Dialysis applied to the selectivity study of cation exchange membranes in contact with strong electrolytes

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Preliminary tests allowed us to improve an experimental device and to define a measurement protocol leading to a choosing criterion among different membranes through leakage flux determinations. This method presents the advantages of being simple, accurate and allows a continuous monitoring of the leakage process through ion exchange membranes by measuring the conductivity in the downstream compartment.

For well-defined experimental conditions (electrolyte nature and concentration), the electrolyte flux determination allows one to classify different membranes by their selectivity. The higher the membrane selectivity, the lower the electrolyte leakage. From one membrane to another, the electrolyte flux variations are considerable. Thus, a classification through the electrolyte leakage method seems to be more accurate than other methods such as the counter-ion transport number determination.

Dialyse appliquée à l'étude de la sélectivité de membranes échangeuses de cations en contact avec des électrolytes forts. Des essais préliminaires ont permis de mettre au point un montage expérimental et de définir un protocole de mesure de la sélection de différentes membranes par la détermination des valeurs des flux de dialyse. Cette méthode présente les avantages d'être simple, précise et permet un suivi continu du processus à travers les membranes échangeuses d'ions. Cette mesure réside dans le contrôle de la conductivité dans le compartiment aval.

Pour des conditions opératoires bien définies (nature de l'électrolyte et concentration), la détermination du flux d'électrolyte permet de comparer la sélectivité de différentes membranes. En effet, cette sélectivité est d'autant meilleure que la fuite d'électrolyte est faible. D'une membrane à une autre, les variations des flux d'électrolytes sont importantes et la classification obtenue semble être plus précise avec cette méthode qu'avec d'autres, telle que la détermination du nombre de transport du contre-ion.

Let us consider an ion exchange membrane (IEM) separating an upstream compartment containing an electrolyte solution, AY, at a given concentration, C_0, from a downstream one, full of permuted water (Fig. 1). This system corresponds to the initial conditions of a diffusional process named dialysis. Indeed, under its concentration gradient, the electrolyte diffuses through the membrane from the concentrated to the diluted compartment. The literature on the dialysis phenomenon is very extensive[1-4] and is described currently by Helfferich's equation, derived from Donnan's law and the Nernst–Planck equation[1] with some restrictive assumptions: complete membrane control of the diffusion process, uniform and constant membrane swelling and complete exclusion of the electrolyte from the membrane.

Generally speaking, the dialysis phenomenon is not taken into account if another gradient, of pressure or electrical potential, is applied to the membrane.[4-7] However, we will show that this can be a simple way to evaluate the performances of highly selective ion exchange membranes in order to optimize their choice for a given application, by measuring the strong electrolyte fluxes through these membranes. This step is of a great interest in the conception of membrane modules with high chemical and energetical performances and with high purity products. Actually, there are at least three other means to characterize membrane selectivity: the counter-ion transport number, the membrane conductivity under an alternating current and the electrolyte sorption. In these methods there is no matter transport along their determination (static parameters), contrary to the proposed method, qualified to be dynamic.

The structure of this paper is as follows. First, we briefly review the experimental set-up. Then, we present the preliminary tests to qualify the method of strong electrolyte leakage. Finally, we present our experimental results and discuss the influence of the concentration, membrane type and of the counter ions and the co-ion nature on the electrolyte fluxes.

