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A simplified procedure for ion-exchange membrane characterisation†

Christian Larchet,*[a] Lasâad Dammak,[a] Bernard Auclair,[a] Stepan Parchikov[b] and Victor Nikonenko[b]

[a] *Laboratoire des Matériaux Echangeurs d'Ions, Université Paris 12, av. du Général de Gaulle, 94010 Créteil, France. E-mail: larchet@univ-paris12.fr; Fax: +33 (1) 45 17 17 21; Tel: +33 (1) 45 17 14 86*

[b] *Department of Physical Chemistry, Kuban State University, 149 Stavropolskaya St., 350040 Krasnodar, Russia. E-mail: v_nikonenko@hotmail.com; Fax: +7 (8612) 699 517; Tel: +7 (8612) 699 573*

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A new procedure for the characterisation of the transport properties of ion-exchange membranes (IEM) is proposed. Only three characteristics have to be measured: the electrical conductivity, the diffusion permeability coefficient and the apparent transport number. To complete the set of parameters, two complementary characteristics, the true counter-ion transport number and the water transport number, are calculated from the Scatchard equation and from a novel equation deduced earlier. The possibilities to reduce the number of initial measurements are discussed in three cases.

I. Introduction

Ion-exchange membranes (IEM) are used in a great number of processes, such as water desalination, electrolyte solution concentration, *etc*. Many characteristics have been introduced for understanding the membrane behaviour and the membrane structure from their static and dynamic properties.[1–19] However, only some of them are applied in practical characterisation when the membranes are compared or selected for a given application. Our aim is to develop a simple but correct procedure for IEM characterisation.[20–29] In this paper we propose a procedure involving a minimal number of easily measured parameters completed by two computed parameters. This procedure is examined for three particular systems, leading to further simplifications.

There are several levels of IEM characterisation. The simplest one is adopted by the IEM manufactures[30,31] and a large portion of users. It consists of measuring only two properties: (1) the electrical conductivity κ (S m^{-1}) (or, sometimes, the surface resistance d/κ in S^{-1} m^2, d being the membrane thickness) at a given concentration and (2) the apparent transport number of the selectively transported counter-ion, denoted here as $t_{+\text{app}}$ (the case of a cation-exchange membrane is considered, for the sake of simplicity) measured by the potentiometric (emf) method. Such characteristics are cited, mainly at 25 °C, in a number of IEM catalogues.[30,31] The conductivity characterises the energy consumption in electrodialysis (ED) processes. Nevertheless, $t_{+\text{app}}$ is an ambiguous characteristic. It includes two contributions: the true transport number t_+ and the water transport number t_w, according to the Scatchard equation:[32]

$$t_{+\text{app}} = t_+ - z_+\nu_+ m_\text{s} M_\text{w} t_\text{w} \qquad (1)$$

where m_s is the molality of the solution, M_w is the water molar mass, z_i and ν_i are the charge and stoichiometric numbers of ion i.

t_+ determines the membrane permselectivity, which is defined[33] as the ratio of the difference between t_+ and the counter-ion transport number in solution (t_+^s) to (1 − t_+^s). The knowledge of t_+ is often (especially in diluted solutions) sufficient to calculate the current efficiency and the concentration variations in an ED cell formed by two ion-exchange membranes if the water transfer through the membranes is not important. However, in concentrated solutions the water transfer should be taken into account to evaluate the variation in solution volume, hence the knowledge of t_w is needed.

