2 \times 10^{-3} \text{ A}$, where a higher value than the one expected is observed. The deviation of this value from the linear behavior is higher at lower electrolyte concentrations. These results are in agreement with the increase of the electroosmotic permeability that is usually observed at lower electric currents[7,11]. A close inspection of Figs. 6–8 shows that this fact is not practically shown when methanol–water mixtures are used as solvent. Another deviation of the linear behavior was also observed in the case of 2.5 mol/m$^3$ electrolyte concentration for the higher electric current applied and 25% of alcohol on solvent. This deviation is due to the electric current applied is near the corresponding limiting value. In this situation a high increase is observed in the apparent electroosmotic permeability as a consequence of the concentration polarization effect[7]. For this same electrolyte concentration and 50% of methanol percentage, no linear behavior was observed between the volume flow and the electric current applied, probably due to the values of applied electric current in the considered interval are too near to the limiting value, estimated in $3.31 \times 10^{-3} \text{ A}$ under the same experimental conditions. For this reason, the values corresponding to this electrolyte concentration are not presented in Fig. 7. In this case, only the value of the flow corresponding to the lower current, 0.001 A, has been considered.

In the region where a linear behavior was observed between the electroosmotic transport and the electric current, a mean value of $W$ can be estimated, taking into account Eqs. (2)–(5), as follows:

$$J'_V (\text{ml/s}) = \vartheta I$$  

$$J'_V = \frac{1}{2} (|\Delta V_a| + |\Delta V_c|)$$

$$I (10^{-3} \text{ A})$$

$$J'_V (10^{-12} \text{ m}^2 \text{ s}^{-1})$$

Fig. 6. Volume change rate, $J'_V$ vs. electric current at different KCl concentrations: (●) 2.5 mol/m$^3$; (○) 5 mol/m$^3$; (■) 7.5 mol/m$^3$; (□) 10 mol/m$^3$. The data correspond to a 25% methanol percentage on solvent.
and the parameter $\vartheta$ is related to the mean electroosmotic permeability $W$ as follows:

$$
\vartheta = W \left( \frac{m^3}{C} \right) - 1.6 \times 10^{-10}
$$

(8)

Eq. (8) permits to determine a mean value of the measured $W$ for every KCl concentration and percentage of methanol in the electric current interval in which $W$ is independent of the electric current applied. The obtained results are presented in Fig. 9, where $W$ is shown versus methanol percentage at the different electrolyte concentrations. The value showed for 2.5 mol/m² and 50% alcohol is the value corresponding to an electric current of 0.001 A. The discontinuous lines are only a visual guide.

As can be observed in Fig. 9, there exists a strong influence of the composition of the solution on the apparent electroosmotic permeability. At a given electrolyte concentration, as a general trend, the apparent electroosmotic permeability increases in the region of percentages of methanol lower than approximately 40–50%, observing the opposite trend at higher percentages of methanol. This behavior is similar with all the electrolyte concentrations. Thus, the measured electroosmotic permeability shows a maximum value at a certain percentage of methanol. This general behavior is similar with all the concentrations studied, although some differences can be observed. In general, the size of the maximum decreases when the solution concentration increases. An exception occurs in the case of a 10 mol/m³ KCl concentration, where the size maximum increases with respect to the previous lower concentrations.

In relation to the dependence on the electrolyte concentration, for pure water and for 25%, the typical dependence between the apparent electroosmotic permeability and the electrolyte concentration is observed, i.e., the higher concentration, the smaller electroosmotic permeability. This trend was also observed at higher methanol percentages in the 2.5–7.5 mol/m³ interval. However, the value corresponding to a 10 mol/m³ did not follow this trend, and for a methanol percentages higher than 50%, the value obtained for the electroosmotic permeability is higher than for other lower KCl concentrations.

With the exception of the case corresponding to the 2.5 mol/m³, the value of the applied current in the measure of the electroosmotic permeability are far away from the corresponding limiting value, as it is followed from the
linear behavior observed in Figs. 5–8. For this value of the electrolyte concentration, the limiting current values are in the interval \((4–6) \times 10^{-3} \text{A}\). At current near than the limiting current density, an increase of the electroosmotic permeability is observed. This is the cause, as it was previously mentioned, because the value for \(5 \times 10^{-3} \text{A}\) and 25% of methanol is far away from the linear behavior in Fig. 6.

