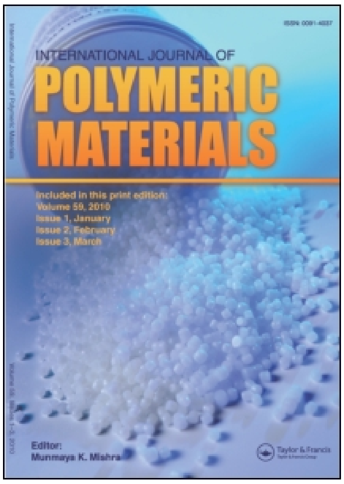

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Methods of Measuring Diffusion Coefficients of Water and Potassium Chloride in Aqueous Solution in Cellulose Acetate Membranes

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Methods of Measuring Diffusion Coefficients of Water and Potassium Chloride in Aqueous Solution in Cellulose Acetate Membranes

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An open-ended capillary cell has been developed to measure thermodynamic diffusion coefficients of electrolytes, in aqueous solution, in swelled polymeric membranes. Also a new method to determine the integral diffusion coefficient of water in membranes is presented. In this work we present a description of the methods as well as the experimental results of the diffusion coefficients of potassium chloride and water in cellulose acetate (CA) membranes. The results are in good agreement with those described elsewhere which shows the reability of the methods.

KEY WORDS Diffusion, polymers, electrolytes, diffusion coefficients.

1. INTRODUCTION

The sorption and diffusion of substances of low molecular weight in polymers is of great practical importance, as shown in recent studies[1,2] of sorption and desorption of solutes in polymers, as well the development of a model of simultaneous transport of water and solute in polymers,[3,4] concerning modelling the kinetics of those phenomena in different cases. However, there are some difficulties in the experimental measurement of some parameters. One of them is the mutual differential diffusion coefficient, D, frequently called thermodynamic diffusion coefficient. An open-ended conductimetric capillary cell[5,6] has been used, with some success,[7] to measure this diffusion coefficient D of electrolytes imbibed in polymers both in powder, and in foam state.[8,9]

In the present work we present a new development of the open-ended capillary cell with a modified design permiting the measurement of the diffusion of an electrolyte (KCl) through polymeric membranes (cellulose acetate). The integral diffusion coefficients of water in the same films help us to understand the mechanism of diffusion as well as to explain the measured results on the basis of free volume theory.[10]

2. METHODS

I. A Method to Measure the Integral Diffusion Coefficients of Water in Membranes

A new method was developed to measure a diffusion coefficient of water in different kinds of polymeric membranes. A cell (Figure 1) with two compartments, A, completely filled with distilled water and B, with poly(ethylene glycol) has a membrane 30 mm in diameter separating them. A capillary positioned in the upper side of the cell measures the variation of water volume during the diffusion studies. The poly(ethylene glycol) of molecular weight 400 in compartment B continuously stirred mantains the concentration of water in the bottom of the membrane equal to zero. In order to quickly achieve the equilibrium all the membranes were immersed in water 24 hours before the beginning of the experiment.

The water diffusion coefficients were determined by following an adaptation of Fick's 1st law:

$$(dh/dt) = D(s_m/a_c)l^{-1} \tag{1}$$

dh/dt is the variation of the height of the column of water in the capillary tube with time, s_m is the area of the membrane surface, a_c is the capillary area and l is the membrane thickness.

II. Open-Ended Conductimetric Capillary Cell

The open-ended capillary cell (OECC) consists basically of two capillaries connected to supporting tubes. There are two platinum electrodes, PT, Figure 2, and a third electrode (CE) equidistant from these. The electric contact with the external electric circuit is made by mercury drops. Diffusion takes place at the bottom capillary previously filled with electrolyte solution of concentration 1.25c, and at the top capillary initially filled with electrolyte solution 0.75c, after the cell is immersed in a tank with electrolyte solution of concentration c (bulk solution). At present (Figure

