Simultaneous electroosmotic and permeation flows through a Nafion membrane

2. Methanol–water electrolyte solutions

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Abstract

The volume flow of methanol–water potassium chloride solutions through a Nafion membrane originated by the simultaneous action of electric potential and pressure gradients has been measured at different percentages of methanol. Measurements were conducted when both gradients act in the same and in the opposite directions under different experimental conditions. The results indicate that the simultaneous action of the pressure and potential differences originates a total flow different from the sum of the individual electroosmotic and permeation flows due to each force acting separately. The application of the irreversible thermodynamics theory, which includes second-order terms, allowed the study of the influence of the composition of the solutions on the determination of the different phenomenological coefficients.

Keywords: Electroosmotic flow; Permeation; Nafion membrane; Phenomenological coefficients; Irreversible thermodynamics; Methanol–water solutions

1. Introduction

In order to determine the different phenomenological coefficients in the study of a membrane system, it is usually that only one thermodynamics force acts over the membrane or one of the flows becomes null. When these coefficients are known, in the linear approximation of irreversible thermodynamics theory (TPI), it is possible to estimate the total flow through the system when various forces are acting from the linear phenomenological equations [1]. If second-order terms are considered, more information is necessary to know the total flow under the simultaneous action of various forces.

According to TPI, the isothermal volume flow, $J_V$, and the electric current, $I$, through a membrane under the simultaneous action of a hydraulic pressure difference, $\Delta P$, and an electrical potential difference, $\Delta \varphi$, can be written [2,3] as

$$J_V = L_{11} \Delta P + L_{12} \Delta \varphi + L_{111} (\Delta P)^2 + L_{122} (\Delta \varphi)^2 + \cdots,$$

$$I = L_{21} \Delta P + L_{22} \Delta \varphi + L_{211} (\Delta P)^2 + L_{222} (\Delta \varphi)^2 + \cdots,$$

where $L_{ij}$ and $L_{ijk}$ are the linear and the second-order phenomenological coefficients, respectively.

The estimation of different phenomenological coefficients can be made from the determination of the volume flow through the membrane under different experimental conditions.

If permeation experiments are performed and under the condition $\Delta \varphi = 0$, the volume flow will be given by the following equation:

$$(J_V)_{\Delta \varphi=0} = L_{11} \Delta P + L_{111} (\Delta P)^2.$$

In the absence of a pressure difference, as has been shown elsewhere [4], there is a linear relationship between the flows...
through the Nafion membrane and the electric potential difference in the experimental interval studied. This fact leads to assume that the second-order coefficients \( L_{22} \) and \( L_{222} \) can be considered as negligible under the given experimental conditions. Consequently, in the case of electroosmotic measurements, with \( \Delta P = 0 \), it can be written that

\[
(J_V)_{\Delta P=0} = L_{12} \Delta \phi, \tag{4}
\]

\[
(I)_{\Delta P=0} = L_{22} \Delta \phi. \tag{5}
\]

Moreover, the following relation is obtained,

\[
\left( \frac{J_V}{T} \right)_{\Delta P=0} = \frac{L_{12}}{L_{22}} = W, \tag{6}
\]

where \( W \) is the electroosmotic permeability, which can be determined experimentally.

With the previous assumptions, if simultaneous electroosmosis and permeation processes are considered, the phenomenological Eqs. (1) and (2) can be written as follows:

\[
J_V = L_{11} \Delta P + L_{12} \Delta \phi + L_{111} (\Delta P)^2 + L_{112} \Delta P \Delta \phi, \tag{7}
\]

\[
I = L_{21} \Delta P + L_{22} \Delta \phi + L_{211} (\Delta P)^2 + L_{212} \Delta P \Delta \phi. \tag{8}
\]

On the other hand, as was shown elsewhere [4], in the absence of an electric voltage difference, a quadratic dependence is observed between the volume flow and the pressure difference and only second-order terms must be considered in the dependence of the volume flow on the pressure gradient. By taking this fact into account in Eqs. (7) and (8), it seems reasonably to make the following assumptions:

\[
L_{112} \Delta P \ll L_{12}, \quad L_{212} \Delta P \ll L_{22}. \tag{9}
\]

