Transport of methanol and water through Nafion membranes

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Abstract

The mass flow originated when two methanol–water solutions of different methanol concentrations are separated by a membrane has been studied for two Nafion membranes. From the experimental results, the methanol and water permeabilities have been estimated. The experiments were carried out in absence and in presence of an electrolyte in the solutions. The obtained results show that, in the absence of the electrolyte, the methanol diffusion flow is higher than the osmotic water flow at all the methanol concentration gradient established, observing that the total mass flow takes place always from the concentrated toward the dilute solution. In contrast, in the presence of the electrolyte, an inversion of the total mass flow is observed at percentages of methanol higher than 40 wt.%. These experimental results could be important in relation to the problem of the methanol crossover in direct methanol fuel cells.
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1. Introduction

As it is well known, when two solutions of different concentrations are separated by a membrane, a diffusion flow of the solute takes place across the membrane from the more concentrated into the more dilute solution [1]. This transport process gives rise to one of the major chemical problems in direct methanol fuel cells, where a difference of methanol concentration exists between the anodic and the cathodic compartments. The methanol transport through perfluoro-sulphonate membranes, typically used in direct methanol fuel cells, usually known as methanol crossover, occurs by diffusion as a result of the concentration gradient and also due to electro-osmotic drag. The methanol crossover causes depolarization losses at the cathode and conversion losses in lost fuel, affecting the performance of direct methanol fuel cells [2,3].

Polyperfluorosulfonic acid Nafion membranes are commonly used as electrolyte in direct methanol fuel cells, owing to good chemical and thermal resistance and ionic conductivity. However, the high methanol permeability and hydration dependence of this kind of membranes affect, as it can be previously said, the performance of direct methanol fuel cells and make necessary to look for alternative polymer electrolytes. For this reason, intensive interest has arisen in the study of transport phenomena across ion-exchange membranes in electrolyte aqueous and organic solutions [4–11]. Nevertheless, studies in organic systems have not been so exhaustive as those conducted in aqueous systems. In addition, transport phenomena in organic systems are still unclear, and more research studies are needed to shed light on development of alternative membranes more resistant to methanol crossover and not so sensible to the hydration.

In this experimental work, the transport of methanol and water through Nafion membranes originated by a methanol concentration gradient has been studied under different experimental conditions. The influence of the presence of an electrolyte in the methanol–water solutions on both the methanol and water flows through the membrane has also been analyzed.

2. Experimental

2.1. Materials

Two commercial membranes Nafion 115 and Nafion 117 with a nominal equivalent weight of 1100 g/equiv. and thickness in the as-received dry state of 1.27×10^{-4} and 1.83×10^{-4} m, respectively, were used in this study. Prior to the experiments, the membrane was previously boiled for 1 h in deionized and bidistilled water. The active area of the membrane was $25.2\,cm^2$.

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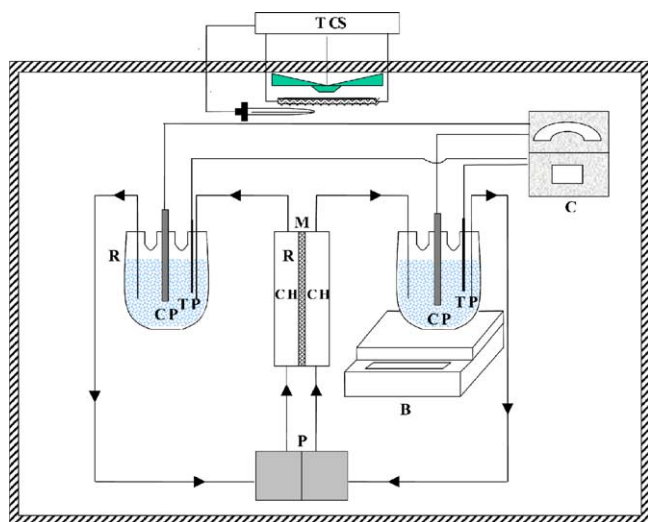
Fig. 1. Sketch of the experimental device used in the experiments. B: Mass balance; C: digital conductivimeter and thermometer; CH: chamber cell; CP: conductivity probe; M: membrane; P: peristaltic pump; R: solution reservoir; TCS: ambient temperature control system; TP: temperature probe.

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 solutions were degassed in order to prevent bubble formation during the measurement process.

2.2. Apparatus and methodology

The experimental device used in this research is sketched in Fig. 1. The cell consisted of two independent compartments made of PTFE of approximately 100 ml of volume separated by the membrane. Each chamber was provided with two orifices communicating to the exterior used as solution inlet and outlet. The solutions circulated by means of a peristaltic pump. The circulation velocity of the solutions was 200 ml/min. Two different solution reservoirs of about 1000 ml of capacity were used to contain the solutions in both chambers. These reservoirs permitted to measure the temperature and the conductivity of the solutions contained in them by means of conductivity and temperature probes connected to a digital conductivimeter and a thermometer. One of the reservoirs was placed over a mass balance, which permitted to measure the mass change in the reservoir as a function of time. The complete unit was contained in a large ambient thermostat. All the measurements were carried out under isothermal conditions at 25 °C.