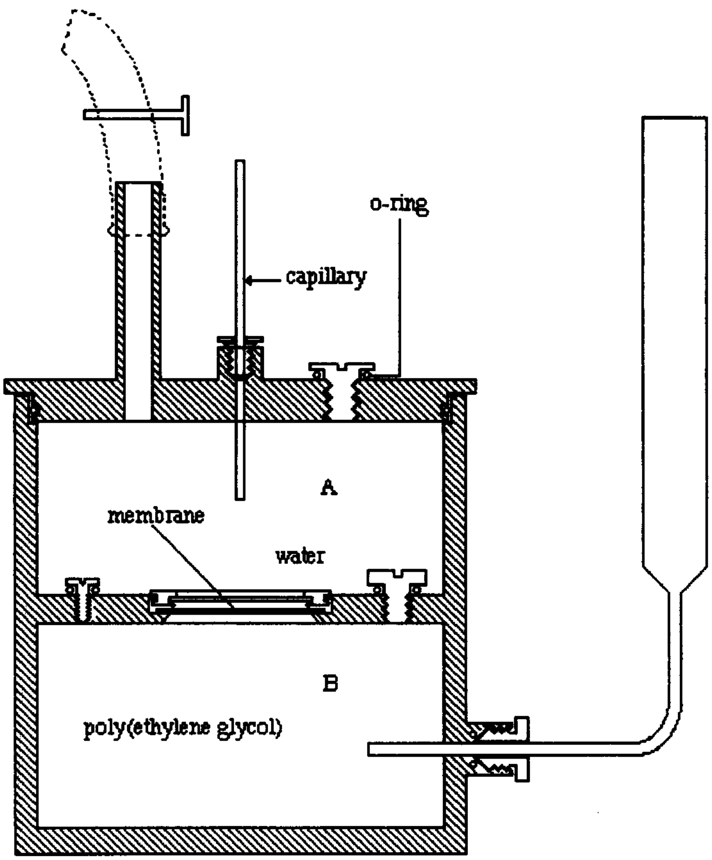

FIGURE 1 Schematic representation of the cell developed to measure the integral diffusion coefficients of water in membranes.

3), the capillaries have also a steel piece, *S*, which adjusts the membrane to the open mouth of each capillary, resulting in a hermetic system (the contact between the electrolyte inside the capillary and in the tank is only possible through the membrane). Experiments carried out using this system with 0.1 M KCl aqueous solutions, showed that the stainless steel pieces do not affect the streamlined flow of solution across the mouth of capillaries.[6,11]

The diffusion process is followed by measuring, at recorded times (t), the electrical resistance ratio $W = R'/R''$ where R' is the resistance of the solution inside the top capillary, and R'' that of the bottom capillary.

In order to calculate D_T we have to bear in mind the following approximations: i) We treat the system as binary. We will not consider the possible interactions between polymer-solvent and polymer-ion. ii) The diffusion coefficient D is constant in both the membrane and the capillary. iii) Diffusion proceeds in the membrane along a path with a diameter equal to that of the diffusion capillary. iv) The diffusion process inside the capillary is independent of the diffusion process in the membrane. v) According to iv), we apply identical boundary conditions[12] to both membrane and capillary. That is to membrane