Experimental

Experimental device

The experimental device used to measure a strong electrolyte leakage is shown in Fig. 2. The cell has been described in detail by Dammak *et al.*[8] It is composed of two symmetrical bodies and two covers containing magnetic stirring stars. The membrane is sandwiched between the two cell bodies, making a seal. Once assembled, the cell is centered on a stand with respect to two watertight magnetic stirrers.
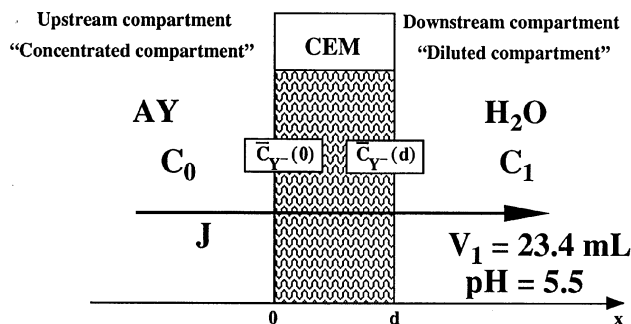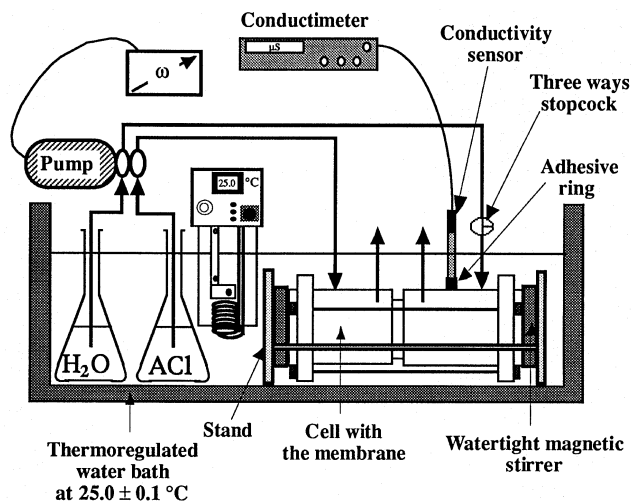

Fig. 1 Initial experimental conditions

Fig. 2 Experimental device

The whole device is placed in a thermoregulated water bath at $25.0 \pm 0.1\,°C$ and the solution circulation is achieved with a peristaltic pump, fitted with a pair of similar heads and a speed variator. The strong electrolyte leakage is measured with a conductivity sensor, suitably calibrated and placed in the diluted compartment. At the inlet of this compartment, a three-way stopcock deviates the pure water circulation during a measurement. The stirring rate in each compartment is locked at 900 ± 10 rpm, using watertight magnetic stirrers and magnetic stars, reducing the diffusion boundary layer thickness, on both sides of the membrane, to 40 μm.[9] 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 (Tacussel XE 120) so that the conductivity sensor position is always the same in the downstream compartment. Connected to a conductimeter (Tacussel CD 78), it allows the conductivity *versus* time recording. The strong electrolyte leakage measurements are repeated at least twice.

Membranes and conditioning

In order to generalize the interpretation of our results, we have selected six different cation exchange membranes (CEM) designated by CM1, CM2, CMx, CRP, MK-40 and Nafion 117 (noted N117). We have used only CEMs because they are generally more stable with time than anion exchange membranes. CM1, CM2 and CMx are three homogeneous polystyrene and divinylbenzene sulfonated membranes provided by Tokuyama Soda (Japan). N117 is a homogeneous perfluoro-sulfonated membrane provided by Du Pont De Nemours (USA). CRP and MK-40 are heterogeneous membranes prepared with cation exchange resin inclusions, finely pulverized in a binder of polyvinyl chloride. CRP is provided by Rhône-Poulenc (France), while MK-40 is provided by Azot (Russia).

Before new membranes can be used, their properties must be stabilized and eventual impurities, resulting from their elaboration, eliminated. These treatments have been carried out *via* a succession of exchange cycles. Then we have determined their characteristics according to French standards[10] and obtained the parameters grouped in Table 1: the dry membrane weight in the H^+ form (m_E), the humid membrane weight in the H^+ form (m_H), the thickness of the wet membrane in the H^+ form (e), the exchange capacity in milliequivalent per gram of dry membrane in the H^+ form (C_E), the swelling rate in water (t_g) and the membrane density in the H^+ form (D_{20}^{20}).

Preliminary Tests

To evaluate a strong electrolyte leakage through a CEM, by measuring the flux, we have chosen the conductimetric method, which presents the advantages to be continuous and very accurate. In order to improve this method, we have performed some preliminary tests.

