Electrolyte diffusive flux determination through a highly selective cation exchange membrane

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A new method for evaluating highly selective ion exchange membranes is devised, which is competitive with the counter-ion transport number determination method. It is based on the evaluation of a strong electrolyte leakage through a membrane. This study uses a CM2 polystyrene and divinylbenzene sulfonated cation exchange membrane, separating two solutions, one containing the electrolyte at a given concentration C_0 and the other permuted water. The electrolyte diffuses under its concentration gradient and induces an increase of the conductivity in the diluted compartment, allowing the determination of its flux. This new method is shown to be reliable and sufficiently accurate over a large concentration range. The bilogarithmic variation of the flux *versus* the concentration, for the KCl ($10^{-2} \leqslant C_0 \leqslant 4$ mol L^{-1})/CM2/H_2O system, shows the existence of three linear sections, each one corresponding to a diffusion state. The concentration range 10^{-1}–2 mol L^{-1} seems to be the most interesting one for experimental and theoretical studies of the diffusion phenomenon of a strong electrolyte through an ion exchange membrane. In this domain the concentration is high enough that the proton contribution to the measured values of the conductivity can be neglected and sufficiently low that the osmosis flux, which would slow down the electrolyte as it diffuses, is not important.

Une nouvelle méthode simple d'évaluation des performances des membranes échangeuses d'ions (MEI) fortement sélectives est proposée. Cette méthode est concurrentielle à celle de la détermination du nombre de transport du contre-ion. Elle est basée sur l'évaluation de la fuite d'un électrolyte fort à travers une membrane (dans cette étude, nous avons utilisé une membrane sulfonique échangeuse de cation, CM2) séparant deux solutions, l'une contenant cet électrolyte à la concentration C_0 et l'autre initialement de l'eau permutée. L'électrolyte diffuse alors sous l'effet de son gradient de concentration et fait augmenter la conductivité du compartiment dilué, laquelle nous permet de déterminer son flux. Nous avons montré que cette nouvelle méthode est sûre et suffisamment précise sur une large gamme de concentrations. La variation bilogarithmique du flux en fonction de la concentration pour le système KCl ($10^{-2} \leqslant C_0 \leqslant 4$ mol L^{-1})/CM2/H_2O montre l'existence de trois domaines linéaires dont chacun correspond à un régime de diffusion. La gamme de concentrations 10^{-1}–2 mol L^{-1} semble être la plus intéressante pour les études expérimentales et théoriques du phénomène de diffusion d'un électrolyte fort à travers une MEI. Dans ce domaine la concentration est suffisamment élevée pour pouvoir négliger la contribution des protons aux valeurs mesurées de la conductivité et suffisamment faible pour ne pas générer un important flux osmotique qui ralentit l'électrolyte lors de sa diffusion.

Nowadays, ion exchange membranes (IEM) find their principal applications in many processes like dialysis, electrodialysis, electro-electrodialysis, fuel cells.... In electromembrane processes, the membrane conductivity measurement is necessary to determine the order of magnitude of the ohmic drop on which depend the energetic performances. Nevertheless, this parameter only is not sufficient to choose the best ion exchange membrane for a given application. Indeed, the membrane must have not only a high conductance but also a very good selectivity towards counter-ions *vs.* co-ions. That means that for electromembrane processes and those appealing to more than one counter-ion, the used membrane must minimize the co-ion fluxes and maximize the counter-ion fluxes. Thus, the membrane selectivity is the ability of this membrane to favour the counter-ion transmembrane transfer over the co-ion one.

Estimation of the last criterion, selectivity, is generally carried out by determining the counter-ion transport number. For recent membranes, we have shown in a previous paper[1] that the former technique is no longer adapted because the transport number values often range between 0.95 and 1.00. Because of the restricted variation of this parameter and of the low accuracy on its determination (in the best case ± 0.005), it is impossible to get a reliable classification of ion-exchange membranes according to their selectivity. Additionally, the transport number determination requires a relatively complex instrumental set-up, not available to all membrane users.