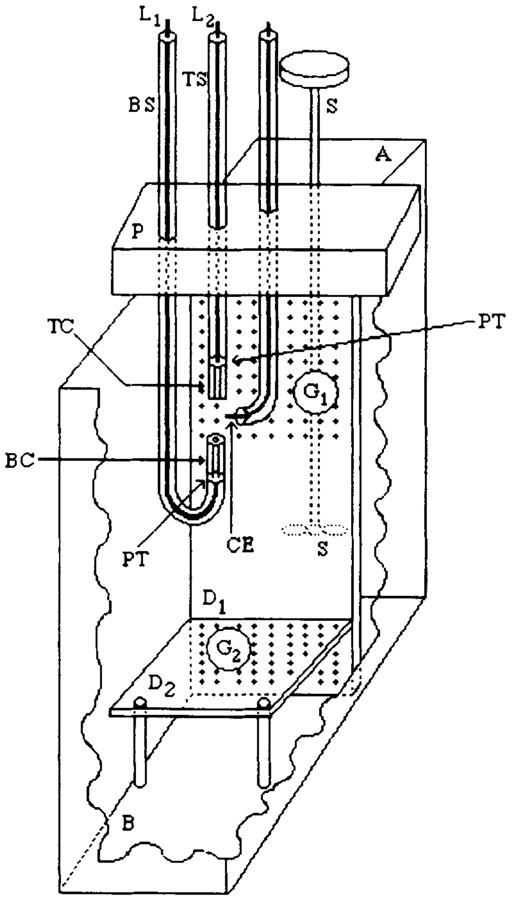

FIGURE 2 Illustration of the open-ended capillary cell. TS, BS—support capillaries; TC, BC—top and bottom diffusion capillaries; CE—central electrode; PT—platinum electrodes; D_1, D_2—perspex sheets; S—glass stirrer; P—perspex block, G_1, G_2—perforations in perspex sheets, A, B—sections of the tank; and L_1, L_2—small diameter coaxial leads.

at $t = 0$ seconds, $c = c_0$ to $0 < x < a$ and $c = c_b$ to $x > a$;

at $t > 0$ seconds, $c = c_b$ to $x > a$ and $(\partial c/\partial x) = 0$ to $x = 0$

and to capillary

at $t = 0$ seconds, $c = c_0$ to $0 < x < a$;

at $t > 0$ seconds, $c = c_b$ to $x > a$ and $(\partial c/\partial x) = 0$ to $x = 0$

c_0 and c_b are, respectively, the initial concentration of the electrolyte solution inside a capillary and the concentration of bulk electrolyte solution; x represents the coordinate of an axis where the diffusion proceeds, with $x = 0$ the ended side and $x =$

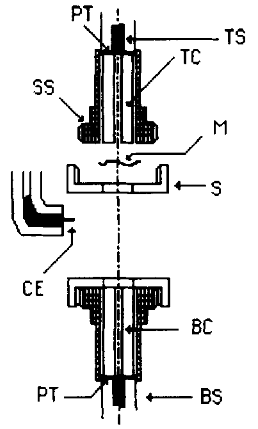

FIGURE 3 Simplified scheme of the modified conductimetric cell. TS, BS—support capillaries; TC, BC—top and bottom diffusion capillaries; S—screw and membrane support; SS—screw support; M—membrane; CE—central electrode; PT—platinum electrodes.

a the open mouth of capillary. In the case of the diffusion process in the membrane the $x = 0$ represents the point where the membrane is adjacent to the open mouth of the capillary, and $x = a$ represents the thickness of the membrane. The solution of the Equation (2),

$$(\partial c/\partial t) = D(\partial^2 c/\partial x^2), \tag{2}$$

for the boundary conditions above mentioned and discussed, is given by the general expression (3):

$$c = \sum_{n=0}^{\infty} B_n \exp[-\pi^2(2n + 1)^2 Dt/4a^2]\cos(\pi(2n + 1)x/2a) + c_b \tag{3}$$

where

$$B_n = (-1)^n(4(c_0 - c_b)/\pi(2n + 1)), \tag{4}$$

D is the diffusion coefficient, t is the time, a is the length of the path diffusion, c is a concentration in a coordinate x, and c_0 is the initial concentration inside the capillary and membrane.

If we consider c_m as the concentration average inside the capillary (or membrane) defined as $c_m = 1/a \int_0^a c\, dx$, and c_b as $c_b = 1/a \int_0^a c_b\, dx$, then

$$(c_m - c_b) = \frac{1}{a}\int_0^a (c - c_b)\, dx. \tag{5}$$

Using Equations (3) and (5) we obtain

$$\frac{c_m - c_b}{c_b} = q(t) = \frac{c_0 - c_b}{c_b} \sum_{n=0}^{\infty} \frac{8}{\pi^2(2n+1)^2} \exp[-\pi^2(2n+1)^2 Dt/4a^2] = q_0 M(\lambda t) \tag{6}$$

where

$$M(\lambda t) = \sum_{n=0}^{\infty} \frac{8}{\pi^2(2n+1)^2} \exp[-\pi^2(2n+1)^2 Dt/4a^2] \tag{7}$$

and

$$\lambda = \pi^2 D/4a^2 . \tag{8}$$

Experimental measurements are taken many hours after starting an experiment when only the first term of the series is significant. Then