In this previous work [4], it was also observed that, for aqueous solutions, when the flow volume was plotted as a function of the electric current, the slope of the obtained lines did not depend on the pressure difference. The slopes have a similar value than the value obtained in the absence of pressure difference, \( W \), given in Eq. (6). By assuming this hypothesis to be valid and taking into account Eq. (9), Eq. (7) can be written as follows,

\[
J_V = L_p \Delta P + L_p' (\Delta P)^2 + WI, \tag{10}
\]

where \( L_p \) is the so-called hydraulic permeability, which is given by the expression

\[
L_p = L_{11} - \frac{L_{21} L_{12}}{L_{22}}, \tag{11}
\]

and the second-order coefficient \( L_p' \) is given by

\[
L_p' = L_{111} - \frac{L_{112} L_{21}}{L_{22}}. \tag{12}
\]

Moreover, Eq. (10) may be rearranged as

\[
J_V = \chi + WI, \tag{13}
\]

where \( \chi \) is given by the following expression:

\[
\chi = L_p \Delta P + L_p' (\Delta P)^2. \tag{14}
\]

Finally, it is possible to estimate the value of the electric current, \( I_0 \), necessary to make the volume flow through the membrane zero. In Eq. (10), if \( J_V \) is set to zero, the following expression can be obtained:

\[
-I_0 = \frac{L_p}{W} \Delta P + \frac{L_p'}{W} (\Delta P)^2. \tag{15}
\]

The study of the behavior of a membrane system where various forces are acting is important in a lot of membrane processes of technical interest, and different approaches have been used to this end [1,5–9].

In a previous work [4], the study of the volume flow through a Nafion membrane under the simultaneous action of a pressure difference and an electric potential difference was carried out. In that first part, the study was carried out using aqueous electrolyte solutions. The obtained results showed that the knowledge of the linear phenomenological coefficients is not enough to describe the process, and that it is possible to make zero the volume flow through the system when both thermodynamics forces act in opposite directions. In the present work, we study a similar system but with methanol–water electrolyte solutions. Understanding the behavior of this system is very important in direct methanol fuel cells, where a difference of electrical potential and a pressure difference operate in opposite directions [10,11].

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 thickness, water content, and ion-exchange capacity were reported in a previous paper [4]. The membrane was previously boiled in deionized and bidistilled water for 1 h. The materials used in the experiments were methanol–water solutions of potassium chloride (KCl) of 0.01 N of different volume methanol percentages. Pure pro-analysis grade chemicals and distilled pure water were used. Before measurements were carried out, the solutions were degassed in order to prevent the bubbles formation during the measurement process.

2.2. Apparatus and procedures

The experimental device and the procedures used in this research were essentially the same that those described elsewhere [4]. In order to achieve equilibrium the membrane was immersed in the corresponding methanol–water solution for a minimum of 48 h, before the measurements were conducted.
The effective surface area of the membrane exposed to the flow was $5.7 \times 10^{-4} \text{ m}^2$. All the experiments were carried out under isothermal conditions at 298 K. The solutions were stirred by a magnetic stirrer assembly, and the stirring rate was 365 rpm in all the experiments. Under these conditions, the temperature was constant within $\pm 0.1 \text{ K}$.

3. Results and discussion

3.1. Permeation measurements

The volume change in the left chamber of the membrane cell have been measured as a function of time, when a pressure difference is established between the two sides of the membrane. Measurements were performed at three different values of the pressure difference by using solutions with three different methanol weight percentages: 25, 50, and 75%. The results obtained for methanol–water solutions were similar than those obtained for aqueous solutions [4], because the volume flow was observed from the high-pressure chamber (right chamber) towards the low-pressure chamber (left chamber). Fig. 1 shows, as an example, the results obtained with a 75% methanol percentage solution. The behavior was similar in all the studied cases. A transitory step was observed at the beginning of the experiment, and after a time the volume variation became linear, indicating that the steady-state conditions had been reached. As it was expected, the flow increased with the pressure difference. It is also observed higher flow values at higher methanol percentages, under the same experimental conditions. This behavior is in agreement with the results obtained in previous works [12]. As in the case of aqueous solutions, the permeation volume flow through the membrane was obtained from the slope of the linear part of the curve. The values obtained are shown in Fig. 2 as a function of the pressure difference.