A second level of IEM characterisation corresponds to a full determination of the set of phenomenological parameters. It is more convenient for mathematical modelling of IEM structure and processes. It is clear that a more complete characterisation requires more experiments, and many of them are too sophisticated for everyday use. Therefore, only a few results are available in the literature. For example, Narebska *et al.*[9,10] have measured the six following properties of an IEM in contact with a single electrolyte solution: the electroosmotic and osmotic volume fluxes, diffusion flux (J_s), specific conductivity under alternating current (κ), apparent transport number of counter-ion ($t_{+\text{app}}$) and pressure-driven flux variation with the pressure. These six parameters allow the determination of the six coefficients of the Kedem–Katchalsky equations [including the true transport number, by using eqn. (1)] or the six L_{ij} coefficients of the Onsager phenomenological equations[11,22]. Recall that the Kedem–Katchalsky coefficients are as follows: (1) electrical conductivity (κ), (2) transport number of the counter-ion (t_+), (3) diffusion permeability (P), (4) water transport number (t_w) or electroosmotic permeability (β), (5) hydraulic permeability (L_p) and (6) Staverman's reflection coefficient (σ).

Since the filtration permeability properties are not important in many applications of IEMs, such as ED, Gnusin *et al.*[13] have proposed to restrict IEM characterisation to the measurement of four properties: the specific conductivity under alternating current (κ), diffusion permeability (P), apparent transport number of counter-ion ($t_{+\text{app}}$) and the water transport number

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† A list of symbol definitions and acronyms is given in Appendix 2.

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(t_w). The true transport number is to be evaluated from eqn. (1). Hence, four of the six independent coefficients of Kedem–Katchalsky can be determined in this way. The knowledge of these coefficients is sufficient for calculation of the ionic electrodiffusion flux, the water electroosmosis flux and the electric potential difference through the membrane, in the case of a single electrolyte.

We will show later that the procedure proposed by Gnusin *et al.*[13] can be simplified almost without losing precision. Namely, the measurement of t_w may be omitted. Instead, we will use a relation between P, κ, t_+ and $t_{+\text{app}}$. This relation, combined with the Scatchard equation,[32] enables t_+ and t_w to be calculated. The proposed method for the t_+ and t_w evaluation will be verified by using known data obtained for one Nafion® 120, one MF-4SK and two MK-40 membranes. Then, several examples of the characterisation procedure with original data will be considered. The possibilities to further simplify the proposed procedure will be discussed.

II. Characterisation procedure

II.1. Static properties

A standard set of static properties is assumed to be determined by conventional methods:[21–23] the ion-exchange capacity (Q), the water content (w_c) and the membrane thickness (d). The values of these magnitudes for several ion-exchange membranes, the properties of which will be discussed here, are given in Table 1. Four commercial sulfonate cation-exchange membranes are considered. The data on their properties (Table 1) are taken from refs 9, 10, 13–16 and 24 or were determined by the authors.

II.2. Specific conductivity

The specific conductivity should be measured in the range of 0.1–2.0 M NaCl concentration or in more concentrated solutions if it is necessary. In principle, the conductivity should be measured under direct current because, firstly, ED works by using a direct current and, secondly, just this quantity enters into relation (9) considered later and used for the evaluation of t_+ and t_w. A difference between the conductivities under direct and alternating currents was observed experimentally[25] and interpreted theoretically[4,17,25] to be a consequence of the concentration polarisation at the internal interphase boundaries inside the membrane. However, the measurement of the conductivity under direct current is more difficult and few of these data are available. At the same time, following theory,[4,17,25] this difference should decrease as the concentration increases and if the membrane structure is sufficiently homogeneous. In this paper, we will use data on the conductivity under alternating current, obtained with a "clamp"-type cell described in the literature.[18]

II.3. Diffusion permeability

This characteristic is determined in the system where an electrolyte diffuses from a solution with a given molar concentration c_s into pure water through the membrane under consideration. The salt diffusion permeability coefficient P is defined as the proportionality coefficient in the integral form of Fick's law:

$$P = (J_s d / c_s)_{\Delta p,\ i\,=\,0} \tag{2}$$

where J_s is the electrolyte flux density, d is the membrane thickness and the subscripts denote that the pressure gradient across the membrane and the current must be zero. The cell and the protocol for diffusion flux measurements used in this paper are described in refs 26 and 27.