$$q = q_0(8/\pi^2)e^{-\lambda t} + \text{neglected terms} \tag{9}$$

Concerning the diffusion inside the capillary and membrane, we can write identical expressions to (9) considering the subscripts 1 and 2 the description of the process in capillary and in membrane, respectively:

$$q_1 = q_{01}(8/\pi^2)e^{-\lambda_1 t} + \text{neglected terms;} \tag{10}$$

$$q_2 = q_{02}(8/\pi^2)e^{-\lambda_2 t} + \text{neglected terms.} \tag{11}$$

On the other side, and as a consequence of the assumptions iv) and v), we can define the resistance between the central electrode and, e.g., the top electrode as a sum of three different terms

$$R = r + \frac{a_1}{A}\int_{\xi_1=0}^{1} \rho_1 \, d\xi_1 + \frac{a_2}{A}\int_{\xi_2=0}^{1} \rho_2 \, d\xi_2 \tag{12}$$

where ρ is the resistance from the interface membrane-bulk solution until central electrode, ρ_1 and ρ_2 the specific resistance inside the capillary and the membrane, respectively, $\xi_1 = x/a_1$ and $\xi_2 = x/a_2$, and A the cross section.

If now we consider a function h defined as

$$h = (c - c_b)/c_b, \tag{13}$$

the specific resistance may be expanded as a power series in h in the form

$$\rho = \rho_b \sum_{m=0}^{\infty} b_m h^m \tag{14}$$

where ρ_b corresponds to concentration c_b ($h = 0$). However as D is computed from readings at high values of time t, h values are much lower than one, and the Equation (14) can be simplified:

$$\rho = \rho_b(1 + bh). \tag{15}$$

Using Equations (12) and (15) we obtain

$$R = r + \frac{a_1}{A}\rho_{b1} + \frac{a_1}{A}b_1\rho_{b1}\int_0^1 h_1\,d\xi_1 + \frac{a_2}{A}\rho_{b2} + \frac{a_2}{A}b_2\,\rho_{b2}\int_0^1 h_2\,d\xi_2 \tag{16}$$

If we assume that $\rho_{b1} = \rho_{b2} = \rho_b$, and $a_1 \gg a_2$ then we can define the resistance R at infine time (R_∞) as

$$R_\infty = r + (a_1/A)\rho_b. \tag{17}$$

Using the equation (17) we can rewrite the equation (16) as

$$\begin{aligned} R &= r + \frac{a_1}{A}\rho_b + \frac{\rho_b}{A}\left(a_1b_1\int_0^1 h_1\,d\xi_1 + a_2b_2\int_0^1 h_2\,d\xi_2\right) \\ &= R_\infty + (R_\infty - r)\left(b_1\int_0^1 h_1\,d\xi_1 + \frac{a_2}{a_1}b_2\int_0^1 h_2\,d\xi_2\right). \end{aligned} \tag{18}$$

From the relations

$$q_1 = q(t) = \int_0^1 h_1\,d\xi_1 \tag{19}$$

and

$$q_2 = q(t) = \int_0^1 h_2\,d\xi_2 \tag{20}$$

Equation (18) can be reformulated as

$$R = R_\infty + (R_\infty - r)(b_1q_1 + b_2q_2). \tag{21}$$

For a question of simplicity we maintian the symbol b_2 as a constant. However this constant in Equation (18) does not have the same value as in the Equation (21). In the latter, b_2 is also affected by a fraction (a_2/a_1).

Considering the total resistance between the top and bottom capillaries (R_t) as the sum of the resistances of top capillary (R') and bottom capillary (R''),

$$R_t = R' + R'', \tag{22}$$

and a measured resistance ratio W_t given by

$$R' = W_t R'' = (W_t/(W_t + 1))R_t, \tag{23}$$

we may derive from it the quantity Y_t defined by

$$Y_t = (W - 1)/(W + 1) = \frac{R'/R'' - 1}{R'/R'' + 1}. \tag{24}$$

If both capillaries and membranes are initially filled with bulk solution (c_b), we achieve the same situation as would occur at infinite time in a diffusion experiment starting with a finite concentration difference. For this case we have

$$Y_\infty = (W_\infty - 1)/(W_\infty + 1) \tag{25}$$

Ideally W_∞ should be unity and Y_∞ should be zero.