In this paper, we propose a simple dialysis experiment to characterize the type of ion exchange membranes under study. This new and competitive method for evaluating the selectivity of highly selective IEMs is proposed to replace the transport number determination method. Our method is based on the measurement of a strong electrolyte leakage through a highly selective cation exchange membrane (CEM) when it separates two solutions, one initially containing a strong electrolyte at a given concentration and the other permuted water. In this system, the electrolyte diffuses through the membrane under its concentration gradient. The literature on this phenomenon is very extensive, but we must emphasize that if another gradient, of pressure or electrical potential, is applied to the membrane,[2–5] the transfer under the concentration gradient is not generally taken into account.

Thus, our main goal in this paper is to determine the concentration domain allowing reliable, fast and reproducible measurements of the transmembrane electrolyte flux and for which the number of factors influencing this flux is reduced to minimum.

Theory

The study of the strong electrolyte leakage through an IEM allows us not only to evaluate its selectivity with the aim of optimizing its choice for a given application, but also to verify some transfer equations, in order better to understand the diffusion process. Many authors[6–9] have derived equations for the diffusion flux, such as in the case of the gel model and complete membrane control, using simplifying assumptions and Fick's law or the Nernst–Planck equation.

Fig. 1 schematicizes the system AY (C_0)/CEM/H_2O under study, with the initial experimental conditions. Here, the upstream compartment initially contains a concentrated electrolyte solution and the downstream compartment, permuted water; but just after the beginning of the experiment it will contain the electrolyte in low concentration, thus it is called the 'diluted compartment'.

The flux, J_i, of a species i with a concentration C_0, an activity coefficient γ_i, a charge z_i, a mobility u_i and put in an electric field $\vec{E}$, derived from an electric potential Ψ, is generally given by the Nernst–Planck equation:

$$J_i = -RTu_i\left(\frac{\mathrm{d}C}{\mathrm{d}x} + C_i\frac{\mathrm{d}Ln\gamma_i}{\mathrm{d}x} + z_i\frac{F}{RT}C_i\frac{\mathrm{d}\Psi}{\mathrm{d}x}\right) \qquad (1)$$

If γ_i is independent of x (for example in the case of an ideal solution $\gamma_i = 1$):

$$J_i = -RTu_i\left(\frac{\mathrm{d}C_i}{\mathrm{d}x} + z_i\frac{F}{RT}C_i\frac{d\Psi}{\mathrm{d}x}\right) \qquad (2)$$

For a 1 : 1 electrolyte, A^+Y^-, the Nernst–Planck equation applied to the counter-ion and to the co-ion, in the case of complete membrane control of the diffusion process, gives:

$$J_{A^+} = \overline{J_{A^+}} = -\overline{D_{A^+}}\left(\frac{\mathrm{d}\overline{C_{A^+}}}{\mathrm{d}x} + \overline{C_{A^+}}\frac{F}{RT}\frac{\mathrm{d}\overline{\Psi}}{\mathrm{d}x}\right) \qquad (3)$$

$$J_{Y^-} = \overline{J_{Y^-}} = -\overline{D_{Y^-}}\left(\frac{\mathrm{d}\overline{C_{Y^-}}}{\mathrm{d}x} - \overline{C_{Y^-}}\frac{F}{RT}\frac{\mathrm{d}\overline{\Psi}}{\mathrm{d}x}\right) \qquad (4)$$

where $\overline{D_i}$ is the diffusion coefficient of species i in the membrane and is given by the Nernst–Einstein relation: $\overline{D_i} = RT\overline{u_i}$. The symbols with a bar refer to the membrane phase.

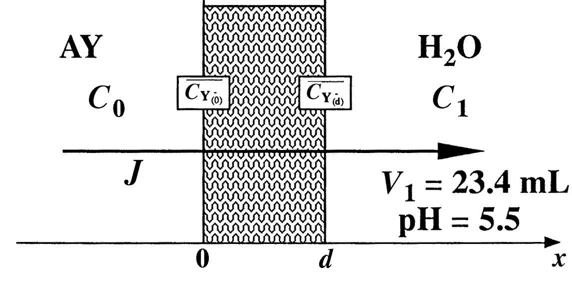

Fig. 1 Initial experimental conditions.

