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Study of the activation energy for transport of water and methanol through a Nafion membrane

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ABSTRACT

This study investigates the influence of different operating parameters in the transport of water and methanol through a Nafion membrane when it is used to separate water from a methanol–water solution. For this purpose, measurements of mass flux and concentration change have been performed at different values of circulation velocity, concentration of the methanol–water solutions and temperature conditions. From the experimental data, the water and methanol partial fluxes have been estimated, and it was found that the water flux is always lower than the methanol flux, but it cannot be neglected. Whereas total and methanol fluxes seem to have predictable and similar behaviors, the water flux seems to be less predictable and it exhibits a very distinct behavior.

Methanol and water permeabilities have been calculated, and from these values the activation energy of methanol and water fluxes in the membrane has been estimated. The results have been discussed in terms of the methanol and water solubilities in the membrane.

1. Introduction

Poly(perfluorosulphonic) acid ionomer (Nafion) is extensively used as membrane in an important number of processes in chemistry and biochemical industry. The wide-ranging applications of this membrane are due to its excellent properties, as can be good water ion exchange, high electrical conductivity, excellent thermal and chemical stability and low gas permeability. For that, a comprehensive study of the transport processes through this membrane is a very important issue [1–3]. This is the reason why one of the main subjects of this paper has been to contribute to the study of this transport by means of the analysis of process dependence on some physical parameters when a Nafion membrane is separating water and methanol–water solution.

Paying attention to particular applications of Nafion membrane, one of its most important uses is in direct methanol fuel cell (DMFC). In this area, the membrane is employed as the polymer electrolyte membrane. However DMFC with these kinds of membranes is hindered by high methanol permeability which produces the methanol crossover and reduces the energy density obtained. This is the cause which the major research focus has been the suppression of methanol crossover [4–13]. To get a better design and control of DMFC, the study of methanol permeability in this membrane is required. For that reason, other of the aims of this work has been to study the sorption and permeation when a Nation membrane is separating water and methanol–water solutions. In a previous paper [14] we obtained that not only methanol was permeating through the membrane, also water crossover was observed, this has leaded us also to study the water sorption and permeability at different experimental conditions in the present work.

In this paper, the total, methanol and water fluxes due to a methanol concentration difference have been obtained at different circulation velocity, methanol concentration and temperature conditions. In this sense we have made measured at 200, 250 and 300 ml/min circulation velocity, 10%, 20%, 30%, 40% and 50% (w/w) methanol concentration and 15, 20, 25, 30, 35 and 40 °C temperature. Our purpose has been to study the influence of these three parameters (methanol concentration, circulation velocity and temperature) on the total, methanol and water transport through a Nafion-117 membrane. To evaluate the influence of the experimental condition over the water and methanol permeabilities, and the activation energy of methanol and water, from the obtained fluxes the methanol and water their values have been calculated. For a more complete characterization, in addition to methanol and water permeabilities, the pure liquid, water and methanol uptake, have been also measured. The calculated uptake values have permitted the discussion of activation energy in terms of methanol and water solubilities.

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2. Experimental

2.1. Materials

The membrane used was a commercial Nafion-117 with a nominal equivalent weight of 1.1 kg/eq and thickness of 183 μm. The maximum water uptake and the ion-exchange capacity given by the manufacturer are 35% and 1.13 kmol/m^3, respectively. Nafion membranes were used as received just converted into acid form. The membranes were immersed in a 0.25 M HCl solution during 48 h at room temperature, after this period, the membranes were washed with deionized bidistilled water and dried with filter paper to remove the superficial water. The active membrane area was 25.3×10^{-4} m^2. Pure pro-analysis grade methanol and deionized bidistilled pure water were used in this study.

The experimental device is similar to one used in previous works [11,15,16], a schema of the experimental device is shown in Fig. 1. The membrane cell has two PTFE independent chambers of an approximate volume of 10^{-4} m^3 separated by the membrane. Each chamber has three orifices communicating to the exterior. In both chambers a temperature probe was introduced in one of the orifices, so the temperature was measured very close to the membrane (2 cm from the membrane). The other two orifices were used as solution inlet and outlet.