If we rearrange the measured parameter (W) as

$$Y_t - Y_\infty = \frac{W - 1}{W + 1} - \frac{W_\infty - 1}{W_\infty + 1} = \frac{R' - R''}{R_t} - \frac{R'_\infty - R''_\infty}{R_{t\infty}} \tag{26}$$

and in conductimetric cell the R_t is equal to a $R_{t\infty}$, then the Equation (26) has the same denominator. Then

$$Y_t - Y_\infty = \frac{R' - R'_\infty}{R_{t\infty}} - \frac{R'' - R''_\infty}{R_{t\infty}}. \tag{27}$$

Considering now a function P given by

$$P_\infty = R_\infty - r \tag{28}$$

and using the Equations (27) and (28) we find

$$Y_t - Y_\infty = \frac{b_1(P'_\infty q'_1 - P''_\infty q''_1) + b_2(P'_\infty q'_2 - P''_\infty q''_2)}{R_{\text{total}\infty}} \tag{29}$$

Using the Equation (21), the Equation (29) can be rewite as

$$\begin{aligned} Y_t - Y_\infty &= \frac{b_1 \frac{8}{\pi^2} e^{-\lambda_1 t}(P'_\infty q'_{01} - P''_\infty q''_{01}) + b_2 \frac{8}{\pi^2} e^{-\lambda_2 t}(P'_\infty q'_{02} - P''_\infty q''_{02})}{R_{\text{total}\infty}} \\ &= c_1 e^{-\lambda_1 t} + c_2 e^{-\lambda_2 t} \end{aligned} \tag{30}$$

where c_1 and c_2 are constants. Equation (30) is the fundamental expression of the method from which we compute the thermodynamic diffusion coefficients.

After obtaining the experimental values of resistance ratio versus time, the first step is to analyse if there is linearity of the results obtained with Equation (31). This equation corresponds at a particulary case of the Equation (30)

$$\ln(Y_t - Y_\infty) = c - \lambda t \tag{31}$$

The linearity of the results (for electrolyte experiments linearity is reached after approximately 1000 minutes) allows us to neglect the second and higher terms of the solution equation of Fick's 2nd law,[13] but is not possible to have more information about diffusion coefficients through the above equation. As we can see in Figure 4, and considering a set of results for KCl 0.1 M and cellulose acetate of thickness 2.0 × 10^{-3} mm, the desired linearity (correlation coefficient $R = 0.985$) is only reached three days after the starting of the experiment. After this procedure we will apply Equation (30) to the experimental results best fitting the Equation (4)—Figure 4c).

The aim of this procedure is to select the experimental values to compute the parameter λ_2, and consequently the thermodynamic diffusion coefficient of the electrolyte in the membrane, knowing the membrane thickness (a_2). Using a computerized least-squares procedure, which finds the best c_1 and c_2, we obtain λ_1 and λ_2 from Equation (30). λ_1 is a measure of the diffusivity of KCl inside the capillary in the presence of a restriction, and λ_2 is a measure of the thermodynamic diffusion coefficient of electrolyte inside the membrane.

4. EXPERIMENTAL PROCEDURE

The apparatus used for measuring thermodynamic diffusion coefficients in the present study has been discussed in previous section and is essentially the same as that described elsewhere,[6] which has been successfully used in the study of differential diffusion coefficients of electrolytes in aqueous solutions.[14] The water diffusion coefficient was determined by using the cell showed in Figure 1.

Experiments were performed with aqueous solutions of KCl 0.1 M, prepared from Merck *pro analysi* reagent. That solution was obtained by mixing equal volumes of 0.075 M and 0.125 M of KCl solutions, previously prepared. The upper and lower tubes, were initially filled with solutions 0.075 M and 0.125 M, respectively. The acetate cellulose films after 24 hours of immersion in top and bottom solutions were placed in the mouth of the respective diffusion capillary. The system is then placed in a tank with 0.1 M KCl solution, the bulk solution, and the time is recorded.