As can be observed in Figs. 1 and 2, the higher the pressure difference, the higher the slope of the corresponding curve; consequently the higher the volume flow. Therefore, the behavior is similar than in the case of aqueous solutions with a positive deviation from linearity at higher pressure differences, which increases with the methanol content of the solutions. These results are in agreement with the results reported in a previous work [12] where the permeation flow of the Nafion 117 membrane was studied under different experimental conditions.

In the experimental pressure interval studied, a nonlinear dependence was also found between the volume flow and the hydrostatic pressure when methanol–water mixtures were used as solvent. In agreement with Eq. (3), the experimental data have been fitted to a second order polynomial, with correlation coefficients higher than 0.99. The values obtained for the mechanical conductance were $0.6 \times 10^{-16}$, $0.7 \times 10^{-16}$, and $0.2 \times 10^{-16} \text{ m}^3 \text{s}^{-1} \text{Pa}^{-1}$, respectively, for 25, 50, and 75% methanol percentage solutions, and $3.0 \times 10^{-21}$, $7.7 \times 10^{-21}$, and $10.5 \times 10^{-21} \text{ m}^3 \text{s}^{-1} \text{Pa}^{-2}$ were the values obtained for the second-order phenomenological coefficients with 25, 50, and 75% methanol percentages, respectively. The fitting lines are shown in Fig. 2 together with the experimental data. The comparison of these data with the corresponding values for aqueous solutions, which was reported in part 1 of this work [4], shows that the values of $L_{11}$ for methanol–water solutions are one order of magnitude lower than in the case of aqueous solutions. It is also found that the mechanical conductance decreases with increasing the methanol content of the solution. These findings are in agreement with the results found by other authors [3] where a decreasing trend in the values of $L_{11}$ was observed with an increase in the concentration of methanol in the mixture. This may be attributed to the fact that $L_{11}$ varies...
inversely with the viscosity of solution which, in the composition interval studied, decrease with the methanol content. On the contrary, the higher the methanol content of the solution, the higher the value of the corresponding second order coefficient $L_{111}$. These results would indicate that the increase observed in the permeation flow with the methanol content of the solution would be due to the behavior of the second order term, and the validity of Poiseuille’s low cannot be neither assumed in the entire experimental interval when methanol–water mixtures are used as solvent. This results are in agreement with the results reported in [13], where a different mechanism from the viscous flow was found in membranes with low pore diameter.

3.2. Electroosmotic measurements

Electroosmotic volume change was measured as a function of time in the absence of pressure difference. Measurements were performed at different electric currents with solutions containing a methanol percentage of 25, 50, and 75%, respectively. The volume flow was estimated when the steady state was reached. The steady state was considered to be achieved when, in the same time interval, the same displacement of the meniscus in the capillary tube connected to the left compartment was observed. In all the cases, the shape of the curves was similar than that obtained with aqueous solutions [4]. The volume increased or decreased in the left chamber when it was the cathodic or anodic compartment, respectively. As an example Fig. 3 shows the time variation of the volume change with different electric currents in the case of a 50% methanol percentage solution. Similar behaviors were observed when solutions with different percentages of methanol were used. In addition, Fig. 4 shows the volume change as a function of time under the same experimental conditions for three methanol percentages. The data correspond to an electric current of 3 mA. It is clearly observed that the higher differences were found at the beginning of the experiments. As it was previously stated, the volume change rates were calculated from the slope of the straight lines obtained from linear fits of the experimental data. As it could be expected, it was observed that the volume change increased when the applied electric current increased. It should be pointed out that the flow was considered positive when it went in the same direction as the permeation flow.