The maxima observed in Fig. 9 may not be due, thus, to the increase of the electroosmotic permeability originated by polarization concentration effects at electric currents near from the limiting value.

It is well known that the formation of polarization layers gives rise to the existence of a concentration difference between the two sides of the membrane. The effect of this concentration difference is to contribute an osmotic component to the solvent flow that can never be definitely neglected. That is, under these conditions, the total solvent flow through the membrane is determined by the current density, which controls the electroosmosis, and the values of the solution concentrations at the membrane/solution interfaces, which control the normal osmosis. Thus, the measured or apparent electroosmotic permeability is the sum of two terms:

\[ W = W_e + W_{\text{osm}} \] (9)

where \(W_e\) is the net electroosmotic contribution (in the absence of polarization effects) and \(W_{\text{osm}}\) is the osmotic contribution due to the polarization effect. However, it is not possible from the experimental results to know if the behavior observed for the apparent electroosmotic permeability when the composition of the external solution changes is due to the osmotic contribution or to the net electroosmotic contribution.

For a \(c_0\) bulk electrolyte concentration and an electric current \(I \leq I_L\), from the classical polarization concentration theory, the following relationship is obtained:

\[ W_{\text{osm}} = 2c_0 \frac{\beta}{I_L} \] (10)

where \(\beta\) is a coefficient directly related to the osmotic coefficient [7].

With reference to the net electroosmotic permeability, according to the theory of electroosmosis developed by Schmid
it may be written as

$$W_e = \frac{FkXpLp}{k}$$

where $Lp$ is the hydraulic permeability, $d$ is the membrane thickness, $k$ and $X$ are, respectively, the specific conductance and the concentration of fixed charge of the membrane. It is worth mentioned that this equation does not include the ion hydration of water, which is also depends on the nature solution in contact to the membrane.

It can be seen that, from Eqs. (10) and (11), both terms would be depend on the percentage of methanol. As can be observed from Fig. 3, at a given electrolyte concentration $c_0$, the limiting current value depends on the methanol percentage, showing a minimum in an interval of the methanol percentage similar to the interval in which the maximum in the curve showing the apparent electroosmotic permeability versus methanol percentage is shown. From studies about the osmotic behavior of a similar charged membrane in methanol–water solutions [24], the term corresponding to the osmotic contribution $B_e$ also seems depend on the percentage of methanol. By other hand, taking into account the behavior observed for the limiting current and the cell resistance, the value of the specific conductance of the membrane will also depend on the alcohol content. From studies about the membrane potential in charged membranes some authors have obtained that the fixed charge decreases when the proportion of methanol in the solution increases, due to the formation of the ion pairs in the membrane [25]. The hydraulic permeability also seems depend on the percentage of methanol [22,26]. The behavior observed in the apparent electroosmotic permeability may be due to the dependence on the methanol content of the solvent of the different parameters that appear in the two terms of Eq. (9).

To achieve a better and more complete understanding of the behavior of the electroosmotic permeability with the percentage of methanol, more information about the specific dependencies of the net electroosmotic and osmotic contributions to $W_e$ on the methanol content is required. Further work is in progress in this direction.
4. Conclusions

From the current–voltage curves, the values of the limiting current for a Nafion membrane were obtained at different methanol–water KCl solutions with different volume percentages of methanol on solvent. The obtained results showed that the limiting current value decreases with increasing percentage of methanol and a minimum value seems to be reached at a certain percentage of alcohol.

The electroosmotic behavior of a Nafion membrane has been studied under different experimental conditions. The apparent electroosmotic permeability depends on the solution methanol content, showing a maximum at a certain percentage of methanol. This behavior has been observed with all the studied electrolyte concentrations.

In the 2.5–7.5 mol/m³ KCl concentration interval, the dependence of the apparent electroosmotic permeability on the electrolyte solution shows the usual behavior, i.e., the higher concentration, the smaller electroosmotic permeability; at all the percentages of methanol on solvent. The obtained results showed that the limiting current value decreases with increasing percentage of methanol and a minimum value seems to be reached at a certain percentage of alcohol.

The electroosmotic behavior of a Nafion membrane has been studied under different experimental conditions. The apparent electroosmotic permeability depends on the solution methanol content, showing a maximum at a certain percentage of methanol. This behavior has been observed with all the studied electrolyte concentrations.

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