Determination of the experimental duration

To determine the flux values, it is necessary to reach a steady state in which the strong electrolyte flux is constant and thus the electrolyte concentration in the downstream compartment varies linearly with time. It has been shown that we must wait for 24 h at an initial concentration (C_0) of 0.1 mol L^{-1}, 3 h at $C_0 = 0.3$ mol L^{-1} and only 1 h at $C_0 \geqslant 0.6$ mol L^{-1}. The experimental durations are then chosen to be equal to 30 h, 5 h and 3 h for the preceding concentrations, respectively. This parameter is an important factor in the determination of the flux value because it depends on the choice of the steady state zone on the experimental curve of the electric conductivity in the diluted compartment *versus* time. This choice constitutes the major restriction of the method, essentially to very low concentrations ($C_0 \leqslant 0.1$ mol L^{-1}).

Comparison of the conductimetric and spectrophotometric methods

In order to verify the validity of the calculated diffusion flux values from the conductimetric method, we have compared them with those determined by a spectrophotometric method.

For this comparative study, we have used the CM2 membrane at KCl concentrations varying from 0.1 to 2 mol L^{-1}. The membrane sample is immersed for 12 h in 250 mL of a potassium chloride solution at the concentration C_0 (all solutions are prepared with permuted water whose conductivity is in the range 1.4–2.5 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 centering it with respect to the two stirrers. Once assembled, the cell is symmetrical with respect to the membrane (Fig. 2). 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. After having introduced the conductivity sensor in the downstream compartment, we record the conductivity *versus* time until

Table 1 Membrane characteristics

Membranes	CM1	CM2	CMx	CRP	MK-40	N117
m_E/g	0.146	0.151	0.183	0.360	0.513	0.381
m_H/g	0.201	0.191	0.239	0.530	0.735	0.454
C_E/mequiv. g^{-1}	2.37	2.12	1.62	2.10	2.52	0.94
t_g/%	27	21	23	32	30	16
e/μm	147	135	175	356	495	215
D_{20}^{20}	1.29	1.26	1.25	1.26	1.16	1.84

we observe a linear variation lasting for 1 to 3 h. At the end of an experiment, and after pulling out the conductivity sensor, we take a sample of the downstream compartment solution ($\approx$ 10 mL). Removal of the sensor and the solution collection must be executed rapidly (2 or 3 min) to avoid an excess of electrolyte diffusion with respect to the experimental time used to calculate the flux value. The solution analysis is performed with a flame emission spectrophotometer (Varian, AA-1275), allowing an accurate determination of the counter-ion concentration in the diluted compartment.

In Fig. 3, we have gathered the two experimental data sets. We note a very small difference between these two methods (less than 1% relative) and for each concentration, the flux value obtained from the conductimetric method is higher. This is explained at high concentrations by the fact that when we perform a conductimetric measurement, the sensor detects not only the potassium ions but also the other ions in solution. The total conductivity variation *versus* time, which allows the flux value determination, is a sum of different contributions due to K^+, Cl^-, H^+, HCO_3^-, *etc.*, whereas the spectro-photometric detection involves only the potassium ion. So the subsequent flux values are lower.

This spectrophotometric method is used by many authors[11–14] but it requires sophisticated equipment and it does not allow a continuous dialysis follow-up. So the use of this technique is limited[15] to discontinuous analytical mea-surements and cannot be generalized for industrial or routine uses. Consequently we have selected the conductimetric method for our study.

Membrane symmetry

Usually, ion exchange membranes do not have two identical sides. For some membranes, this difference can be visible to the naked eye, but in most cases, we are not able to confirm it easily. However, such an asymmetry can have important con-sequences on the matter transfer (membranes treated on their surfaces) and so they must be correctly set up in the cells or modules.