The cellulose acetate membranes were prepared from portions of the polymer (1.5 g or 3.0 g) (49% acetilated, from Sigma Chemical Company, Poole, Dorset, England) dissolved in 15 cm^3 of tetrahydrofuran, stirring for 24 hours. The solution was evaporated on a glass plate. Membranes with 20 μm and 35 μm were obtained. In order to characterize the membranes through its water sorption, each membrane was introduced in a excicator containing a saturated solution of $CuSO_4 \cdot 5H_2O$ at 20°C,

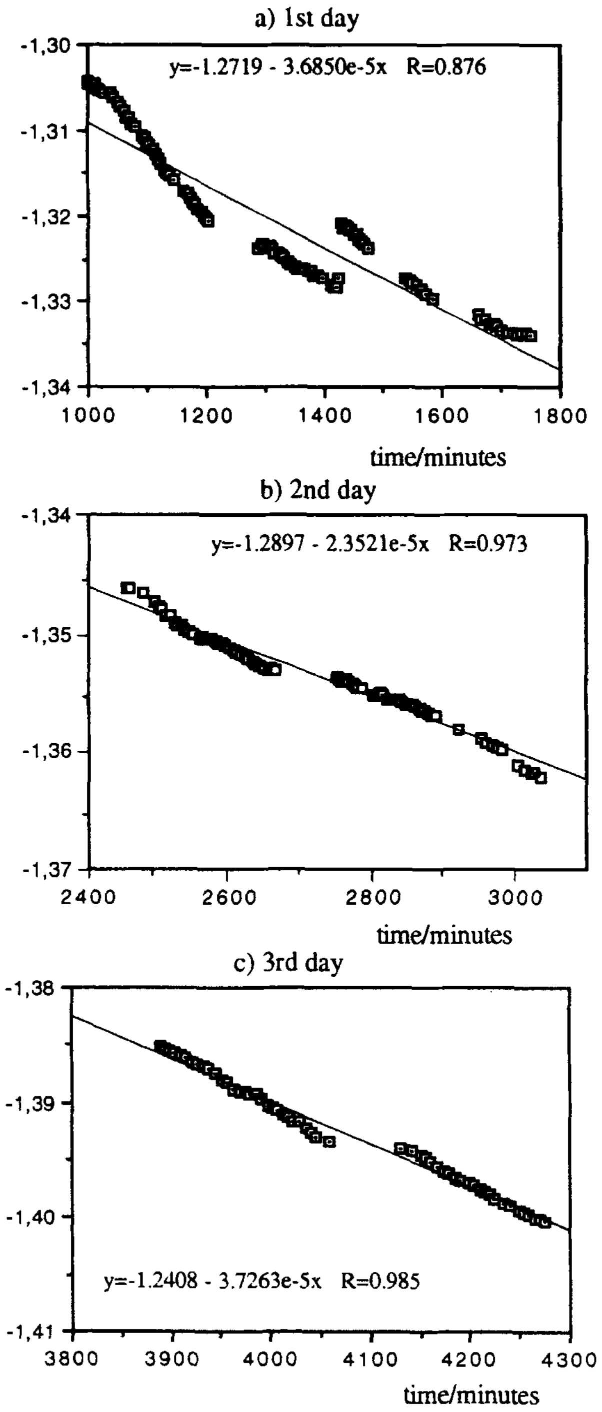

FIGURE 4 Plots of a function of a resistance ratio, Equation (3), versus time *t*, for the 1st, 2nd and 3rd days of running of the diffusion experiment, respectively a), b) and c).

remaining there until constant weight. This ensures an atmosphere with 98% humidity. The percentage of water absorption was calculated from

$$\%\ \text{water sorption} = (w_f - w_i)/(w_i) \times 100 \tag{32}$$

where w_f and w_i are the final and initial weights of the membrane respectively.

5. RESULTS AND DISCUSSION

Table 1 presents the integral (D) and thermodynamic (D_T) diffusion coefficients of water and of 0.1 M KCl solutions in cellulose acetate membranes of different thicknesses at 298 K. D_T values were computed considering the λ_2 obtained by Equation (30).