In ED applications, this characteristic is very important for concentrated solutions, because the diffusion permeability (as well as the water transport) limits the performance of the electrolyte concentration process. In diffusion dialysis it is desirable to know this characteristic in a sufficiently large range of concentrations: at 0.1 M and higher. The knowledge of the electrolyte diffusion permeability as a function of the concentration permits to calculate the diffusion flux through the membrane if the interfacial concentrations in the left- (c_s^{II}) and right-hand (c_s^{II}) side solutions are known.[4,22] However, for computing t_+ and t_w, the local coefficient of the diffusion

Table 1 Main characteristics of different ion-exchange membranes in 1.0 M NaCl solution

Membrane		Nafion 120 Du Pont de Nemours (USA)	MF-4SNPO PlastPolymer (Russia)K	MK-40NPO Plastmassy (Russia)	CM2 Tokuyama Soda (Japan)
Type		Homogeneous Perfluorinated Cation-exchanger	Homogeneous Perfluorinated Cation-exchanger	Heterogeneous Polystyrene and divinylbenzene Cation-exchanger	Homogeneous Polystyrene and divinylbenzene Cation-exchanger
Water content	in g H_2O per g of dry IEM	0.30	0.16	0.52	0.27–0.30
	in mol H_2O per mole of fixed groups	20.0[14]	11.9[15]	11.6[c]	7.1–7.8[c]
Exchange capacity (mol kg^{-1} dry membrane)		0.83[14]	0.77[15]	1.64[c]	2.12[c]
Thickness mm		0.29–0.30[a]	0.22[b]	0.51[c]	0.135[c]
Conductivity (S m^{-1})		1.77[13]	0.82[15]	1.26[c]	0.75[c]
Salt permeability (10^{-11} m^2 s^{-1})	Integral (P)	3.50[9]	0.86[13]	1.10[13]	0.11,[24] 0.093[c]
	Local (P*)	4.60	1.29	1.22	0.14,[24] 0.15[c]
Counter-ion apparent transport number t_{app}		0.85[9]	0.90[13]	0.87[13]	0.943[c]
True transport number t_i	Calcd from t_{app} and t_w [eqn. (1)]	0.97	0.99	0.985	—
	Calcd from κ, t_{app} and P* [eqn. (9)]	0.945	0.97	0.974 (sample 1) 0.979 (sample 2)	0.996
Water transport number t_w	Exptal	6.6[10]	5.0[16]	6.5[13]	—
	Calcd from eqn. (1)	5.2	3.7	5.8	3.0

[a] Result communicated by S. Koter. [b] Result communicated by N. Berezina. [c] Our experimental results.

permeability P^* is needed. This quantity plays the role of the coefficient in the differential equation of diffusion under the form:

$$J_s = -P^*(dc_s/dx)_{\Delta p,\ i\,=\,0} \quad (3)$$

where c_s is the concentration of the "virtual" electroneutral solution in equilibrium with a thin layer of the membrane localised at the normal coordinate x.[22] P^* can be calculated from the (integral) coefficient P as a function of c_s:[4,22,24]

$$P^*(c_s) = P(c_s) + c_s(dP/dc_s) \quad (4)$$

ż

It is convenient to present the function $P^*(P)$ in the $P^* = P\beta_s$ form.[19] The coefficient $\beta_s = 1 + d(\log P)/d(\log c_s)$ may be easily obtained by differentiating the function $\log P = \text{funct}(\log c_s)$ by using, for example, a polynomial regression of the experimental data.

II.4. Apparent transport number

The apparent transport number is determined from emf measurements described, for example, in ref. 2 when the membrane separates two solutions with concentrations c_s^{I} and c_s^{II}. The problem of relating the value t_{+app} to an equilibrium solution concentration c_s being between c_s^{I} and c_s^{II} is resolved by a graphical interpolation known as Prigent's method.[21]

II.5. True transport number and water transport number

The true transport number of the counter-ion is defined by the following equation as the fraction of the electric charge transported by this ion through the membrane under the conditions where there are no concentration and no pressure gradients across the membrane:

$$t_+ = \left(\frac{z_+ J_+ F}{i}\right)_{\Delta p, \Delta c = 0} \quad (5)$$

where i and J_+ are the current density and the flux of cation considered as the counter-ion.