At the beginning of the experiments, two solutions with different concentrations of methanol were placed between the two sides of the membrane. Initially, 800 g of an aqueous solution was placed in one of the reservoir and 800 g of a water–methanol solution is placed in the other reservoir.
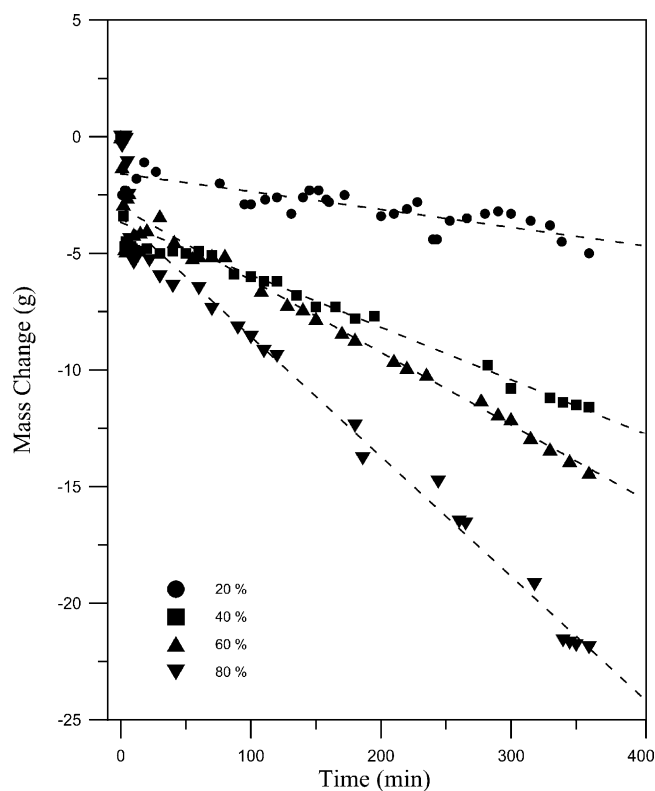

Fig. 2. Mass change as a function of time when a Nafion 115 membrane separates pure water and a methanol–water mixture, at different weight percentages of methanol.

Thus, the dilute solution did not contain initially methanol, and the initial concentration of the concentrated solution coincided with the concentration difference of methanol established between both sides of the membrane at the beginning of the experiment. When the temperature conditions were achieved, the solutions were made circulate through the cell and the mass change was measured as a function of time in the reservoir containing the concentrated solution. The duration of the measurements was 6 h in all cases.

The densities of the initial and final solutions were measured by a means of a pycnometer at a temperature of 25 °C.

3. Results and discussion

3.1. Nonelectrolyte methanol–water solutions

Figs. 2 and 3 show the results obtained, for membranes Nafion 115 and Nafion 117, respectively, for the mass change in the reservoir containing the concentrated solution as a function of time. In all the cases studied, a decrease of the mass in the concentrated reservoir was found, observing that the mass change increased when the percentage of methanol of the mixture increased. Moreover, after a period of time, a linear dependence was observed between the mass change and time indicating that pseudosteady-state conditions prevailed during the experiment after an initial tran-
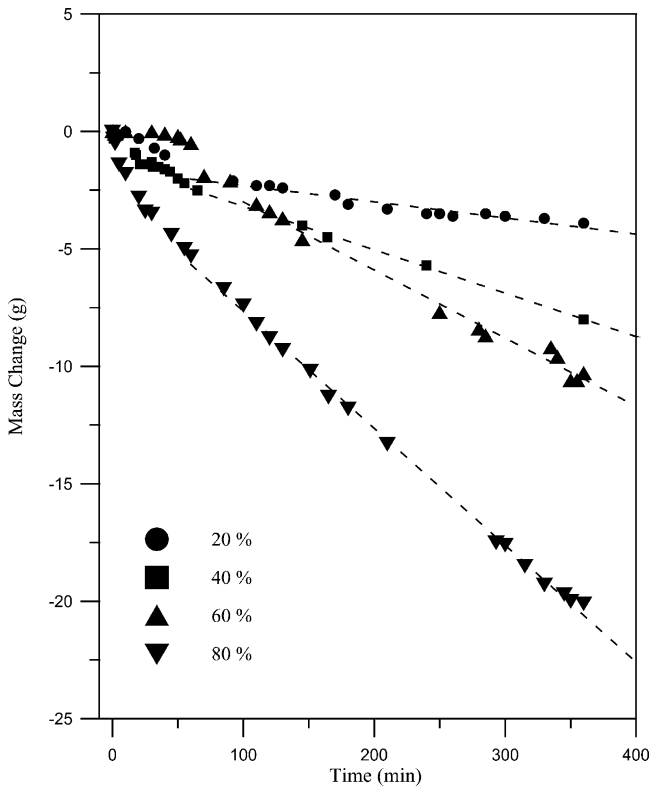
Fig. 3. Mass change as a function of time when a Nafion 117 membrane separates pure water and a methanol–water mixture, at different weight percentages of methanol.