The null electric current is given by:

$$J_{A^+} - J_{Y^-} = 0 \qquad (5)$$

and the electroneutrality condition in a cation exchange membrane gives the relation:

$$\overline{C_{A^+}} = \overline{C_{Y^-}} + \overline{X} \qquad (6)$$

where $\overline{X}$ is the concentration of fixed charges in the membrane.

The swelling is assumed to be uniform and constant, whatever the equilibrating solution concentration may be, so that:

$$\mathrm{d}\overline{C_{A^+}} = \mathrm{d}\overline{C_{Y^-}} \qquad (7)$$

Eliminating the electric potential term from eqns. (3) and (4) we obtain:

$$J = J_{A^+} = J_{Y^-} = -\frac{\mathrm{d}\overline{C_{Y^-}}}{\mathrm{d}x}\left[\frac{(\overline{C_{A^+}} + \overline{C_{Y^-}})\overline{D_{A^+}}\,\overline{D_{Y^-}}}{(\overline{D_{A^+}}\,\overline{C_{A^+}} + \overline{D_{Y^-}}\,\overline{C_{Y^-}})}\right] \qquad (8)$$

In a typical ion exchange membrane and at moderate and low concentrations, the fixed charges concentration, $\overline{X}$, is high enough to imply a complete exclusion of the electrolyte from the membrane. In this case, it is possible to neglect the co-ion concentrations relative to the counter-ion ones so that:

$$J = -\overline{D_{Y^-}}\frac{\mathrm{d}\overline{C_{Y^-}}}{\mathrm{d}x} \qquad (9)$$

Integrating between both sides of the membrane, we obtain:

$$J = -\frac{\overline{D_{Y^-}}}{\mathrm{d}}(\overline{C_{Y_{(d)}^-}} - \overline{C_{Y_{(0)}^-}}) \qquad (10)$$

This equation shows that J depends only on the co-ion diffusion coefficient, $\overline{D_{Y^-}}$, and on its concentration in the membrane. The diffusion process is then controlled by the co-ion, for which the internal concentration is difficult to quantify. This is why Helfferich[7] expressed this concentration as a function of the external one, C, through Donnan's relation:

$$\overline{C_{Y^-}} = \frac{C^2}{\overline{X}K_{\mathrm{sel}}} \qquad (11)$$

where K_{sel} is the selectivity coefficient, assumed to be constant by Donnan. This equation is only an approximation, valid in the limit of good co-ion exclusion: $\overline{X}/C_0 \ll 1$.

In this case, the internal co-ion concentration on the side of the diluted compartment, $\overline{C_{Y^-}}$, is negligible compared to that on the other side, $\overline{C_{Y_{(0)}^-}}$. In addition, the membranes in this study are highly selective so that the overall matter flux is too small to modify the initial concentration value (C_0) in the upstream compartment. So the flux equation is given by:

$$J = J_{A^+} = J_{Y^-} = \frac{\overline{D_{Y^-}}}{\mathrm{d}}\overline{C_{Y_{(0)}^-}} = \frac{\overline{D_{Y^-}}}{\mathrm{d}}\frac{C_0^2}{\overline{X}K_{\mathrm{sel}}} \qquad (12)$$

This equation, also called the Helfferich equation for a strong electrolyte diffusion, shows a linear relationship between the logarithm of J and the logarithm of C_0 with a slope of 2, over the whole concentration range for which the approximations inherent in this result are valid.

The various studies in this field are usually carried out for $C_0 \geqslant 0.1$ mol L^{-1}. Hence the concentration domain $C_0 \leqslant 0.1$ mol L^{-1} has never been dealt with, neither experimentally nor theoretically. To generalize our method, we have decided to perform our study over a large concentration range, from 10^{-2} to 4 mol L^{-1}.