As it was done in our previous paper [14], we have checked experimentally that there is a linear relation between the flow of methanol–water solutions through the membrane and the electric potential difference, in the absence of a pressure difference. Moreover, it should be pointed out that the limiting current values were determined under the same experimental conditions as reported in our previous paper [14], which allows us to assure that the values of the electric current used are far away from the corresponding limiting values. This fact is very important in order to avoid concentration polarization effects. Thus, we can consider that the second-order coefficients $L_{122}$ and $L_{222}$ are also negligible under the given experimental conditions with methanol–water solutions. Consequently, the electroosmotic permeability, $W$, can be estimated from the slope of the curves of the volume flow versus the applied electric current in the absence of pressure difference, as it is given in Eq. (6).

In this way, the electroosmotic permeability has been estimated as $1.40 \times 10^{-9}$, $1.45 \times 10^{-9}$, and $1.20 \times 10^{-9}$ m$^3$ C$^{-1}$, respectively, for 25, 50, and 75% methanol percentages. The fact that the correlation coefficients of the fittings were about 0.999 indicates that the contribution of the second order terms can be effectively considered as negligible. These results are in agreement with the results reported for the same membrane in a previous work [14]. In contrast, it is found

![Fig. 3. Electroosmotic volume change as a function of time at different electric currents, in the absence of pressure difference. The data correspond to a solution with a 50% volume content of methanol.](image)

![Fig. 4. Electroosmotic volume change as a function of time at different volume methanol percentages: (●) 25%, (▲) 50%, (■) 75%. The data correspond to an electric current of 3 mA (filled symbols) and −3 mA (unfilled symbols) in the absence of pressure difference.](image)
some differences with respect to previous reported values of the electroosmotic permeability for a similar membrane system. This fact is probably related to the different treatment of the membrane. Thus, in our previous work, the membrane was only immersed in the corresponding solution for 24 h in order to achieve equilibrium, while in this work the membrane was also previously boiled. It seems that when the membrane is boiled, the value of the electroosmotic permeability increases with respect to the corresponding value for the unboiled membrane.

3.3. Simultaneous electroosmosis and permeation measurements

The volume change in the left chamber of the membrane cell has been measured as a function of time when simultaneously a pressure difference is applied and an electric current circulates through the system. These measurements were conducted at different pressure differences with solutions of different methanol content. As an example, Fig. 5 shows data obtained by using a 25% methanol percentage solution with a pressure difference of 0.3 bar and several electric currents. The results obtained with solutions with different percentages of methanol were similar to those obtained with aqueous solutions. Moreover, it was also found that, when both the pressure and the electric potential gradient are applied in the same direction, i.e., the left compartment is the cathodic chamber, the curves are similar to the one corresponding to the permeation measurements, with a transitory step at the beginning of the experiments and a steady-state regime after a time. In this situation, the volume always increases in the chamber of measurement. If the applied electric current is increased, an increase of the slope of the linear curves is observed, which indicates that both flows take place in the same direction and they are added.

In this case, the higher the electric current, the higher the slope of the linear part of the curve. On the other hand, when the electric potential gradient and the pressure difference are opposite, i.e., the left compartment is the anodic chamber, a change of the slope of the curves is observed after a time. At the beginning of the experiments the volume flow is established from the high- to the low-pressure chamber, but after a few minutes the direction of the flow is reversed, and the volume decreases in the low-pressure chamber. It is also observed that this change of tendency takes place at longer times and it is more significant at higher electric currents. This behavior indicates that both volumes go in opposite directions, and they are subtracted.

It is observed that it is necessary a higher value of the electric current for the flow inversion to occur when the pressure difference increases, mainly due to the higher value of the permeation flow. Moreover, the slope of the curves decreases for the highest pressure difference, but the volume flow is not reverted. The same effect was observed when the methanol percentage was increased. Fig. 6 shows the volume change as a function of time under a pressure difference of 0.3 bar and an electric current of 4 mA at different methanol percentages. For a same value of the electric current, a decrease of the slope with increasing methanol content is observed in all the cases, but the inversion of flow is observed only in the case of the lower percentage of methanol. As previously stated, this is due to the fact that an increase in the methanol content of the solutions originates a higher permeation flow.