Fig. 4. Total mass flow as a function of methanol concentration difference for the two Nafion membranes studied.

sient. For each methanol concentration difference, the results have been fitted to a straight line. The dotted lines in Figs. 2 and 3 correspond to these fits. The total mass flow per unit area A through the membrane can be defined by

$$J_m = \frac{1}{A} \frac{dm}{dt} \tag{1}$$

In the pseudosteady-state region, the total mass flow through the membrane can be estimated from the slope of the linear straight. The obtained values are shown in Fig. 4 as a function of the initial percentage of methanol in the concentrated chamber, which indicates in this case the concentration difference, for the two membranes used. In this figure, the total flow had been considered positive when the mass transfer had placed from the concentrated toward the dilute chamber. As it can be observed, the total mass flow increases when the methanol concentration gradient increases. In addition, as it can be expected, the total mass flow is higher through the membrane Nafion 115, which is the thinner membrane [12,13].

It can be expected that the measured total mass flow, J_m, is due to the contribution of the methanol flow, J_{MeOH}, for diffusion and the water flow, J_{water}, for osmosis, originated as a consequence of the methanol concentration difference. Thus, if the osmosis water transport is not negligible
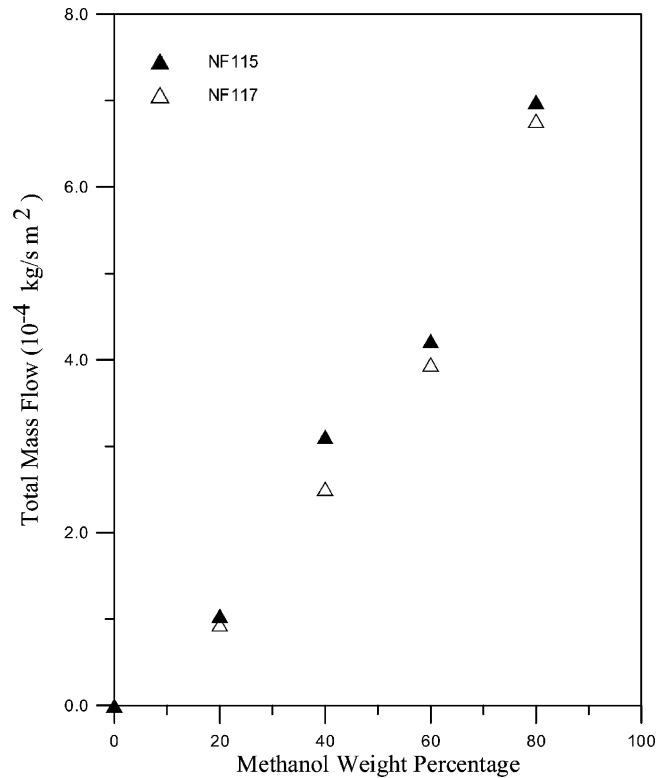
$$J_m = J_{MeOH} + J_{water} \tag{2}$$

It would be important to know which are the contributions of these two flows to the total value. This can be done if the total mass change, Δm, and the initial and final methanol concentrations are known in the dilute and concentrated chambers, as well as the initial masses of methanol and water in each chamber. Both the total mass change and the initial mass of the solution components in the chambers are measured in the experiments, whereas the methanol concentration in the chambers can be estimated as follows.

The final concentrations of methanol in the dilute chamber, c_1, and in the concentrated chamber, c_2, expressed in weight percentages, will be given by

$$c_1 = \frac{(m^f_{MeOH})_1}{m^i_1 + \Delta m} \times 100, \qquad c_2 = \frac{(m^f_{MeOH})_2}{m^i_2 + \Delta m} \times 100 \tag{3}$$

where m^i_1 and m^i_2 are the initial total masses in the dilute and concentrated chambers, respectively. From Eq. (3), the final methanol masses in the diluted chamber, $(m^f_{MeOH})_1$, and in the concentrated chamber, $(m^f_{MeOH})_2$, can be estimated, if c_1, c_2 and Δm are known and thus the corresponding mean mass flows of methanol and water through the membrane.

To this purpose, the densities of the initial and final solutions were estimated under each experimental condition. Using the data for the dependence of the density with the concentration (wt.%) of methanol found in the literature [14] at 25 °C, it is obtained that the density of a methanol–water solution as a function of the concentration of methanol in
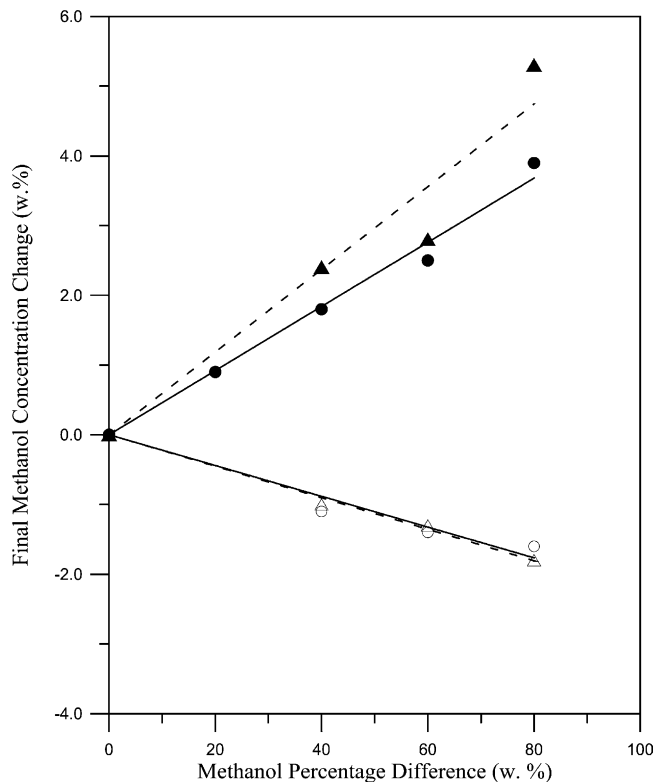
Fig. 5. Final methanol concentration change in the dilute (filled symbols) and concentrated (open symbols) chambers as a function of the initial methanol concentration difference, for the two studied membranes—circles: Nafion 115; triangles: Nafion 117.