Experimental

In this part, we describe our continuous method for evaluating the leakage of a strong electrolyte (ACl) through an IEM separating a concentrated solution from permuted water.

Table 1 Characteristics of the CM2 membrane

Dry membrane weight/g	0.151
Humid membrane weight/g	0.191
Exchange capacity/equiv L^{-1}	2.1
Swelling rate/%	21
Thickness/μm	135
Density D_{20}^{30}	1.26

We chose to work with a polystyrene and divinylbenzene sulfonated cation exchange membrane (CM2) provided by Tokuyama Soda (Japan). Before making any measurements, the CM2 has been treated in order to stabilize its physicochemical properties and to eliminate the eventual impurities resulting from its elaboration. The French standards[9] have been adopted to achieve this treatment, *via* a succession of two exchange cycles, and to measure the main characteristics of the membrane. The results are reported in Table 1.

The experimental device used to measure the electrolyte flux is shown in Fig. 2. The cell itself has been well-described by Dammak *et al.*[10] To follow the evolution of the concentration in the diluted compartment, we chose a conductimetric method, which presents the advantages of being continuous and very accurate if the conductivity sensor is suitably calibrated, for example, by determining daily the calibration constant of the sensor with a reference solution. This method needs also a high temperature stability. Hence the cell, stand, magnetic stirrers and solution flasks are placed in a thermoregulated water bath at 25.0 ± 0.1 °C. The solution circulation is achieved through a peristaltic pump, fitted with a pair of similar heads and a speed variator. The stirring rate in each compartment is locked at 900 ± 10 rpm, using watertight magnetic stirrers. Magnetic stirring stars reduce the thickness of the diffusion boundary layers on both sides of the membrane at 40 μm.[11]

The membrane sample is immersed for 12 h in 250 mL of a C_0 concentration KCl solution (all solutions are prepared with permuted water whose conductivity is in the range of 1.4 to 2.5 μS cm^{-1}). After a fast rinse with permuted water, the membrane is sandwiched between the two compartments of the cell and locked in a stand centring it with respect to the two stirrers. Once assembled, the cell is symmetrical with respect to the membrane. Before an experiment, the concentrated compartment is filled with a given KCl solution and the diluted one with permuted water. Possible air bubbles in the cell are carefully eliminated.

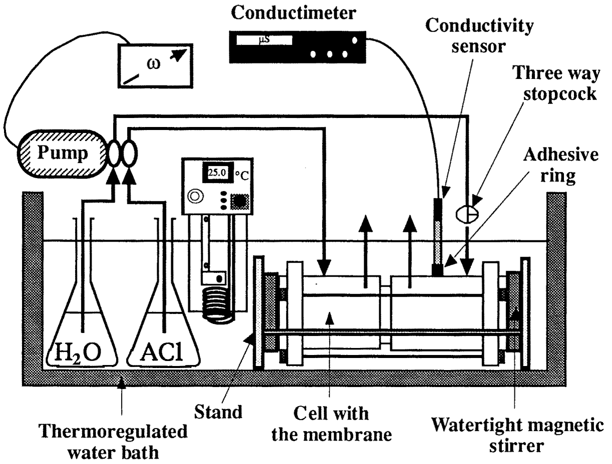

Fig. 2 Experimental device.

Table 2 Required times for different concentrations

Concentration/mol L^{-1}	Experimental time/h
1-6 × 10^{-2}	100
10^{-1}	30
0.3	5
0.6-4	3

The concentration calculation from a conductivity measurement requires the exact knowledge of the diluted compartment volume. To avoid the determination of this volume for each experiment, we pasted an adhesive ring on the sensor stem, which serves to fix the electrode length penetrating the measurement cell. Thus, before each experiment, this ring is maintained in contact with the cap of the stuffing box that assures the watertightness of the cell. The error on this length is equal to one screw step of the stuffing box: 1 mm. Thus, the volume of the dilute compartment is reproducible to within 0.1 mL and the conductivity sensor position (Tacussel XE 120) is always the same in the downstream compartment. Connected to a conductimeter (Tacussel CD 78), it allows the conductivity *vs.* time recording.