In a first analysis of those results, we conclude that the precision of the method developed to measure the Fickian diffusion coefficients of water is very high, though not an absolute one. The results are also of the same order of magnitude of those reported in the literature.[15]

On the other hand, the precision of the results with KCl is not so high, particularly concerning the experiments with 3.5×10^{-2} mm thickness membranes. In the open-ended capillary cell, the precision can be easily affected by some lost of homogeneity of the membranes. In fact, when the sample membranes of the top and bottom capillaries are not exactly the same, the experimental results show a deviation, leading to a different value. This is a consequence of the symmetry of the method which makes it is sensible enough to detect any kind of irregularity on the system. However the D_T results obtained are of the same order of magnitude of the Fickian diffusion coefficients of NaCl in identical membranes,[16] measured through another conductimetric method. This comparison can also prove the validity of the mathematical theory of the method previously described. Therefore, we believe that the reported average diffusion coefficient is an accurate value due to the design of the cell and its operation, within the indicated error.

TABLE I

Thermodynamic diffusion coefficients (D_T) of KCl 0.1 M solutions and integral diffusion coefficients (D) of water, in cellulose acetate membranes of different thicknesses at 298 K

Polymer content*	Thickness/ 10^{-2} mm	Water sorption	$D \pm \sigma$/ 10^{-12} m^2 s^{-1}	DC/ 10^{-9} m^2 s^{-1}	D_T/ 10^{-13} m^2 s^{-1}	$D_T \pm \sigma$/ 10^{-13} m^2 s^{-1}
10%	2.0	13.5%	1.63 ± 0.05	1.827	3.260	3.466 ± 0.615
				1.845	2.980	
				1.831	4.158	
20%	3.5	14.4%	2.44 ± 0.02	1.831	8.063	3.826 ± 3.696
				<<1.845	2.155	
				1.831	1.261	

*Percentage (w/v) of cellulose acetate in solvent tetrahydrofuran.

Table 1 also presents the diffusivity coefficients (DC) of KCl inside the capillary for each experiment. We can see that these diffusivity coefficients are smaller than the diffusion coefficient of KCl in aqueous solution, which is $D = 1.845 \times 10^{-9}$ m^2 s^{-1},[17] as we expected. In fact, the process inside the capillary and membrane is not totally independent as assumed above. In the same way, the results show that the boundary condition concerning the capillary at $t > 0$ is very close to reality. Firstly, if the membrane is impermeable at the interface capillary-membrane, (a boundary condition in a restrict point of view), the total resistance would be infinite and thus, it would not be possible to obtain any measurements. On the other hand, the method permits measuring differential changes of concentration, which is done after at least 1000 minutes. Therefore the real situation is not that at $t > 0$, $c = c_b$ at $x > a$, but c is approximately equal to c_b.

The diffusion coefficients of water are approximately one order of magnitude lower than the thermodynamic diffusion coefficients of KCl in the same polymers, and both increase with the increasing thickness of the membrane. In fact, we should not expect alterations of the reported values for the diffusion coefficients of water and KCl in cellulose acetate because we only change the thickness of the polymer. Because the surface of the membrane has a different polarity than the bulk, such alterations may occur. This may explain the different values obtained for the diffusion coefficients concerning the same polymer. The increase of the values of D and D_T with the membrane thickness can be explained by the differences in the membrane densities, as a measure of the structure ordering. This was verified experimentally and was confirmed that the thinner membrane presents a higher density.[18] When the intermolecular forces between the polymer chains are weak, the water can diffuse without expending so much energy. Another factor helping the explanation of the results is that the increase of the membrane thickness is followed by an increase of water sorption, and in consequence the diffusivity of water is also easy. If the membrane sorves more water, the free volume is also higher, and therefore the system becomes closer to a water-electrolyte system, and the D_T also increases. Then, it seems reasonable to believe that the KCl diffusion process inside a membrane in the same way as in aqueous medium.

For all the above reasons the open-ended conductimetric cell applied to polymeric membranes, and the method to measure the Fickian diffusion coefficients of water, seems to be a very feasible and reliable method to study diffusion in systems such as polymer-electrolyte-water and polymer-water.

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