Table 1

Estimation of the methanol and water masses, in absolute value, interchanged between the two chambers separated by the membrane at the end of the experiment, as a function of the initial methanol concentration difference, for the two Nafion membranes used

Methanol concentration difference (wt.%)	$|\Delta m|$ (g)			
	Nafion 115		Nafion 117	
	MeOH	H_2O	MeOH	H_2O
20	7	2	–	–
40	14	1	18	10
60	23	8	20	10
80	31	9	36	16

the mixture, c, can be fitted to a quadratic polynomial, with a correlation coefficient of 0.9998, as

$$\rho \, (\mathrm{g \, cm^{-3}}) = 0.9971 - 1.349 \times 10^{-3} c - 7.42 \times 10^{-6} c^2 \quad (4)$$

Using this expression, it is possible, from the value of the density, to obtain the corresponding values of the methanol concentration at the beginning and at the end of each experiment. The results obtained for the two membranes are shown in Fig. 5, in which the final methanol concentration change in both chambers is presented as a function of the initial methanol concentration difference. As can be expected, the concentration of methanol increases in the chamber containing initially water, and it decreases in the chamber containing initially the mixture. The behavior is linear and similar for the two membranes.

From the total mass change and the final methanol concentrations in the dilute and the concentrated chambers, it is possible to estimate the quantity of water and methanol that has passed through the membrane during the experiment. Table 1 shows these results as a function of the initial methanol concentration difference between the chambers. As it can be observed, a net flow of methanol is originated from the concentrated to the dilute chamber, while a net flow of water is originated in the opposite sense, as it can be expected in diffusion and osmotic processes. For the two membranes, the general trend is that the interchanged masses of

methanol and water increase with the methanol concentration, and the mass of water is always smaller than the mass of methanol, but not negligible. For this reason, the total flow is always observed from the concentrated reservoir towards the dilute reservoir, and a decrease of the mass is observed in the chamber containing the initial methanol–water mixture. From these data, it can be estimated that the methanol and water permeabilities are of the order of magnitude of 10^{-6} and 10^{-7} m/s, respectively, in agreement with the results obtained by other authors [15].

3.2. Electrolyte methanol–water solutions

In order to study the influence of the presence of an electrolyte on the membrane behavior, similar experiments were carried out when the membrane separates two solutions of equal concentration of electrolyte but different percentage of methanol. In this case, one of the reservoirs contained initially an aqueous 10^{-2} M KCl solution and the other one a methanol–water 10^{-2} M KCl solution of different percentages of methanol. In this way, the electrolyte concentration was the same at both sides of the membrane but a methanol concentration difference exited through it. The time of the experiments was also 6 h in all the cases. Figs. 6 and 7 show, for membranes Nafion 115 and Nafion 117, respectively, the mass change measured as a function of time in the concentrated reservoir at different methanol concentrations.

An observation of these figures shows a fundamental difference with respect to the experiments carried out without the presence of KCl. At 20 and 40% (w/w) methanol, a mass decrease is observed in the concentrated chamber, indicating that the mass total flow takes place in the same sense that in the absence of electrolyte. It is also observed that the mass decrease is lower when the methanol percentage increases from 20 to 40%. For percentages higher than 40% a mass increase is observed in the concentrated chamber, indicating that the total mass flow occurs in the opposite sense. This behavior is similar for the two membranes used.