At the inlet of the diluted compartment, a three-way stopcock deviates the pure water circulation during a measurement. Its duration depends on the concentration, from 3 h at high concentrations to 100 h at low concentrations (Table 2). These periods are selected in order to obtain near-stationary states.

Results and discussion

We report in Fig. 3, the variation of the conductivity, *vs.* time, for two limiting cases; one in the low concentration range [system: KCl (3 × 10^{-2} mol L^{-1})/CM2/H_2O], and the other in the high concentration range [system: KCl (2 mol L^{-1})/CM2/H_2O].

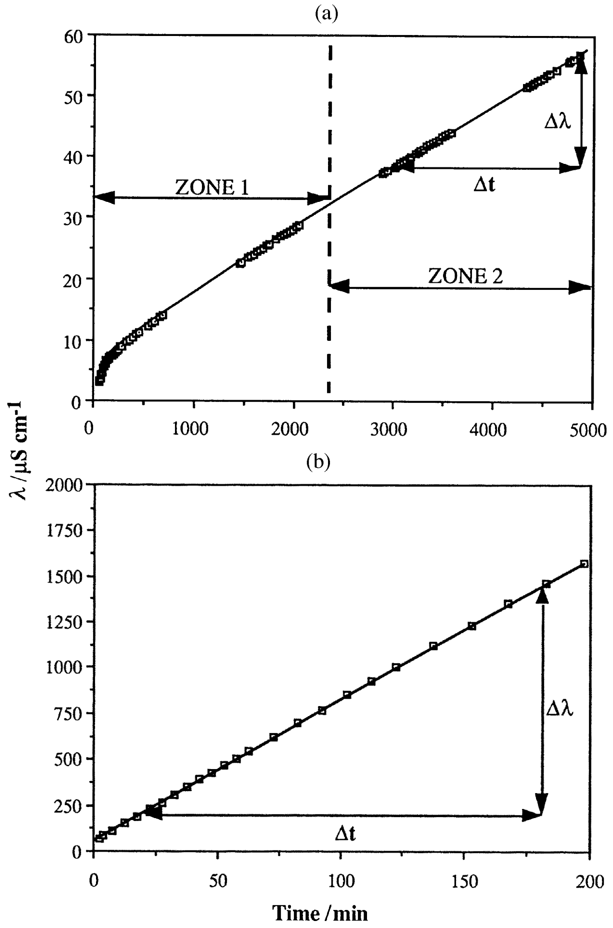

Fig. 3 (a) Conductivity *vs.* time for the system KCl (3 × 10^{-2} mol L^{-1})/CM2/H_2O. (b) Conductivity *vs.* time for the system KCl (2 mol L^{-1})/CM2/H_2O.

The low concentration range [Fig. 3(a)] shows two different domains. In the first one (Zone 1), the variation of the conductivity *vs.* time is not linear, as it is in the second one (Zone 2), which appears to be a steady state. This second zone is used to calculate the flux, J. At high concentrations [Fig. 3(b)], we observe that the steady state is reached from the begining of the experiment.

The slope of the linear part of a curve is converted into a variation of concentration *vs.* time through a conductivity-concentration calibration curve. Given the real concentrations in the downstream compartment ($C_1 \leqslant 10^{-3}$ mol L^{-1} in all cases), the conductivity varies linearly with the concentration:

$$\lambda = kC_1 \tag{13}$$

where C_1 is the concentration in the diluted compartment (mol m^{-3}) and k the standardization constant (S m^2 mol^{-1}) Therefore:

$$\frac{\Delta C_1}{\Delta t} = \frac{1}{k}\frac{\Delta \lambda}{\Delta t} \tag{14}$$

Knowledge of the diluted compartment volume, V_1, and the membrane area in contact with the two solutions, S, allows the calculation of the transferred electrolyte flux, J:

$$J = \frac{V_1 \Delta C_1}{S \Delta t} = \frac{V_1 \Delta \lambda}{S k \Delta t} \tag{15}$$

In our case, $V_1 = 23.4 \times 10^{-6}$ m^3 and $S = 4.5 \times 10^{-4}$ m^2.