The water transport number t_w is defined from the equation:

$$t_w = \left(\frac{J_w F}{i}\right)_{\Delta p, \Delta\pi = 0} \quad (6)$$

where J_w is the water flux density through the membrane.

We have mentioned that t_+ may be found from the Scatchard eqn. (1) if the apparent transport number t_{+app} and the water transport number t_w are known. Note that the membrane potential and, therefore, t_{+app}, are relatively easy to measure, but the determination of t_w is delicate.

Another possibility to determine t_+ is the use of the well-known Hittorf method.[21,28] This method can give reliable information on the true transport number because it consists in direct determination of the ionic flux J_+ from the changes in the electrolyte concentration in a compartment formed by two membranes, one of them being that under study. However, there are many difficulties in the practical realisation of this method:[4,28] the ion transport number through the auxiliary membrane should be known and the variation in the solution volume due to the water transfer through the membranes should be taken into account (normally it can be neglected in diluted solutions).

II.6. Relation between the transport parameters

It can be shown by comparing the Onsager and the Kedem–Katchalsky equation systems written down for a 1 : 1 electrolyte that:[22]

$$P^* = \frac{2RTg}{c_s}\left[\frac{\kappa t_- t_{+app}}{F^2} + (L_{+-} - m_s M_w L_{-w})\right] \quad (7)$$

where L_{ij} are the phenomenological coefficients in the Onsager equations, t_- is the transport number of the co-ion ($t_+ + t_- = 1$) and g is the activity factor[7,22] relating to the equilibrium virtual solution:

$$g = 1 + \frac{d \ln y_\pm}{d \ln c_s} \quad (8)$$

$y_\pm$ being the mean molar activity coefficient.

If the term $l_1 = L_{+-} - m_s M_w L_{-w}$ is small compared to $\kappa t_- t_{+app}/F^2 = L_{--} t_{+app}$, it can be neglected and the following relation between the transport parameters is obtained:[22]

$$t_- = \frac{P^* F^2 c}{2RT\kappa t_{+app} g} \quad (9)$$

Eqn. (9) can be considered as a generalisation of the Nernst–Einstein relation.[22] The l_1 term is positive if the contribution of the co-ion–counter-ion interaction (L_{+-}) is greater than that of the co-ion–water interaction ($m_s M_w L_{-w}$). In this case the membrane studied may be considered as rather hydrophobic following the classification by Kedem and Perry:[8] the polymer matrix is hydrophobic and the concentration of charged sites is not large; hence, the water content is relatively low. Obviously, in the case $l_1 < 0$ the membrane should be considered as relatively hydrophilic with a less hydrophobic matrix and higher concentration of charged sites. Eqn. (9) becomes exact when there is a balance between the membrane hydrophobic and hydrophilic properties, the water content being rather medium.

An equation equivalent to eqn. (9) was deduced by Paterson and Gardner.[34] In the case of zero volume transport ($t_w = 0$) similar relations were obtained and tested by Kedem and Perry,[8] Narebska and Koter,[35] Gnusin *et al.*,[19,29] Zabolotsky and Nikonenko[4,17] and Parchikov;[20] the latter has taken into account $g \neq 1$.

Paterson and Gardner[34] have studied two sulfonated styrene-DVB membranes in normal and expanded forms. They have found t_- from the t_{+app} and t_w experimental values using the Scatchard equation, and then calculated the diffusion flux of NaCl through the membranes by an equation equivalent to eqn. (9). The calculated and observed NaCl fluxes were 3.3 and 3.9 ($\times 10^{-6}$ mol m^{-2} s^{-1}), respectively, for the normal and 12.9 and 12.2 ($\times 10^{-6}$ mol m^{-2} s^{-1}) for the expanded forms. Hence, if using our notation, $l_1 > 0$ for the normal and $l_1 < 0$ for the expended form, this correlates with the sense of this term presented above.