In general, after an initial transient period, a linear variation of the mass change with time is observed. In the case of 20% (w/w) methanol solution, a change in this tendency is observed at the end of the experiments. In a similar way
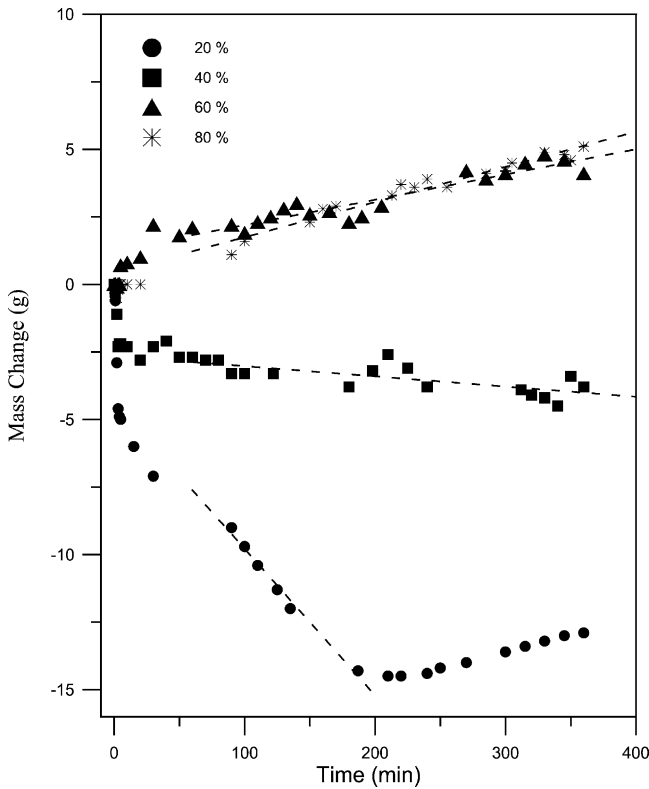
Fig. 6. Mass change as a function of time when a Nafion 115 membrane separates an aqueous solution and a 10^{-2} M KCl methanol–water solution at different weight percentages of methanol.
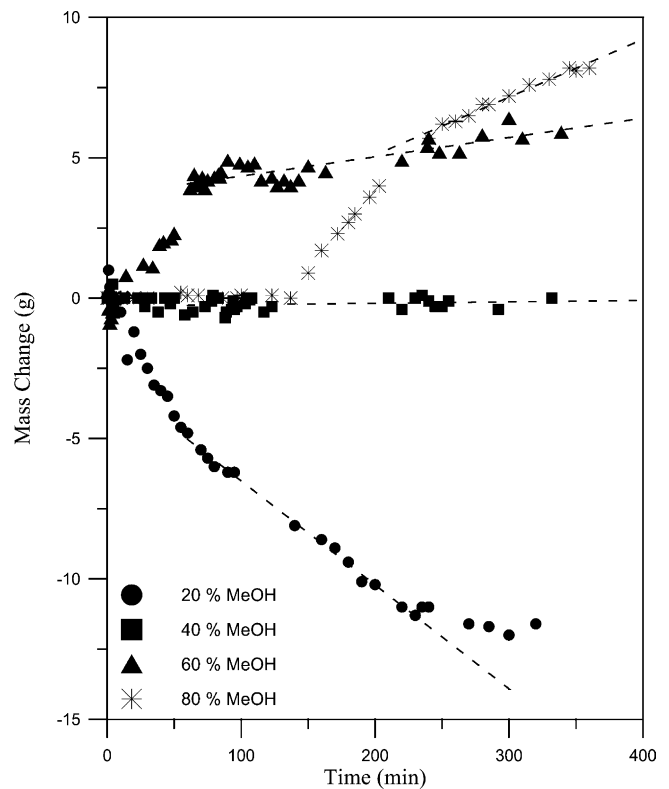

Fig. 7. Mass change as a function of time when a Nafion 117 membrane separates an aqueous solution and a methanol–water 10^{-2} M KCl solution at different weight percentages of methanol.

that in the case of nonelectrolyte solutions, in order to obtain the total mass flow through the membranes, the experimental values were fitted to straight lines in the corresponding region. The results are shown in Fig. 8, and as it can be observed, the behavior is similar for the two membranes.

In order to estimate the concentration from the value of the density, we have determined experimentally the density of mixtures of methanol–water with a 10^{-2} M KCl electrolyte concentration. In this case the dependence between density and methanol weight percentage can be also fitted to a quadratic polynomial, with a correlation coefficient of 0.99986, as

$$\rho\,(\mathrm{g\,cm^{-3}}) = 0.99754 - 1.398 \times 10^{-3} c - 6.58 \times 10^{-6} c^2 \tag{5}$$

where c is the methanol concentration in the solution expressed in weight percentage.

Using this calibration curve, it is possible to obtain the methanol concentration changes in the dilute and concentrated chambers as a function of the initial methanol concentration difference. The results are shown in Fig. 9. As can be observed, as in the case of nonelectrolyte solutions, the methanol concentration increases in the chamber with an initial aqueous solution (dilute chamber) and decreases in the chamber with the initial methanol–water mixture (concentrated chamber). However, a nonlinear behavior is now
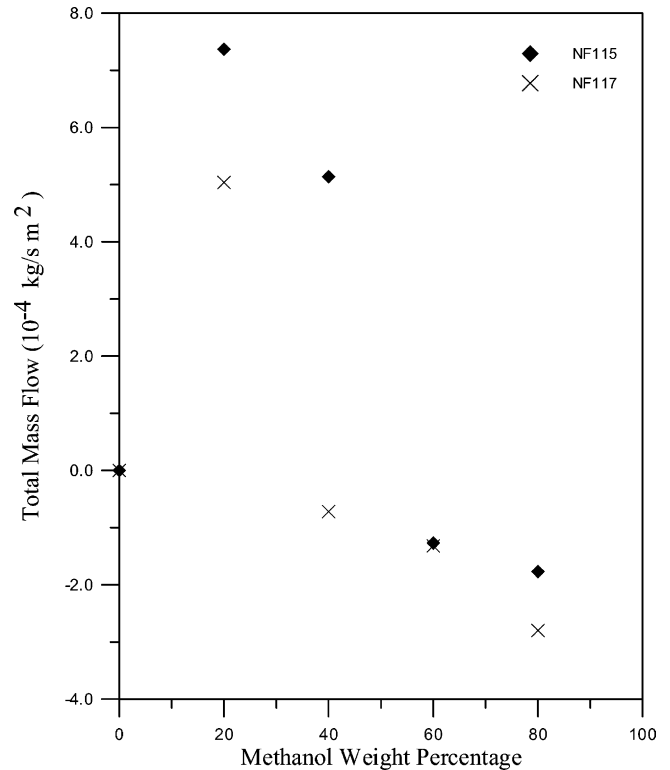