From a reproducibility study, it appears that J can be measured with a good accuracy for each concentration, with respect to the required time for an experiment. The errors on the J values do not exceed 4% and in several cases are lower than 1%. Taking into account the reproducibility and the simplicity of the experimental setup, we consider that the electrolyte flux measurements are reliable.

In Fig. 4, we plot the logarithm of J *vs.* the logarithm of C_0 for the system KCl (C_0)/CM2/H_2O, where C_0 varies between 10^{-2} and 4 mol L^{-1}. This curve can be divided into three sections, noted 1, 2 and 3.

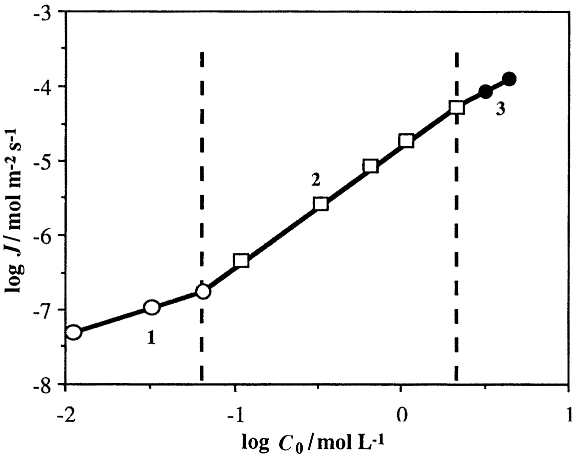

Fig. 4 Bilogarithmic variation of the electrolyte flux *vs.* the concentration for the system KCl ($10^{-2} \leqslant C_0 \leqslant 4$ mol L^{-1})/CM2/H_2O.

The first domain concerns concentrations varying from 1–6 × 10^{-2} mol L^{-1} and where the slope is equal to 0.7, a value less than 2, predicted by theory and even less than unity, the expected value when all occurs as in an aqueous solution. In order to explain this "anomaly", we studied the particular case of HCl electrolyte in the concentration range 3 × 10^{-3}–1 mol L^{-1}. The results are reported in Table 3.

In Fig. 5, we show the results for the systems KCl ($10^{-2} \leqslant C_0 \leqslant 4$ mol L^{-1})/CM2/H_2O and HCl ($3 \times 10^{-3} \leqslant C_0 \leqslant 1$ mol L^{-1})/CM2/H_2O. We remark that unlike the KCl/CM2/H_2O one, the HCl/CM2/H_2O system presents a bilogarithmic variation of J *vs.* C_0 that is linear for all concentrations, with a slope equal to 1.78. Since HCl does not show any particular behaviour in the membrane, we can expect the bilogarithmic variation of the KCl flux *vs.* C_0 to be linear over the entire concentration range and the slope to have a single value. This is not observed experimentally. So the difference between slopes at low and high concentrations needs to be explained.

Before each experiment, circulation of the solutions is performed for 15 min at the rate of 8 mL min^{-1}, so that a volume of 120 mL of permuted water flows through the downstream compartment. At the pH of the used permuted water (5.5), this quantity contains $n_0 = 3.8 \times 10^{-7}$ moles of protons that are assumed to be immediately fixed by the CM2 exchange membrane. As soon as the experiment begins (just after the insulation of the downstream compartment), H^+ ions are released progressively into the solution. The conductivity sensor detects not only the KCl flux but also the contribution of the H^+ions. This contribution depends on the upstream concentration C_0. In fact, the higher the concentration C_0, the lower the H^+ contribution, because the KCl flux becomes important enough to drag out rapidly all the H^+ initially accumulated in the membrane. In the downstream solution, the K^+ concentration becomes rapidly greater than the H^+ concentration.