Two glass reservoirs of capacity of 500 ml were used to contain the circulating solution in both chambers. Each reservoir was provided with three orifices. Two of them were used as solution inlet and outlet. At the third one, a temperature probe was introduced in order to control the solution temperature outside the membrane chamber. For this purpose an electronic device (Jenco 1671 model) with an accuracy of ±0.1 °C was used. In the inlet orifices one L-shape capillary tubes were also introduced to avoid the pressure difference built-up between the reservoirs. These tubes were kept at the same height. The reservoir had a glass made jacket where water was circulated by means of a Techne TU-16D thermostat to keep the solution temperature constant.

The solutions were circulated between the cell and the reservoirs by means of a peristaltic pump (Masterflex L/S model, Cole-Parmer).

2.2. Determination of the total mass flux through the membrane and the change of the concentration of the methanol–water solutions

The solutions were placed in the reservoirs. One of the reservoirs contained pure water and the other a methanol–water solution. When the selected temperature of the solution in each reservoir was achieved, the solutions were made to circulate through the cell. The water reservoir was placed over a mass balance (Sartorius BL3100 model) in order to measure mass change in this reservoir as a function of the time. The accuracy in the mass measurements was $\pm 10^{-4}$ kg.

At the initial conditions, and during the experiment samples were taken out. The temperature of these samples was leaded to 20 °C and then the density of the solutions were measured by means of an AP Paar Density Meter, model DMA58, with an accuracy of $\pm 10^{-2}$ kg/m^3. It is known that the density of a methanol–water solution varies with its composition. Consequently, it is possible to estimate the corresponding methanol concentration of the solution from the density measured values if the curve of dependence density–concentration is known. This calibration curve has been determined from the data found in the literature for the methanol–water solution density dependence on methanol concentration in the mixture at 20 °C [17].

The method to determine the total mass flux through the membrane and the change of the concentration of the methanol–water solutions in the reservoirs are similar to those described elsewhere [14]. Basically, the mass change in the diluted chamber (reservoir that initially contains pure water) was measured as a function of time. The curve presents at short times a transitory followed at longer times by a steady state region in which the mass is a linear function of time. For all experimental situations, the results were fitted to a straight line, whose slope allowed to estimate the total mass flux, β.

It is worth mentioning that, over each experiment, the methanol concentration in the concentrated chamber (reservoir that initially contains the methanol–water solution) was determined as a function of the time. Once the steady state conditions were reached, it was found a linear variation of the methanol concentration with time in all cases. This fact allowed to estimate the concentration change velocity, α, from the slope of experimental mass curves.

2.3. Determination of methanol and water flux

In this case, the method to determine the methanol and water flux through the membrane is similar to that described in a previous work [14]. By using the obtained data of α, β and the initial mass at the concentrated chamber, the methanol and water fluxes can be estimated. The methanol, J_{m}, and water, J_{w}, fluxes through the membrane were obtained by means of the following expressions:

$$J_{\mathrm{m}} = \frac{1}{100A}(c\beta + \alpha m) \qquad (1)$$

$$J_{\mathrm{w}} = \frac{1}{100A}(100\beta - c\beta - \alpha m) \qquad (2)$$

where c and m are the initial concentration and initial mass, respectively, in the concentrated chamber, A is the effective area of the membrane, and α and β are the coefficients that determine, respectively, the concentration and total mass variations with time.

2.4. Determination of water and methanol solubility in the membrane

In order to determine the total, methanol and water membrane solubilities, a swelling study was performed by using binary mixtures of methanol and water of 10%, 20%, 30%, 40% and 50% (w/w) methanol content.

Before experiments a membrane sample was dried in a vacuum oven at 100 °C for 24 h. After that, the sample was weighed and, then immersed in a close bottle containing a known mass of the corresponding solution and allowed to equilibrate at room temperature. After 48 h of immersion, when the equilibrium conditions are achieved, the swollen membrane was taken out of the solutions, wiped carefully with filter paper and weighted again. The initial and equilibrium concentrations of methanol at the solution in the bottle were also determined.

The overall solubility, S, was calculated from the weight of the swollen and the dry membrane sample according to the following expression:

$$S = \frac{m_{\mathrm{w}} - m_{\mathrm{d}}}{m_{\mathrm{d}}} \qquad (3)$$

where m_{w} and m_{d} are the masses of the swollen and dry membrane, respectively. This expression is in agreement with that used by other authors [18].