Fig. 8. Total mass flow as a function of initial methanol concentration difference for the two studied Nafion membranes. The concentration of KCl electrolyte in the solutions was 10^{-2} M.
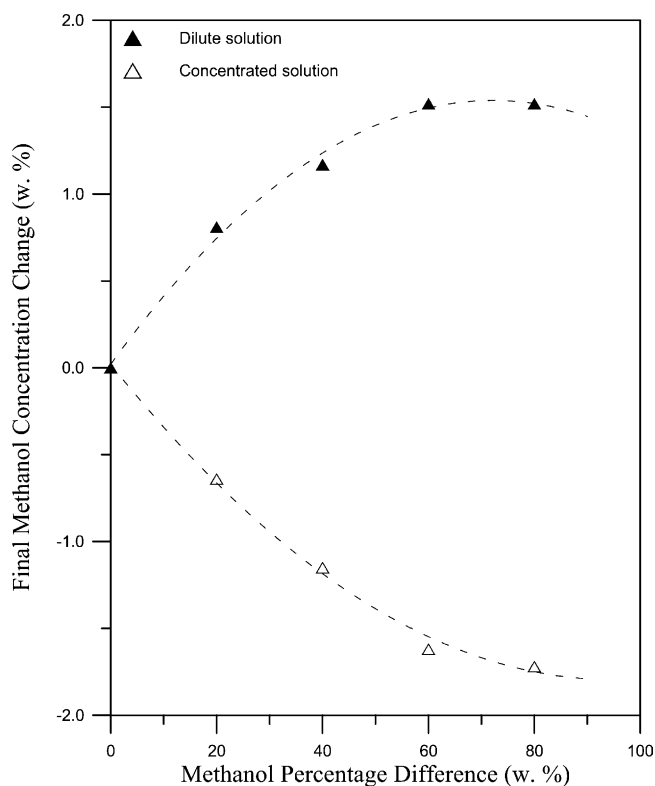
Fig. 9. Final methanol concentration change in the dilute and concentrated chambers as a function of the initial methanol concentration difference for membrane Nafion. The concentration of KCl electrolyte in the solutions was 10^{-2} M.
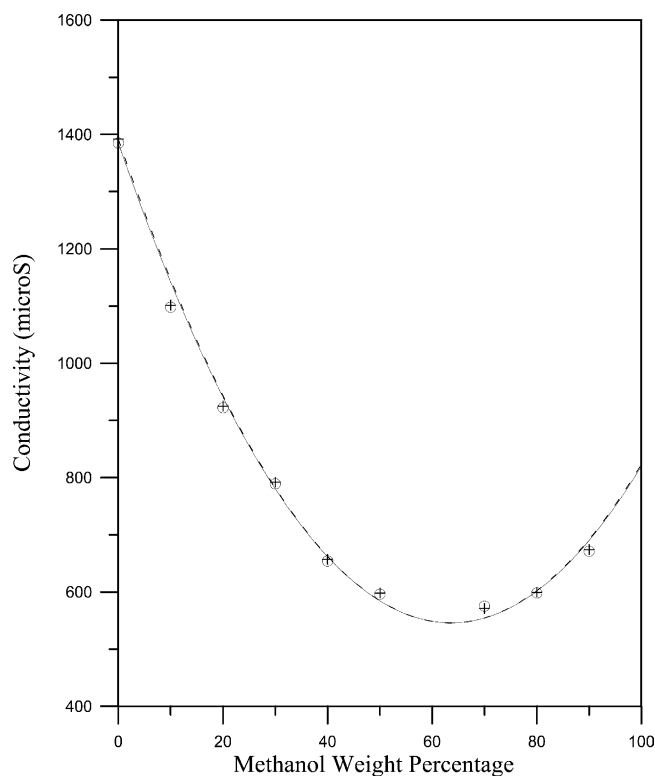

Fig. 10. Conductivity of methanol–water 10^{-2} M KCl solutions at different methanol weight percentages using two conductivity probes at 25 °C: (○) concentrated chamber conductivity probe; (+) dilute chamber conductivity probe.

observed between the concentration change and the initial concentration difference. A quadratic behavior can be considered.