It is possible to estimate the time Δt necessary so that the amount of H^+ is negligible compared to that of K^+ in the downstream solution. At a given instant t, the n_0 moles of H^+, previously calculated, are distributed between the solution,

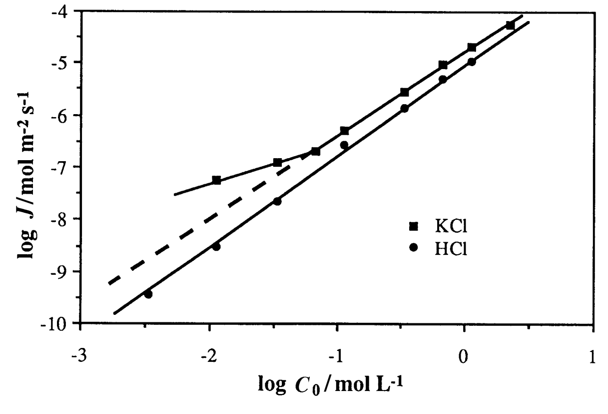

Fig. 5 Comparison between the systems KCl (C_0)/CM2/H_2O and HCl (C_0)/CM2/H_2O.

Table 3 Flux values for the system HCl ($3 \times 10^{-3} \leqslant C_0 \leqslant 1$ mol L^{-1})/CM2/H_2O

	Flux/10^{-10} mol m^{-2} s^{-1}			
C_0/mol L^{-1}	Value 1	Value 2	Average	Variation/%
0.003	2.67	2.70	2.68	1.30
0.01	23.46	23.49	23.47	0.13
0.03	170.4	168.9	169.6	0.88
0.1	2090	1991	2040	4.00
0.3	10 890	10 550	10 720	3.13
0.6	38 060	36 640	37 350	3.79
1	80 650	80 660	80 650	0.02

n_{Hs^+}, and the membrane, $n_{\mathrm{H_m}^+}$;

$$n_0 = n_{\mathrm{Hs}^+} + n_{\mathrm{H_m}^+} \tag{16}$$

If we combine this equation with that for electroneutrality, in which we neglect the sorbed co-ions $[\overline{\mathrm{H}^+}] + [\overline{\mathrm{K}^+}] = \overline{X}$ and with the following assumptions:

(*i*) in the downstream compartment and at Δt, $[\mathrm{K}^+] = 100 \times [\mathrm{H}^+]$,

(*ii*) an instantaneous equilibrium is established at the membrane/downstream solution interface,

(*iii*) the affinity coefficient is considered to be constant and equal to unity:[12]

$$K_{\mathrm{aff}} = \frac{[\overline{\mathrm{H}^+}][\mathrm{K}^+]}{[\overline{\mathrm{K}^+}][\mathrm{H}^+]} \approx 1.00 \tag{17}$$

(*iv*) the flux values at low concentrations are obtained by extrapolating the results corresponding to high concentrations (dashed line, Fig. 5),

we can estimate the time Δt by the equation:

$$\Delta t = \frac{C_0 V_1}{JS} \tag{18}$$

Some calculation results are reported in Table 4.

We note that the lower the concentration C_0, the longer the time necessary for the contribution of H^+ to the conductivity value to become negligible, compared to that of K^+. So the anomaly observed for low concentrations can be attributed first to an exchange competition between H^+ and K^+ at the level of the membrane/downstream solution interface and secondly to the fact that we previously considered the conductivity value of the solution to be imposed only by the ions K^+ and Cl^-. Futhermore, at low concentrations, the calculated times Δt are greater than those fixed for the experiments. In the high concentrations domain, Δt has the same order of magnitude as the experimental flux measurement times (Table 2).

These results show that reliable flux measurements in the low concentration domain are difficult to obtain because of long experimental times, necessary to reach steady state. In future studies of diffusion, this domain ($10^{-2} \leqslant C_0 \leqslant 6 \times 10^{-2}$ mol L^{-1}) will be excluded.