Narebska and Koter[35] have shown that neglecting the term l_1 has a small effect, not exceeding 5–8%, on the evaluation of the permselectivity of a Nafion 120 membrane.

The experiments of Kedem and Perry[8] have shown that two types of deviations from relation (9) are possible: positive ($l_1 > 0$) for hydrophobic membranes and negative ($l_1 < 0$) for hydrophilic membranes.

II.7. Simplified characterisation

In all, five parameters are employed for the characterisation of membrane transport properties: κ, t_{+app}, P^*, t_+ and t_w. The use of the correct Scatchard eqn. (1) and the approximate relation (9) allows measurement of only three of them, the other two can be calculated. It is proposed to determine experimentally κ, t_{+app} and P^* as their measurement is simpler; then the t_+ and t_w values are calculated.

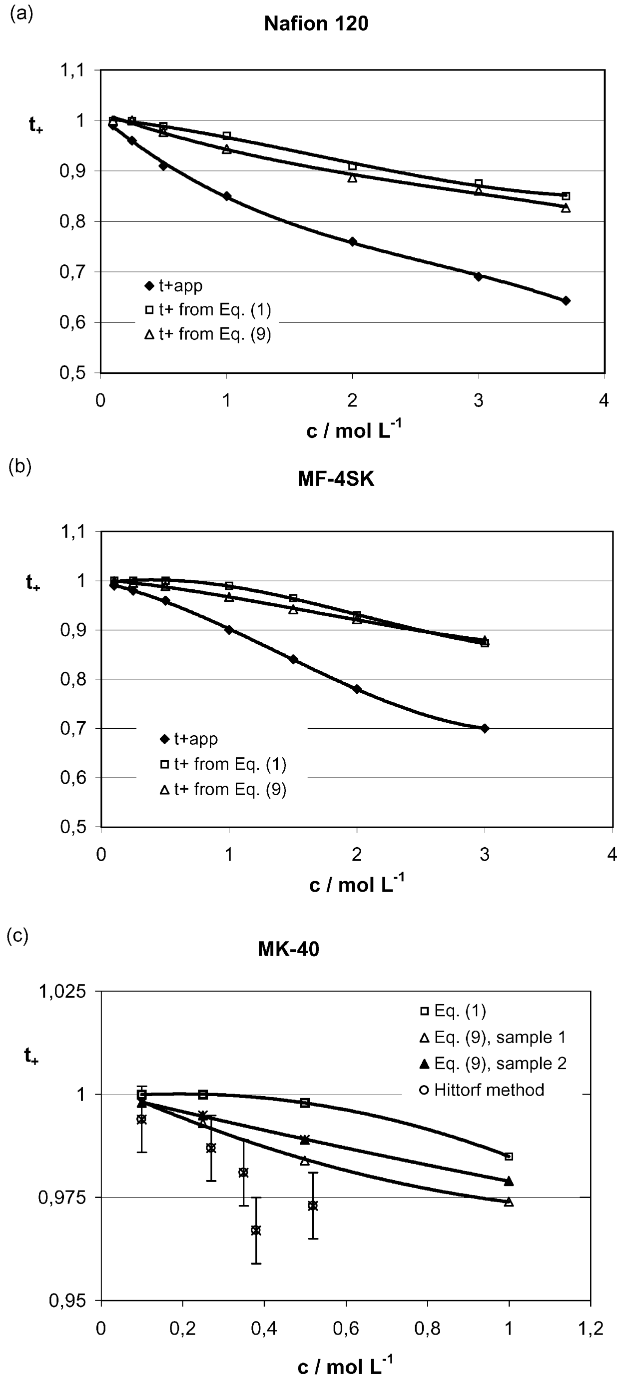

Fig. 1 Apparent experimental and true transport numbers of Na^+ through (a) Nafion®120, (b) MF-4SK and (c) MK-40 membranes. The latter are determined from eqn (1) or eqn (9) or from the Hittorf method. Experimental data (except Hittorf's t_+) are taken from refs 9, 10 and 14 for the Nafion®120 membrane and from refs 13, 15, 16 and 24 for the MF-4SK and the MK-40 ones; for Hittorf's t_+ in MK-40 the data are taken from ref. 28