From the total mass change and the value of the methanol concentration in both chambers, the mass of water and methanol passing through the membrane during the experiments can be estimated. The results obtained for the Nafion 115 membrane have been shown in Table 2 as a function of the initial methanol concentration difference between the chambers. In this case, it is observed that for 20 and 40% (w/w) methanol, the methanol mass change is higher than the water mass change, but this trend is opposite at higher percentages of methanol. As in the case of the absence of

Table 2
Estimation of the methanol and water masses, in absolute value, interchanged between the two chambers separating the Nafion 115 membrane at the end of the experiment, as a function of the initial methanol concentration difference

Methanol concentration difference (wt.%)	$|\Delta m|$ (g)	
	MeOH	H$_2$O
20	7	6
40	10	6
60	11	15
80	11	16

The concentration of the KCl electrolyte was 0.01 M.

electrolyte, the net methanol flow is from the concentrated chamber toward the dilute chamber, and the opposite sense is observed for the net water flow. However, for the same methanol concentration difference, it is also observed that, in general, the methanol flow is lower and the water flow is higher when the electrolyte is present in the solutions. In this case, the methanol and water permeabilities estimated are of the order of 10^{-7} and 10^{-6} m/s, respectively. It seems that the presence of electrolyte favors the osmotic transfer of water and reduces the diffusion of methanol through the membrane at the higher percentages of methanol. This fact may be important in order to decrease the methanol crossover, as well as the dehydration of the membrane in a direct methanol fuel cell.

In order to follow the time variation of the concentration of methanol in both chambers, the conductivity of the solutions have been measured as a function of time during the experiments for Nafion 115 membrane. Previously, we have determined experimentally the conductivity of methanol–water 10^{-2} M KCl solutions at different methanol percentages using the same two conductivity probes used in the experiments. Fig. 10 shows the obtained results as a function of the methanol content of the solutions. These results showed that a quadratic dependence can be considered between the conductivity and the methanol weight percentage on the solution, c. The dashed line in Fig. 10 corresponds to these
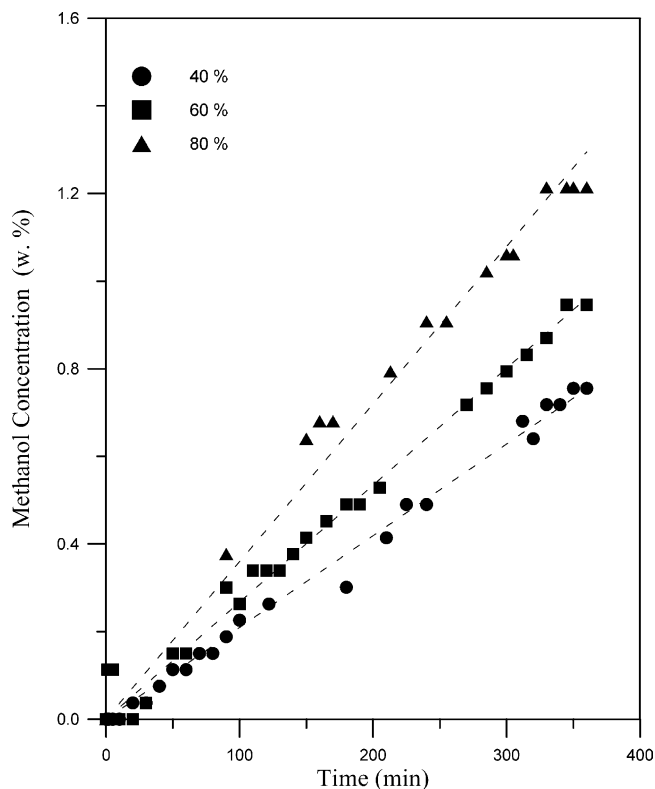
Fig. 11. Methanol concentration in the dilute chamber vs. time at different methanol concentration differences for membrane Nafion 115 when electrolyte solutions are used.
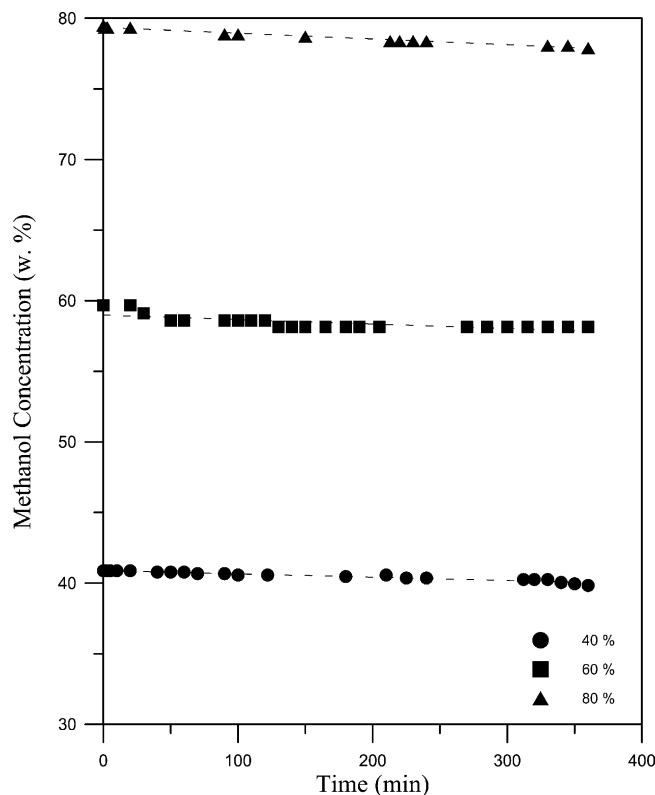