In our case, the symmetry verification has been carried out on a sample of each studied membrane and with the system KCl (0.3 mol L^{-1})/CEM/H_2O for which we have realized two measurement series of the KCl flux. The first series has been performed with side A of the CEM in contact with the KCl solution and the second series under the same experimental conditions, but the membrane has been inverted at the moment of its insertion in the cell (side B in contact with the KCl solution). The obtained results are reported in Table 2
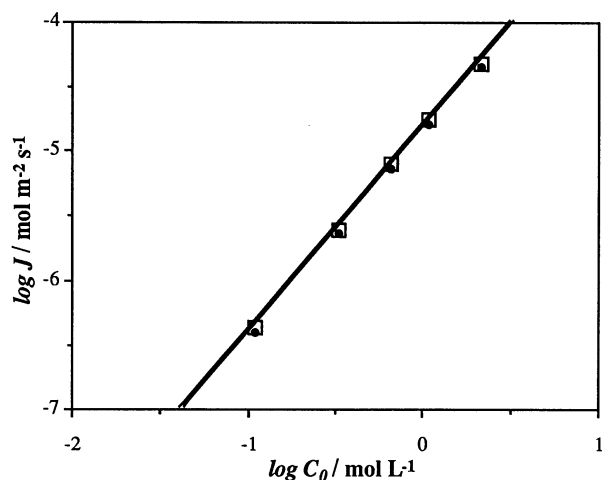
Fig. 3 Bilogarithmic variation of the KCl flux through the CM2 membrane, *versus* the C_0 concentration determined with two analysis methods: ($\square$) conductimetric, ($\bullet$) spectrophotometric

Table 2 Flux values for each membrane as a function of the assembly way for the KCl (0.3 mol L^{-1})/CEM/H_2O system

Membrane	Side	$10^8 \times$ Flux/mol m^{-2} s^{-1}	Rel. difference
CM1	A	668.6	0.21%
	B	669.9	
CM2	A	221.1	0.17%
	B	221.4	
CMx	A	834.1	0.12%
	B	835.0	
CRP	A	1605	1.89%
	B	1635	
MK-40	A	1055	0.55%
	B	1049	
N117	A	334.6	2.90%
	B	324.9	

from which we note that for each membrane, the difference between the two fluxes is less than 3% relative. Taking into account the measurement uncertainties, we can affirm that the six studied membranes are symmetrical and so will be inserted indifferently in the cell.

Influence of the hydrodynamic parameters

It is well-known that hydrodynamic conditions are essentially fixed by the stirring rates on both sides of the membrane. Their influence depends, in some cases, on the solution con-centration.[9] So we have studied the effect of the stirring rate ω on the electrolyte flux. In each compartment, the tested values of this parameter are either the minimum $\omega_0 = 0$ rpm or the maximum $\omega_{max} = 900$ rpm. Three interesting cases have been studied: (*i*) $\omega = \omega_{max}$ in both compartments. The correspond-ing notation is 100%–100%. (*ii*) No stirring in the upstream compartment and maximum speed in the downstream one. The notation is 0%–100%. (*iii*) Maximum stirring in the upstream compartment and no stirring in the downstream one. The notation is 100%–0%.

For the two systems NaCl (0.3 mol L^{-1})/CM2/H_2O and NaCl (0.001 mol L^{-1})/CM2/H_2O, the calculated flux values are reported in Table 3, from which we note that the differ-ence between the three cases is on the order of 1.2% at medium and high concentrations and can reach 2.4% at low concentrations. This last value can be attributed to the fact that ions reach the conductivity sensor not by convection but by diffusion.

This study shows that stirring both compartments has no noticeable influence on the electrolyte flux, whatever the upstream concentration value. For the transfer process, the diffusion boundary layers induce additional barriers with a thickness that decreases with increasing stirring rate.[9,16–19] But in our case, it seems that they do not have a great effect on the diffusion process. This leads us to affirm that only the membrane controls the transfer.

For the rest of the study, we have locked the stirring rate at 900 rpm, because it makes the conductimetric detection easier.

As a conclusion, these preliminary tests allow us to put in evidence the principal and the most favorable experimental conditions to obtain accurate electrolyte diffusion flux values

Table 3 Flux values at high and low electrolyte concentrations

	$10^8 \times$ Flux/mol m^{-2} s^{-1}	
Stirring	$C_0 = 0.3$ mol L^{-1}	$C_0 = 0.001$ mol L^{-1}
100%–100%	93.4	3.8
0%–100%	93.2	3.8
100%–0%	93.3	3.7

and to define a simple procedure to carry out all the experiments.

Results and Discussion

In this section, we examine the influence of three parameters on strong electrolyte leakage in order to understand better the dialysis process. These parameters are the initial upstream concentration, C_0, the membrane type and the electrolyte nature. We have investigated six cation exchange membranes (CM1, CM2, CMx, CRP, MK-40 and N117) for a concentration C_0 varying from 0.1 to 2 mol L^{-1} and five electrolytes: KCl, NaCl, LiCl, KBr and KNO$_3$.