III. Results and discussion

III.1. Determination of the transport numbers by different methods

Fig. 1(a,b) compares the values of the transport numbers calculated from eqn. (1) (where t_{app} and t_w are known from experiment) or from eqn. (9) (where P^*, κ and t_{app} are known) for Nafion® 120 and MF-4SK membranes as functions of the NaCl solution concentration. The experimental data for the Nafion® 120 are taken from publications of Narebska, Koter and Kujawsky.[9,10] The permeability P as a function of the concentration is modelled with a polynomial: $P = (0.0014c_s^4 + 0.0393c_s^3 - 0.5198c_s^2 + 1.9763c_s + 1.9867) \times 10^{-11}$ ($m^2\ s^{-1}$), then by differentiation of this polynomial the local permeability P^* is calculated following eqn. (4). The experimental data for the MF-4SK and MK-40 are taken from publications[13,15,16,24] of Gnusin, Berezina *et al.* The log$P = y$ as function of log$c_s = x$ is modelled with a polynomial: $y = -0.3967x^3 - 0.4015x^2 + 0.5269x - 0.07$. Then $\beta_s = 1 + d(\log P)/d(\log c_s) = 1 + dy/dx$ is calculated and P^* is found (see Section II.3). The values for the activity factor g for the solutions used were determined by treating the data presented in ref. 7 (Table 2, see Appendix 1 for the details of the calculation).

One can see that there is a sufficiently good agreement between the values of the counter-ion transport number t_+ evaluated with the Scatchard eqn. (1) or with approximate eqn. (9) for the two membranes. At least, the difference between two evaluations of t_+ is much less than the difference between the true and apparent transport numbers.

The case of two samples of the MK-40 membrane taken from different membrane sheets, in NaCl solutions, is considered in ref. 22. It was shown that the difference between the "Scatchard" and "approximated" transport numbers is, for several NaCl solution concentrations, less than the difference between the t_+ values obtained for the different samples. An example of the t_+ calculation with eqn. (1) or with eqn. (9) for two samples of MK-40 in the case of 1 M NaCl is presented in Table 1.

Fig. 1(c) gives the data for two samples of MK-40 membrane. The results of the t_+ calculation from eqns. (1) or (9) are compared also with the experimental data[28] obtained by the Hittorf method for another sample of the same material. The values of t_+ calculated using eqn. (9) are within the error bars of the t_+ obtained by the Hittorf method. The values of t_+ calculated using eqn. (1) are a little bit higher than this range. This example shows that the proposed method may be applied for the evaluation of the membrane permselectivity, the uncertainty being of the same order of magnitude as the variation in the properties of different samples. Owing to the fact that the uncertainty of the Hittorf method is relatively high, about 8% in the experiments,[28] and that different samples were used, it is difficult to give a more definitive conclusion about the choice of method for the true transport number determination.

Note that the values of t_+ calculated from eqn. (9) and presented in Fig. 1(a–c) are slightly lower for most concentrations than the true transport numbers obtained from the Scatchard eqn. (1). This means[22] that the coefficient $l_1 = (L_{+-} - m_s M_w L_{-w})$ is positive, therefore the membranes Na-

Table 2 Activity factor $g = 1 + d(\ln y_{\pm})/d(\ln c_s)$ for different electrolyte solutions

	g		
c_s/mol L^{-1}	LiCl	NaCl	KCl
0	1	1	1
0.0001	0.991	0.991	0.991
0.0005	0.985	0.985	0.985
0.001	0.980	0.980	0.980
0.005	0.964	0.963	0.962
0.01	0.954	0.952	0.951
0.05	0.936	0.927	0.922
0.1	0.935	0.918	0.909
0.2	0.949	0.916	0.900
0.5	1.022	0.938	0.905
0.7	1.078	0.960	0.914
1.0	1.162	0.998	0.932
1.5	1.312	1.071	0.974
2.0	1.489	1.152	1.024
2.5	1.707	1.251	1.080
3.0	1.933	1.356	1.141