Fig. 12. Methanol concentration in the concentrated chamber vs. time at different methanol concentration differences for membrane Nafion 115 when electrolyte solutions are used.

fits, obtaining a correlation coefficient higher than 0.999. The empirical curves found were

$$\sigma_{\text{concentrated}} (\mu S) = 1385 - 26.38c + 0.2073c^2,$$
$$\sigma_{\text{dilute}} (\mu S) = 1392 - 26.62c + 0.2093c^2 \quad (6)$$

observing that the conductivities of the system have a minimum value at around 60% (w/w) methanol. The diminution observed in the 0–60% range of composition 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 [16]. Similar behavior has been described for the equivalent conductivity of KCl in methanol–water mixtures, with a minimum at about 80 mol% alcohol [17] and for methanol–water KCl and NaCl solutions using other methods [18].

Using these calibration curves it is possible, from the experimental dependencies of the conductivity with time, to estimate the variations of the methanol concentration in both chambers. The results, for membrane Nafion 115, are shown in Figs. 11 and 12, for dilute and concentrated chambers, respectively, at different initial methanol concentration differences. As can be observed, the variation of the concentration of methanol with time is linear.

As it has been shown, the methanol content in both chambers at the end of the experiments has been estimated from conductivity and density measurements. It would be interest-

ing to compare the reliability of both methods. Table 3 contains the final methanol percentage changes in both chambers obtained by using the two methods. As can be observed, the results obtained by both methods are similar, within the experimental error, in the case of the concentrated chambers. For the dilute chamber, the values are also similar, but the differences are slightly higher. It may be due to the calibration curves that are valid when the concentration of the salt is the same for all the methanol–water mixtures. However, it is possible that, although at the beginning of the experiment the salt concentration is the same in both chambers, when solvent is passing through the membrane, the concentration

Table 3
Methanol percentage change in the dilute and concentrated chambers at the end of the experiment, as a function of the initial methanol percentage difference between the two chambers

Methanol percentage difference (wt.%)	Methanol percentage change (wt.%)			
	Dilute chamber		Concentrated chamber	
	I	II	I	II
20	–	0.8	–	−0.6
40	0.8	1.2	−1.0	−1.1
60	1.0	1.5	−1.5	−1.6
80	1.2	1.5	−1.6	−1.7

I: from conductivity measurements; II: from density measurements.

of electrolyte may change. Taking into account that the mass flow is small with respect to the total mass of the chamber, it is expected that the variation of the electrolyte concentration will be small. However, this possible variation may affect more the determination of the conductivity, where the salt concentration has a high influence than that in the determination of the density. The results obtained show that this influence seems to be higher in the dilute concentrated, in such a way that the influence will be more important at smaller percentages of methanol.

The different behavior of the system observed in presence and in absence of an electrolyte in solution may be due to the presence of electrolyte in the compartments, since the rest of the experimental conditions are similar, as a consequence of the K^+-form of the Nafion membrane. Tricoli [19] observed that the methanol permeability could be reduced when a Nafion 117 membrane was doped with Cs^+ cations at room temperature. This result was explained on the basis of alterations produced by the presence of cesium in the membrane microstructure, which reduces the hydrophilic domains though methanol diffuses primarily. Other authors have also observed the influence of the cation-form of the membrane in its transport properties [20,21]. In this sense, when the salt is added to the solutions in contact with the membrane, the presence of K^+ in the membrane would cause a reduction of methanol permeability, as is observed.

On the other hand, the increase of the water flow observed when electrolyte solutions are used may be due to the diffusion of methanol and water originated by the methanol concentration difference gives rise an electrolyte concentration gradient. This fact would originate an osmotic water flow in the same sense that those due to the methanol concentration difference and thus to a higher water transfer than that in absence of electrolyte. One interesting topic would be the analysis of the cation nature of the electrolyte in the process. Further works are in progress in this sense.

4. Conclusions

The mass flow originated when two methanol–water solutions of different methanol concentration are separated by a membrane has been studied, for two Nafion membranes, in absence and in presence of an electrolyte in the solutions.

The experimental results show that, in all cases, a methanol diffusion takes place across the membrane from the more concentrated solution to the more dilute solution, and a water transport takes place in the opposite sense.

In the absence of the electrolyte, the methanol diffusion flow is higher than the osmotic water flow at all the methanol concentration gradient established, observing that the total mass flow takes place always from the concentrated toward the dilute solution. In the presence of the electrolyte, an inversion of the total mass flow is observed at percentages of methanol higher than 40 wt.%.

This behavior could be due to the fact that the presence of electrolyte cation in the structure of the membrane causes a reduction of the methanol permeability and an increase of the osmotic water effect as a consequence of the electrolyte concentration differences established between both sides of the membrane during the process.

Acknowledgements

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