Influence of the concentration

Fig. 4(a) shows the variation of the flux, J, versus the concentration C_0 for the KCl (C_0)/CEM/H$_2$O systems. The same curve shape is obtained for the six membranes and it is characterized by an increasing evolution of the flux with the concentration. This variation must be of the form $J = kC_0^2$ if we suppose available the Donnan equilibrium at the membrane/solution interfaces. This supposes also that the membrane is homogeneous (on a molecular scale) and that the absorption isotherms of a strong electrolyte are given by the Donnan equation: $\bar{C} = k'C_0^2$, where C_0 and $\bar{C}$ are the

co-ion concentrations in the solution and in the membrane, respectively.

Glueckauf and Watts[20] have remarked that absorption isotherms are rather described by a $\bar{C} = KC_0^{(2-z)}$ law, where the coefficient z is called the heterogeneity factor and characterizes the heterogeneity of the counter-ion distribution in the membrane. To establish the former empirical equation, these authors: (i) supposed that an ion exchange membrane is constituted by a set of elementary volumes characterized by a mean counter-ion concentration, $\mathscr{C}$, when it is equilibrated with pure water, (ii) supposed that in the presence of an electrolyte solution at the concentration C_0, each elementary volume is in equilibrium with this solution, has an electrolyte concentration $\bar{C}$ and a total counter-ion concentration ($\mathscr{C} + \bar{C}$), and (iii) introduced a distribution function, Φ ($\mathscr{C}$), of the counter ion, equilibrating the fixed sites:

$$\frac{d\Phi(\mathscr{C})}{d\mathscr{C}} = k_0 \mathscr{C}^{-z} \quad \text{and} \quad \int_0^{\mathscr{C}_{\max}} d\Phi(\mathscr{C}) = 1$$

where k_0 and z are two constants and $\mathscr{C}_{\max}$ is the maximum of the local counter-ion concentration in the exchanger.

Experimentally, we can determine only the mean counter-ion concentration $\mathscr{C}^*$, given by:

$$\int_0^\beta \mathscr{C}d\Phi(\mathscr{C}) = \mathscr{C}^*$$

Rearrangement of the three equations leads to the following k_0 and $C_{\max}$ expressions:

$$k_0 = \frac{(1-z)^{2-z}}{(2-z)^{1-z}(\mathscr{C}^*)^{1-z}} \quad \text{and} \quad \mathscr{C}_{\max} = \frac{2-z}{1-z}\mathscr{C}^*$$

It appears that the increase of the heterogeneity coefficient shows especially a larger dispersion of the counter-ion concentration with respect to its mean value.

The mean sorbed electrolyte concentration by an exchanger, $\bar{C}^*$, is obtained by summation of all the electrolyte concentrations contained in the elementary volumes:

$$\bar{C}^* = \int_{\Phi=0}^1 \bar{C}d\Phi$$

Supposing that the Donnan relation is available between each elementary volume and the external electrolyte solution, it is easy to prove that $\bar{C} = \bar{C}^* = KC_0^{(2-z)}$. Using this equation (Glueckauf's equation) and the simplified Nernst–Planck equation in the case of dialysis $[J_{A^+} = J_{Y^-} = -\bar{D}_{Y^-}(d\bar{C}_{Y^-}/dx)]$, we obtain:

$$J_{AY} = -\frac{\bar{D}_{Y^-}}{e}(0 - \bar{C}) = KC_0^{(2-z)} = KC_0^\beta$$

The use of bilogarithmic scales leads to a linearization of the $J = f(C_0)$ curves, Fig. 4(b), and so allows the slopes β, reported in Table 4, to be determined. We note that the slopes vary from 1.02 to 1.59, thus less than two, the value expected from the Helfferich treatment.[2] Our results are in agreement with other results from many authors.[21–25] For example, Glueckauf has shown that for homogeneous membranes, β can vary
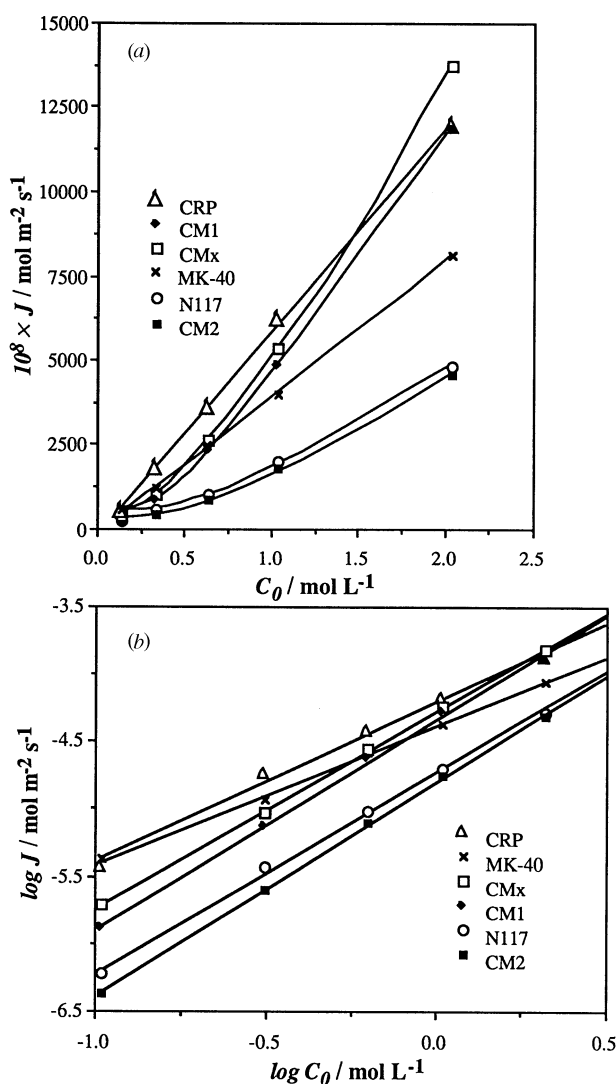

Fig. 4 (a) Variation of the flux *versus* C_0 for the KCl (C_0)/CEM/H$_2$O systems. (b) Bilogarithmic representation of the data in (a)

Table 4 Bilogarithmic slope values and their fit coefficient for each KCl (C_0)/CEM/H$_2$O system

Membrane	β	Fit coefficient
CM1	1.55	0.998
CM2	1.59	1.000
CMx	1.46	1.000
CRP	1.18	0.999
MK-40	1.02	0.999
N117	1.48	0.998

from 1.2 to 1.7. However, for heterogeneous ones (like MK-40), Gnusin et al.[22] found that β can reach a value of 1.2. Once more, for highly selective cation exchange membranes, we confirm the validity of Glueckauf's equation, but not that of the homogeneous model. In a future paper, we will confront our experimental results with the theoretical predictions obtained from a heterogeneous representation of the membrane.

Influence of the membrane nature and selectivity characterization

The essential ion exchange membrane property is its selectivity towards ions. It allows the counter ions to flow and constitutes a more or less impervious barrier to the co-ions. In the dialysis phenomenon, counter ions and co-ions diffuse together and the electrolyte flux is imposed by the slower one, the co-ion. This is why we have measured the electrolyte fluxes through the six cation exchange membranes for different concentrations [Fig. 4(a)]. The choice criterion for characterizing the membrane selectivity should not be the electrolyte flux through the membrane, J, and this for at least the following reasons: (i) from Fick's or Nernst-Planck's laws, the electrolyte flux is proportional to the electrolyte diffusion coefficient in the ion exchange material and to the concentration, and inversely proportional to the membrane thickness. For a same material, a given concentration and the same electrolyte, the membrane selectivity must be independant of its thickness. (ii) We remark the existence of inversions in the membrane selectivity classification from one concentration domain to another. These inversions make the choice of the best membrane for a given application difficult.