From the values of the increase in weight of the membrane, $\Delta m = m_{\mathrm{w}} - m_{\mathrm{d}}$, the mass of the initial solution in the bottle, m_{i}, and the fraction of the immersion solution before and after membrane equilibrium, Q_{i} and Q_{f}, respectively (where fraction means mass of a component versus total mass) it is possible to estimate the fraction of methanol and water inside the membrane after the swelling

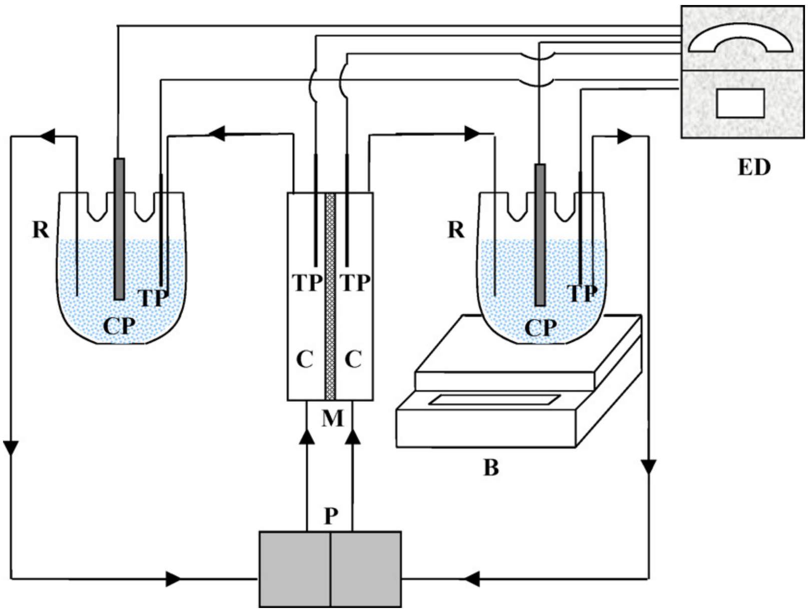

Fig. 1. Scheme of the experimental device: (C) chambers; (M) membrane; (R) reservoirs; (B) mass balance; (P) peristaltic pump; (ED) electronic device; (CP) conductivity probe; (TP) temperature probe.

process:

$$Q^{\mathrm{MeOH}}_{\mathrm{membrane}} = Q_{\mathrm{i}} - \left(\frac{m_{\mathrm{i}}}{\Delta m}\right)\Delta Q_{\mathrm{solution}} \tag{4}$$

where $\Delta Q_{\mathrm{solution}}$ is the change of the fraction in the bottle solution. From these values, the masses of methanol and water absorbed by the membrane can be determined, and thus, the methanol and water membrane solubility for each solution.

3. Results and discussion

3.1. Influence of the circulation velocity

As it was previously stated, measurements were carried out at different circulation velocities of the solutions (200, 250 and 300 ml/min), at two different temperatures (40 and 15 °C), and by using mixtures of methanol and water with methanol contents of 10%, 20%, 30%, 40% and 50% (w/w). It should be pointed out that the flux values are referred to the concentrated chamber, in such a way that a negative flux value indicates that the flux goes from the concentrate to the dilute chamber.

The experimental results showed that the values of the β and α coefficients were negative under all the experimental conditions. Illustrative plots are shown in Figs. 2 and 3, where these values are given as a function of the initial methanol concentration for the different circulation velocities at 40 and 15 °C, respectively. It is observed that both coefficients are not affected by the circulation velocity within the experimental accuracy. According to Eqs. (1) and (2) that β and α were independent from circulation velocity also mean that the methanol and water fluxes were independent as well. This is important in order to estimate the stirring conditions to remove the concentration polarization effect in the 15–40 °C temperature interval. Attending to our results, it could be said that at circulation velocities higher than 200 ml/min, the concentration polarization effect can be considered negligible.

3.2. Influence of the solution composition on the flux through the membrane. Estimation of the methanol and water permeabilities

In order to study the dependence of the methanol and water fluxes on the initial methanol concentration difference between chambers, experiments were performed to determine the values of β and α at different temperatures (15, 20, 25, 30, 35 and 40 °C), by using methanol–water solutions with different composition. The circulation velocity of the solutions was kept at 300 ml/min. The results obtained can be seen in Fig. 4. As a general trend, it is found an increase of β and α with temperature.