The volume flow through the membrane was estimated from the slope of the linear part of the curves, for a given set of experimental conditions. The obtained results are shown in Figs. 7–9, where the volume flow is plotted as a function of the electric current applied, at different pressure differences and with 25, 50, and 75% methanol percentage solu-

Fig. 5. Electroosmotic volume change as a function of time at different electric currents under a pressure difference of 0.3 bar. The data correspond to a solution with a 25% volume content of methanol.

Fig. 6. Electroosmotic volume change as a function of time at different methanol volume percentages: (●) 25%, (■) 50%, (▲) 75%. The data correspond to an electric current of 4 mA (filled symbols) and −4 mA (unfilled symbols) under a pressure difference of 0.3 bar.
that the slope of the lines representing the volume flow as a function of the electric current does not depend on the pressure difference in the case of methanol–water solutions. This behavior is in agreement with the approximations given by Eq. (9) and therefore it justifies the use of Eqs. (10)–(14) to estimate the phenomenological coefficients when methanol–water electrolyte solutions are used. Consequently, it is possible to obtain the values of the electroosmotic permeability in presence of a pressure difference by using Eq. (6), in a way similar to that in the absence of pressure difference.

The fittings of the experimental data for \( J_L \) as a function of \( I \) are given, for each methanol-water solution, in Figs. 7–9. In accordance with Eq. (13), straight lines with the same slope, but different origin coordinates for each applied pressure difference are observed. The values of the origin coordinate, \( \chi \), which are given in Table 1, represent the volume flow due to the pressure gradient when the electric current is zero. It is important to note that they are different from that the corresponding permeation flows in the absence of electric potential difference, which were shown in Fig. 2, due to the fact that the coupling between the volume flow and ion flow cause \( L_{11} \) to be different from \( L_P \). The latter is plotted in Figs. 7–9 with unfilled symbols, and they have not been taken into account in the data fittings. On the other hand, it is possible to estimate the values of \( L_P \) and \( L_P' \) from the fitting of the values of \( \chi \) to a second-order polynomial by using the pressure difference data. The values obtained for solutions containing 25 and 50% methanol percentage

<table>
<thead>
<tr>
<th>Methanol percentage (%)</th>
<th>( W , (10^{-9} , \text{m}^3 , \text{s}^{-1}) )</th>
<th>( \chi , (10^{-12} , \text{m}^3 , \text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 bar</td>
<td>0.3 bar</td>
</tr>
<tr>
<td>25</td>
<td>1.40 (±0.04)</td>
<td>1.31 (±0.04)</td>
</tr>
<tr>
<td>50</td>
<td>1.45 (±0.05)</td>
<td>1.44 (±0.05)</td>
</tr>
<tr>
<td>75</td>
<td>1.20 (±0.06)</td>
<td>1.27 (±0.05)</td>
</tr>
</tbody>
</table>

Fig. 7. Total volume flow as a function of the electric current at different pressure differences with a methanol volume percentage of 25%: (×) 0 bar, (▲) 0.3 bar, (●) 0.4 bar, (■) 0.6 bar. The unfilled symbols correspond to the volume flows in the absence of the electrical potential differences at the corresponding pressure differences.

Fig. 8. Total volume flow as a function of the electric current at different pressure differences with a 50% methanol volume percentage solution: (×) 0 bar, (▲) 0.3 bar, (●) 0.4 bar, (■) 0.6 bar. The unfilled symbols correspond to the volume flows in the absence of the electrical potential differences at the corresponding pressure differences.