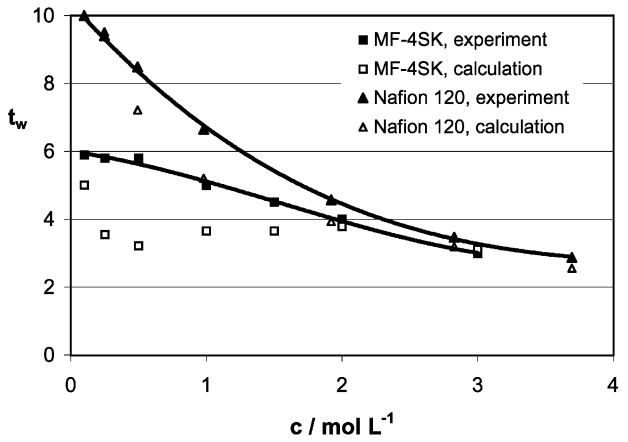

Fig. 2 Experimental and calculated [from eqn. (1) or eqn. (9)] water transport numbers for MF-4SK and Nafion®120 membranes in NaCl solutions. Experimental data are taken from refs 9 and 10 for the Nafion®120 and from refs 13 and 15 for the MF-4SK membrane.

fion 120, MF-4SK and MK-40 should be considered as rather hydrophobic.[8] Hence, omitting l_1 shifts the calculated t_+ down in comparison with the Scatchard transport numbers.

III.2. Calculation of the water transport numbers and comparison of the membranes

Fig. 2 shows the experimental and calculated water transport numbers for the Nafion® 120 and MF-4SK/NaCl systems. The experimental data are taken from refs 9 and 10 for the Nafion® 120 and from refs 13 and 15 for the MF-4SK. The theoretical values are obtained by using eqn. (1), where t_+ was determined previously from eqn. (9), and $t_{+\mathrm{app}}$ is experimental.

The agreement between the experimental and calculated water transport numbers is good in the case of the Nafion® 120 membrane and less good in the case of the MF-4SK membrane (Fig. 2). A sufficiently good agreement between calculated and measured t_w is observed also in the case of the MK-40 membrane, for 1 M NaCl (Table 1). However, in all the considered cases, the calculated values are lower than experimental ones, which is explained by the positive value of the l_1 term as demonstrated in the previous section. Indeed, if we had taken into account this term and used the exact eqn. (7) instead of eqn. (9), the calculated t_+ would be higher, as well as the values of t_w calculated from eqn. (1). We suppose the higher disagreement between calculated and experimental t_w in the case of MF-4SK is due to the fact that this membrane is more hydrophobic (Table 1), hence the l_1 term is higher than that in the case of Nafion® 120.

When comparing two sulfonic perfluorinated membranes, Nafion®120 and MF-4SK, one can note that calculated values of t_+ and t_w are in the same order as the experimental values: t_+ (Nafion) < t_+ (MF-4SK), t_w (Nafion) > t_w (MF-4SK). This order is logical if we take into account that the exchange capacities of the membranes are close, but the water content of the Nafion®120 is significantly higher than that of the MF-4SK.

The same method of calculation of t_w, as used in Fig. 2, was applied for a CM2 membrane in NaCl solutions: t_+ was calculated from experimental κ, $t_{+\mathrm{app}}$ and P^* with eqn. (9) and then t_w was evaluated from t_+ and $t_{+\mathrm{app}}$ with eqn. (1). The results shown in Table 1 allow us to compare the membranes. The CM2 contains the lowest amount of water (expressed in mole H_2O per mole of charged sites, n) and the highest exchange capacity among the cation-exchange membranes presented in Table 1, hence the lowest value of t_w and the highest value of t_+ seems justified.