From the values of β and α, the methanol and water fluxes were determined from Eqs. (1) and (2), respectively, as a function of the initial methanol concentration difference established between two sides of the membrane for each temperature. The results are shown in Figs. 5 and 6 for methanol and water, respectively. The negative value of the methanol flux indicates that the methanol flux is orig-

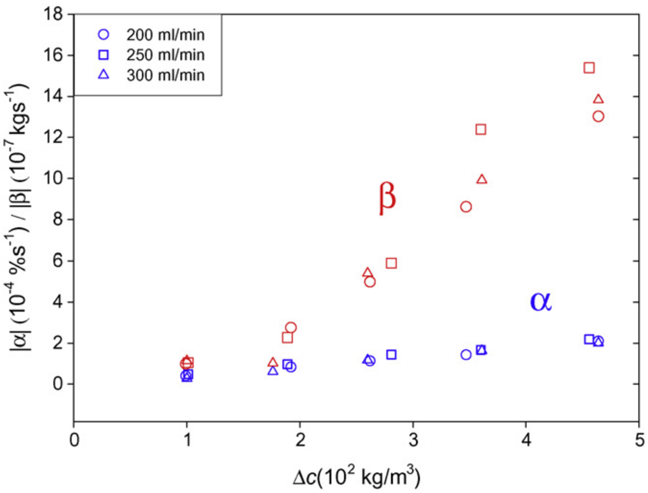

Fig. 2. Concentration change velocity, α, and total mass flux, β, as a function of the initial methanol concentration for different circulation velocities at a temperature of 40 °C.

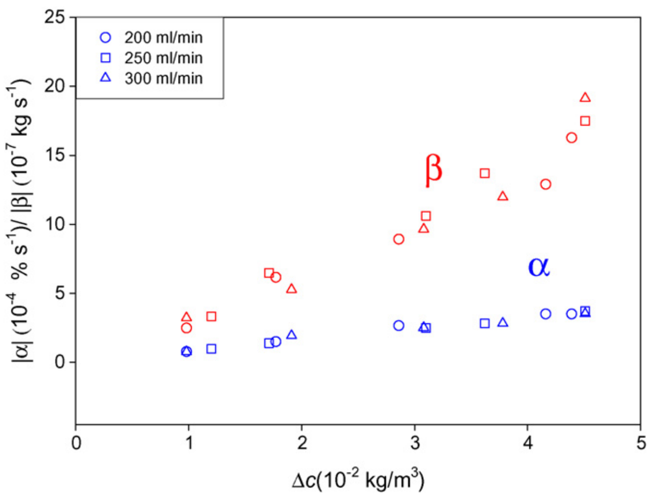

Fig. 3. Concentration change velocity, α, and total mass flux, β, as a function of the initial methanol concentration for different circulation velocities at a temperature of 15 °C.

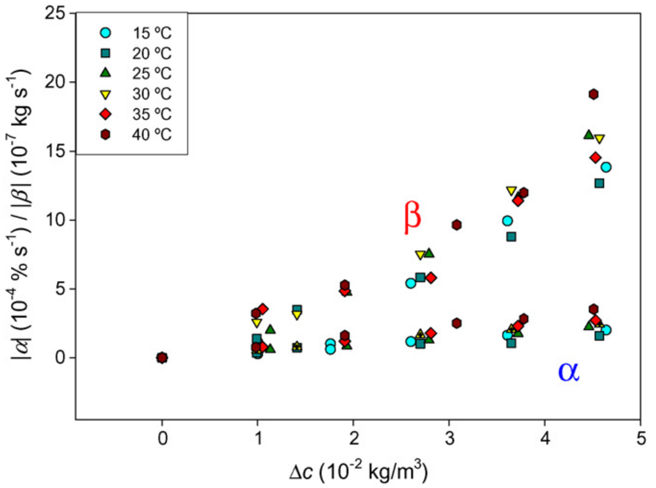

Fig. 4. Concentration change velocity, α, and total mass flux, β, as a function of the initial methanol concentration at a 300 ml/min circulation velocity for different temperatures.