Fig. 9. Total volume flow as a function of the electric current at different pressure differences with a 75% methanol volume percentage solution: (×) 0 bar, (▲) 0.3 bar. The unfilled symbols correspond to the volume flows in the absence of the electrical potential differences at the corresponding pressure differences.
were, respectively, \( L_p = 4.0 \times 10^{-17} \text{ m}^3 \text{s}^{-1} \text{ Pa}^{-1} \) and \( L'_p = 2.9 \times 10^{-21} \text{ m}^3 \text{s}^{-1} \text{ Pa}^{-2} \), and \( L_p = 5.0 \times 10^{-17} \text{ m}^3 \text{s}^{-1} \text{ Pa}^{-1} \) and \( L'_p = 7.1 \times 10^{-21} \text{ m}^3 \text{s}^{-1} \text{ Pa}^{-2} \). The fittings and the data points for \( \chi \) are also shown in Figs. 7–9. As can be observed, in Figs. 2 and Figs. 7–9, the value of the permeation volume flow at electric current zero is lower than the corresponding value at electric potential zero. However, in contrast to the case of the aqueous solutions, the relative deviation has a different tendency with the pressure difference. When water is used as solvent, a decrease of the relative deviation was found if the applied pressure difference is increased, which indicates that the coupling effect with the ion flow decreases the total volume flow, while for methanol–water solutions, under 0.3 and 0.4 bar pressure difference, there is not a general tendency in the presence of methanol, as is shown in Fig. 10. A decrease of the relative deviation is still observed when the pressure difference increases for 25% methanol percentage solutions, but the opposite tendency is found with 50% methanol percentage solutions. Moreover, under 0.3 and 0.4 bar pressure differences, the influence of the methanol content was such as the higher the methanol content, the lower the deviation. The opposite tendency is observed, however, under a 0.6 bar pressure difference. These results would indicate that there is not a general tendency in the presence of methanol, and the coupling effect depends on both the methanol content of the solutions and on the established pressure difference.

As in the case of aqueous solutions, it is possible to estimate the value of the electric current necessary to make zero the volume flow through the system from the values of the slopes and the origin coordinates of the straight lines shown in Figs. 7–9. The values obtained are shown in Fig. 11 as a function of the pressure difference. As it may be expected, the higher the pressure difference, the higher the electric current that must be applied to the system. Moreover, a nonlinear relationship was found between the applied pressure difference and the electric current circulating through the system, in accordance with Eq. (15). The lines in Fig. 11 correspond to Eq. (15). As it can be observed, the value of the electric current \( I_0 \) increases with the methanol content, due to the increase of the permeation flow.

It is possible to estimate the values of \( L_{12} \) and \( L_{22} \) from the values of \( L_{11} \), \( L_p \), and \( W \) by considering Eqs. (6) and (11) and the Onsager conditions. The coupling second order coefficient \( L_{112} \) can be also estimated from Eq. (12). A summary of the results obtained for the phenomenological coefficients is given in Table 2 as a function of the methanol percentage. These results indicate that, for methanol–water system, the simultaneous action of pressure and electric potential gradients also originates a flow different from the sum of the individual flows due to each force acting separately. In addition, in the presence of methanol, a sign change in \( L_{112} \) is observed with respect to the value obtained for aqueous solutions. For aqueous solution the coupling effect decreases the total volume flow, while for methanol–water solution an increase is observed. This increases is higher at higher methanol percentages. A change of sign in the \( L_{112} \) coefficient was also observed by other authors using Zeobarb.
225 (Na\(^+\) form) membranes/aqueous methanol solutions [3]. In relation to \(L_{12}\) and \(L_{22}\) coefficients, lower values are obtained than in the case of aqueous solutions, with a decreasing tendency with increasing methanol content of the solution. The decrease of \(L_{22}\) with increasing proportion of methanol is due to the decrease in the ability of the solvent to dissolve the electrolyte [15], and is in agreement with other previous results [14,16].

4. Conclusions

The volume flow of methanol–water electrolyte solutions through a Nafion membrane originated by the action of a pressure difference, an electric potential difference, and the simultaneous action of both has been measured. As in the case of aqueous electrolyte solutions, the experimental results showed that there is a linear relationship between the flow and the corresponding thermodynamic force for the electroosmotic flow, but terms of second order appear in the equation of the permeation flow.

The application of the irreversible thermodynamics theory, which includes second order terms, allowed the determination of the different phenomenological coefficients. The influence of the methanol content of the solutions on both the electroosmotic permeability and the mechanical conductivity was similar; both decrease with increasing methanol content. Moreover, an increase of the second-order term with the methanol content is also observed.

The obtained results indicated that the simultaneous action of the pressure and electric potential differences originates a flow different than the sum of the individual flows due to the each force acting separately. The coupling effect makes that the total volume flow decreases when aqueous solutions are used, whereas for methanol–water solutions an increase is observed. This increase is more significant at higher methanol percentages.

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