We propose to consider the magnitude $J \times e$ our choice criterion. In Fig. 5, we report the variation of $J \times e$ versus C_0. This eliminates curve intersections and consequently the selectivity order becomes independant of the concentration C_0 and of the membrane thickness. In addition, we remark that the CM2 membrane has the smallest values of $J \times e$, hence it is the most selective membrane. This is probably due to the fact that CM2 has a low swelling rate and a high exchange capacity (the electrolyte exclusion is important). Comparison between the six CEMs allows us to obtain the following classification, in increasing order of selectivity ($\mathscr{S}$): $\mathscr{S}$(CRP) $< \mathscr{S}$(MK-40) $< \mathscr{S}$(CMx) $< S$(CM1) $< S$(N117) $< S$(CM2).

From Table 1, it appears that the characteristics C_E and t_g alone are insufficient to give a complete interpretation of this selectivity order. It is then necessary to consider the structure and the design of the membrane. Moreover, to have a suitable

classification, it is necessary that the membranes belong to the same family. Here, the proposed classification groups heterogeneous membranes, CRP and MK-40, with homogeneous ones, CM1, CM2, CMx and N117, the last one having a particular structure. So, the above classification is not really rigorous but seems to be reliable for characterizing the membrane selectivity from the flux values.

Influence of the electrolyte nature

The nature of both the electrolyte counter- and co-ions has a great influence on the leaked-out quantity.

Counter-ion influence. To illustrate the counter-ion effect on the electrolyte fluxes, we report in Fig. 6 the variation of the flux versus C_0 for the CM2 membrane, with three counter ions: K^+, Na^+ and Li^+, and the same co-ion, Cl^-. We note that for all the upstream concentration values, the LiCl fluxes are lower than the NaCl fluxes, which are lower than the KCl ones. Thus, CM2 appears to be more selective for Li^+ than for Na^+ or K^+. This phenomenon can be interpreted using Glueckauf and Kitt's data[26] relative to the hydrated ion radius, or hydration number, in a sulfonic ion exchange membrane.[27,28] Indeed, they found that the Li^+ ion is much larger (hydration number ≈ 3.3[26]) than the Na^+ ion (hydration number ≈ 1.5[26]) or the K^+ ion (hydration number ≈ 0.6[26]). It is well-known that the higher the ion hydration number, the lower its diffusion coefficient in the membrane and so its flux through it.

In addition, the osmotic flow, in the opposite direction of the electrolyte flux, slows down the voluminous ions, as they diffuse. So the larger ion, Li^+, will be slowed down more than the Na^+ and K^+ ions.

Co-ion influence. The last part of this study deals with the co-ion influence on the electrolyte diffusion. We have chosen the counter ion K^+, the membrane CM2 and different co-ions: Cl^-, Br^- and NO_3^-. The obtained results are reported in Fig. 7. We note that the flux variation versus concentration presents the same evolution as in Fig. 4(a) and remark that the KNO_3 fluxes are higher than the KCl and KBr ones. The distinction between KCl and KBr is not evident because Cl^- and Br^- have close equivalent conductivity values in solution[29] (76.31×10^{-4} m^2 S mol^{-1} for Cl^- and 78.10×10^{-4} m^2 S mol^{-1} for Br^-) and the same hydration numbers (4 for both[2]).

What about the NO_3^- anion on the one hand and the Cl^- and Br^- anions on the other hand? The NO_3^- equivalent

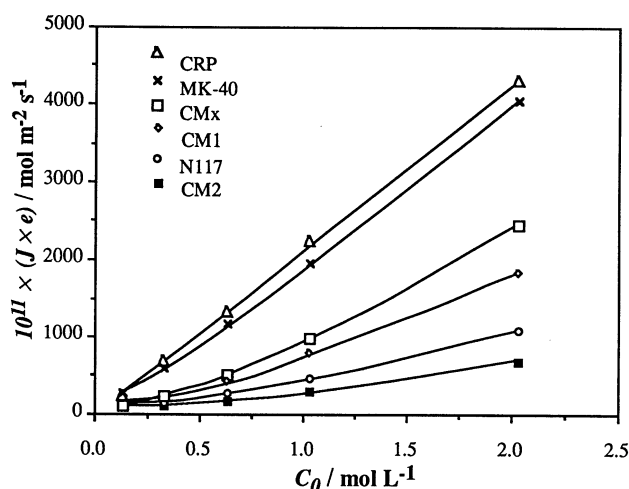**Fig. 5** Variation of $J \times e$ versus C_0 for the KCl (C_0)/CEM/H$_2$O systems