The domain we will treat now is that of very high concentrations ($2 \leqslant C_0 \leqslant 4$ mol L^{-1}), noted 3 in Fig. 4. In this domain, we observe another diffusion state where the bilogarithmic variation is also linear, but the slope is smaller than the one obtained in domain 2, where C_0 varies from 10^{-1} to 2 mol L^{-1}. This observation can be explained by the fact that for a very high solution concentration, the sorbed electrolyte quantity in the membrane, by Donnan's equilibrium, becomes significant and the membrane behaviour evolves gradually to a solution one. The flux tends then to vary linearly with C_0 and the slope on the bilogarithmic scales becomes comparable to unity. Moreover, at high concentrations, the osmotic flux, in the opposite direction to the KCl flux, is no longer negligible and so may slow down sharply the electrolyte transfer. The slope value in this very high concentration domain decreases continuously. So, this domain will be excluded too.

The third and last domain is the one where the concentration varies between 10^{-1} and 2 mol L^{-1}. This is the most interesting domain where all previous authors[13–20] have made their experimental and theoretical studies. In this zone, the bilogarithmic variation is linear with a slope equal to 1.59. This value is less than two, the value expected from Helfferich's treatment [eqn. (12)]. This result is confirmed by many authors.[13,17,20–22]

Table 4 Theoretical estimation of Δt

C_0/mol L^{-1}	Δt/h
0.01	2350
0.1	60
1	1.7
2	0.5

This domain is the best for the study of the transport mechanism and for the characterization of the ion exchange membrane selectivity. In fact, concentrations in this domain are sufficiently high to allow the H^+ contribution to the downstream solution conductivity to be neglected and not high enough to generate an important osmotic flux slowing down the electrolyte when it diffuses through the membrane.

In a future paper, we will present a detailed study of the influence of the membrane, the counter-ion and the co-ion on the diffusion flux values, in order to explain the difference between the experimental slopes and that predicted by the Helfferich treatment.

Conclusion

We present a simple and accurate method to characterize the electrolyte leakage through a highly selective cation exchange membrane under a concentration gradient. For a given concentration and different membranes, the higher the electrolyte leakage the lower the membrane selectivity. The great variation of the electrolyte fluxes (almost two orders of magnitude) with concentration and/or with membrane nature, even for recent ones, leads to an accurate classification of ion exchange membranes with respect to their selectivity.

The determination of the electrolyte flux is achieved using a conductivity sensor allowing a continuous measurement of the electrolyte concentration in the diluted compartment. The curve of the bilogarithmic variation of the electrolyte flux *vs.* the concentration of the upstream solution shows an apparent anomaly at low concentrations. Effectively, for diluted solutions, the H^+ contribution to the conductivity of the downstream solution is important. Taking into account that the electrolyte flux decreases with decreasing concentration, the experimental time must be very long before this contribution becomes negligible. In other words, for these concentrations, the true electrolyte fluxes cannot be obtained within a reasonable experimental time.

For the domain of very high concentrations ($2 \leqslant C_0 \leqslant 4$ mol L^{-1}), the co-ion quantity in the membrane and the osmotic fluxes through this membrane are not negligible. They must be measured and taken into account in the transfer equations. So, the number of parameters influencing the transmembrane electrolyte flux is large and they must be determined experimentally. The method will the be complex and slow. Thus we will not consider this high concentration domain for future studies.

However, for concentrations varying from 0.1 to 2 mol L^{-1}, they are sufficiently high to reduce quickly the H^+ contribution and sufficiently low to neglect both the co-ion quantity absorbed by the membrane and the osmotic flow. So this domain is the best to study the diffusion phenomenon through a highly selective cation exchange membrane, because the diffusion state is linear and the experimental durations are reasonable. In this domain, the obtained slope is less than 2, the value expected from Helfferich's treatment. This discrepancy between theory and experiment can be explained only by the variation of the membrane structure, that is, the membrane charge density or the ion diffusion coefficients, with the external salt concentration C_0.

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