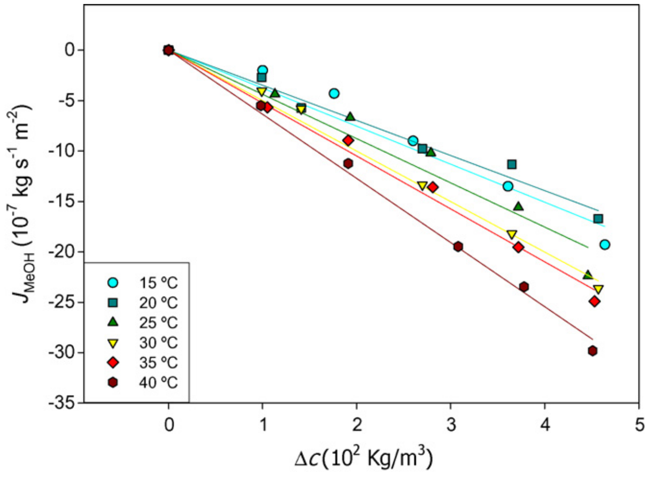

Fig. 5. Methanol flux as a function of the initial methanol concentration at a 300 ml/min circulation velocity for different temperatures.

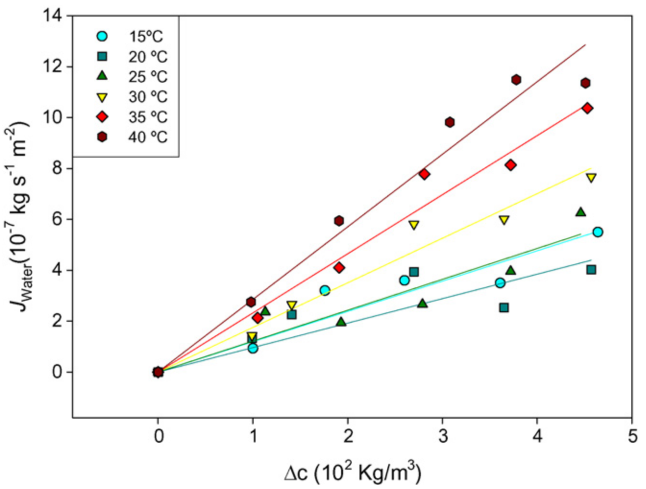

Fig. 6. Water flux as a function of the initial methanol concentration at a 300 ml/min circulation velocity for different temperatures.

inated from the concentrated to the diluted chamber. In contrast, a positive flux of water is found, indicating that the water flux goes in the opposite direction. This behavior was observed regardless of the temperature used. In general, the higher the methanol concentration difference, the higher the corresponding flux. The methanol flux is always higher than the water flux, but this last cannot be neglected.

When the experimental data of Figs. 5 and 6 are fitted to a first-order polynomial, a mean methanol and water permeabilities could be estimated from the slope of the straight line. The results are shown in Fig. 7 as a function of the temperature. It is observed that, in general, the mean permeability increases with temperature, with the exception of the value corresponding to 15 °C. Moreover, at any temperature, the methanol permeability is higher than the water permeability.

3.3. *Influence of the temperature. Estimation of methanol and water flux activation energies*

It is possible to use the obtained experimental data to study the dependence of water and methanol fluxes with the temperature. In this case, the flux was plotted versus the reciprocal of the absolute temperature for methanol–water solutions with the different methanol concentrations (10%, 20%, 30%, 40% and 50% (w/w)). In all

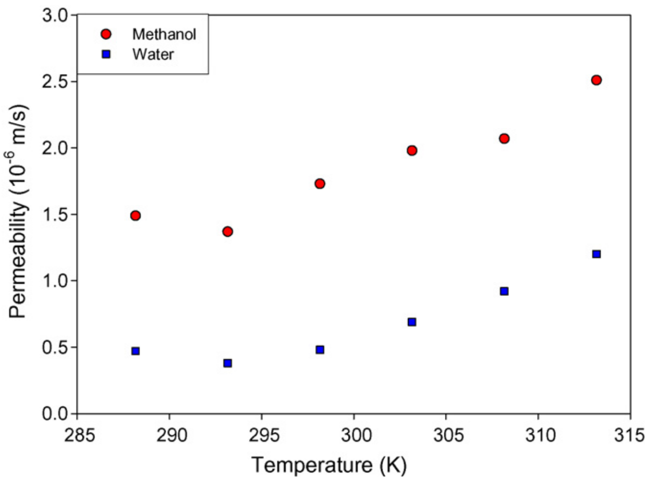

Fig. 7. Methanol and water permeabilities as a function of the temperature.