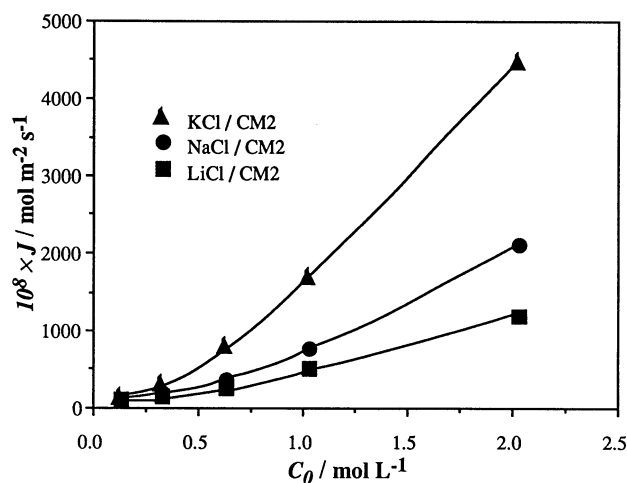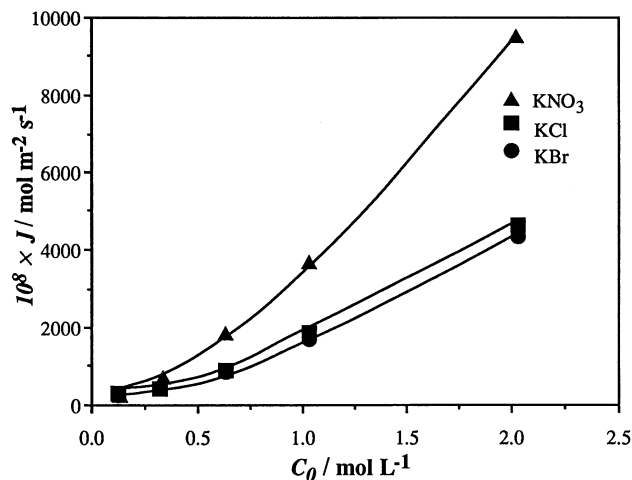**Fig. 6** Influence of the counter-ion nature on the ACl (C_0)/CM2/H$_2$O systems

Fig. 7 Influence of the co-ion nature on the KY (C_0)/CM2/H$_2$O systems

conductivity value in solution,[29] equal to 71.42×10^{-4} m^2 S mol^{-1}, is lower than those of Cl$^-$ and Br$^-$ and its hydration number is equal to 4.5.[2] This means that NO$_3$$^-$ is more voluminous than Cl$^-$ and Br$^-$. So the surface electrical charge density on NO$_3$$^-$ is lower than that of Cl$^-$ and Br$^-$. At the solution/membrane interface, the potential gradient (Donnan's potential) is fixed by the counter ion, K$^+$, which has a constant concentration. The driving force on NO$_3$$^-$ is also lower than those applied on Cl$^-$ and Br$^-$. Thus, NO$_3$$^-$ penetrates the membrane more than Cl$^-$ and Br$^-$ do and its concentration gradient increases, compared to the gradients of Cl$^-$ and Br$^-$. So, for a given co-ion we are in the presence of two opposing phenomena: the increase of its gradient concentration is associated with the decrease of its mobility, and *vice versa*.

According to our experimental results and to the former reasoning, we can deduce that the contribution of concentration gradient variations is more important than the one of mobilities.

Conclusions

From the present study, we conclude that the proposed method to characterize a cation exchange membrane selectivity is more reliable and efficient with respect to the other, static, methods. The selectivity is related to the hydration numbers (sizes) of co-ions and counter ions. However, the variation of this property for the two ion types is in reverse order.

The bilogarithmic variations of the electrolyte flux *versus* the concentration confirm the validity of Glueckauf's model insofar as they are linear and have slopes less than 2. It

remains now to confront our experimental results with different membrane model predictions, in order to explain the effects of various parameters on the electrolyte flux and so on the selectivity.

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