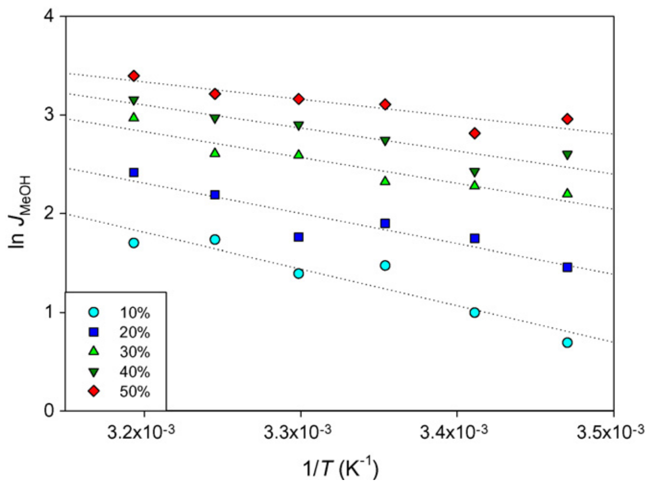

Fig. 8. Natural logarithm of methanol flux against the reciprocal of absolute temperature for the different initial methanol concentrations.

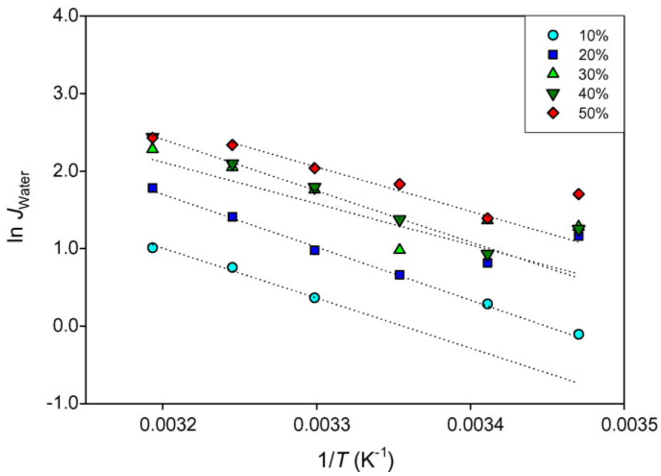

Fig. 9. Natural logarithm of water flux against the reciprocal of absolute temperature for the different initial methanol concentrations.

cases, the circulation velocity was maintained at 300 ml/min. As a general trend, there is a flux increase with the temperature.

The dependence of methanol flux on temperature can be expressed by an Arrhenius-type equation:

$$J \propto \exp\left(-\frac{E}{RT}\right) \tag{5}$$

where R is the gas constant and E is the activation energy associated with the flux. Accordingly, plots representing the natural logarithm of methanol fluxes against the reciprocal of the absolute temperature are straight lines. These results are shown in Fig. 8. From the slope of the corresponding straight line, the activation energy values for the methanol flux are obtained. The results for methanol activation energy at methanol–water solutions with different compositions are given in Table 1. It is worth noting that methanol flux obeys Arrhenius-type equation as reflected by good correlation coefficients (0.9). In the case of water, a general similar behavior was observed, but the Arrhenius behavior is not so clear and depends on the temperature range. As can be observed in Fig. 9, plots representing the natural logarithm of water fluxes against the reciprocal of the absolute temperature are straight lines at high temperature and only the data in this temperature interval are considered in the calculation. The obtained values for the water activation energy are also shown in Table 1. On the other hand, it is found that, in the case of methanol transport, the activation energy associated with flux decrease with the increase in the concentration difference between the chambers. This could mean that the concentrations increase made the process easier. It should be pointed out that the methanol activation energy values obtained in the present work are the same order of magnitude as those found in the literature [19,20]. On the other hand, it seems that the activation energy associated with the water flux have not a clear trend with the methanol concentration of the solution. The water activation energy values are the same order of magnitude as those reported by other authors [21,22]. At a given methanol concentration difference, the activation energy of methanol flux is lower than that of water flux. This may indicate that methanol diffuses easier in the membrane than water does. This fact is in agreement with the higher values of the permeability obtained for methanol in comparison with the water values.

The values of the overall, methanol and water solubilities of the membrane are shown in Table 2 as a function of the methanol percentage of the immersing solution. As can be observed, the overall solubility increases when the methanol percentage increases, in agreement with the results obtained by other authors [23,24]. But this increase is due to an increase of the methanol solubility. The water swelling seems to be independent on the presence of methanol on the solutions. This behavior is in agreement with the results obtained by other authors and it may be explained by the hydrophobic character of the Nafion membrane. In the present of a polar solvent, a hydrophobic/hydrophilic separation takes place in the membrane. The water molecules are inside the hydrophilic domains of the polymer, whereas methanol is also soluble in the hydrophobic backbone. This fact explains the increase of the methanol solubility with the methanol content. Fig. 10 shows the methanol and water activation energies of the membrane as a function of the corresponding solubility. As can be observed, there is a correlation between the energy activation and the solubility of the membrane in the case of methanol, in such way that the higher the solubility, the lower the activation energy. No correlation seems to exist in the case of water. It would indicate that the diffusion process is favored by the presence of the solvent inside of the membrane. An increase of the methanol content of the solutions leads to an increase of the methanol percentage inside the membrane and so, to a lower activation energy. In the case of water, the percentage of methanol on solutions does not affect the water content of the membrane and therefore the activation energy for water is independent on the methanol concentration difference.

Table 1
Activation energy, E, as a function of the initial methanol concentration difference (wt.% MeOH) associated with methanol and water fluxes through a Nafion membrane.

MeOH (wt.%)	E_{methanol} (10^4 J/mol)	E_{water} (10^4 J/mol)
10	3.1	5.3
20	2.6	5.7
30	2.2	4.5
40	1.9	5.5
50	1.5	4.7

Table 2
Overall, methanol and water membrane solubilities, as a function of the initial methanol concentration (wt.% MeOH).

MeOH (wt.%)	S (%)	S_{Methanol} (%)	S_{Water} (%)
10	36	4	32
20	40	8	32
30	45	13	32
40	52	20	32
50	64	31	33

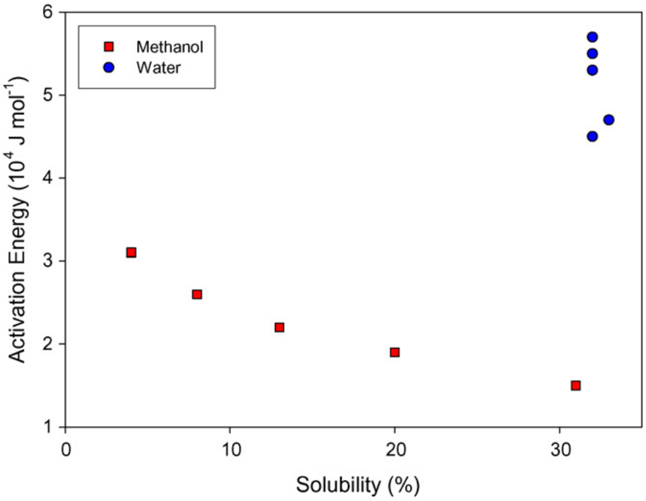

Fig. 10. Methanol and water activation energies of the membrane as a function of the corresponding solubility.

4. Conclusions

The influence of different operating parameters in the transport of water and methanol through a cation-exchange Nafion membrane when it is used to separate water from a methanol–water solution, has been investigated. The results show that the overall, methanol and water fluxes are not affected by the circulation velocity of the solutions between the reservoirs and the membrane cell, in the range studied.

The effect of the solution concentration difference across the membrane on the mass transport through it is straightforward, the higher the methanol concentration difference, the higher the overall, methanol and water fluxes. The analysis of the results show that the partial fluxes of methanol and water increases linearly with the methanol concentration difference in the membrane. Under the same conditions, the water flux is always lower than the methanol flux, but it cannot be neglected.

The temperature dependences of both the methanol and water fluxes through the membrane were studied over the temperature range 15–40 °C. It is found that the methanol flux obeys Arrhenius behavior in all the temperature range, indicating that the methanol transport in the membrane is an activated thermal process. In the case of the water flux, the Arrhenius behavior is only observed at higher temperatures interval. The activation energies associated with the methanol and water fluxes have been estimated and they are the same order of magnitude as those found in the literature. A dependence of the activation energy on the methanol concentration is observed only in the case of methanol. These results have been explained in terms of membrane solubility.

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