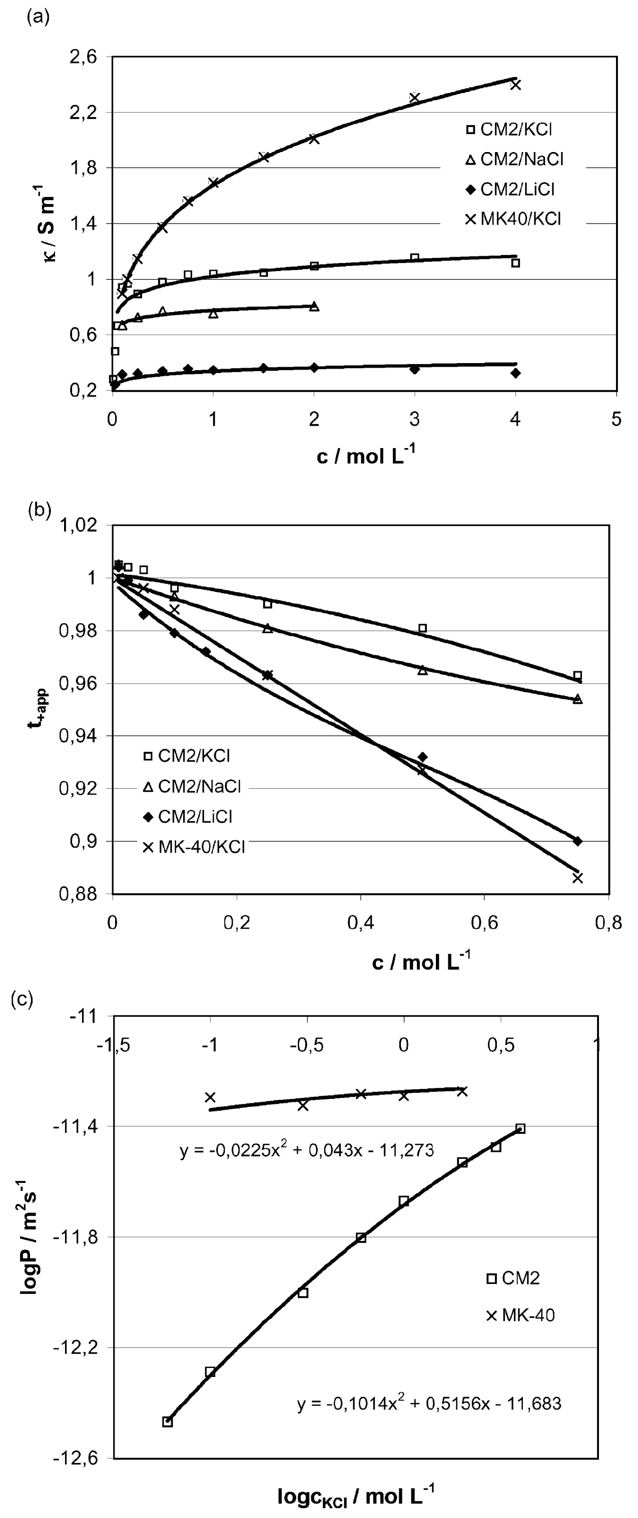

Fig. 3 Results of measurements of the (a) specific conductivity, (b) apparent transport number and (c) integral diffusion permeability as functions of the external solution concentration c for different membrane systems. The equations of the quadratic regression of the functions log$P$ *vs.* log$c$ are shown near the curves.

Note also that the high selectivity of MK-40 is not surprising if its water content n is compared with this value for other membranes, Nafion®120 in particular. Here we agree with Berezina *et al.*[15] about the role of the water content expressed in mole H_2O per mole of charged sites (n): this characteristic is more significant than that expressed in g per g of dry membrane. Really, the higher n, the higher are the κ,P and t_w values, but the less selective is the counter-ion transport (t_+). At the same time, the permselectivity increases with the

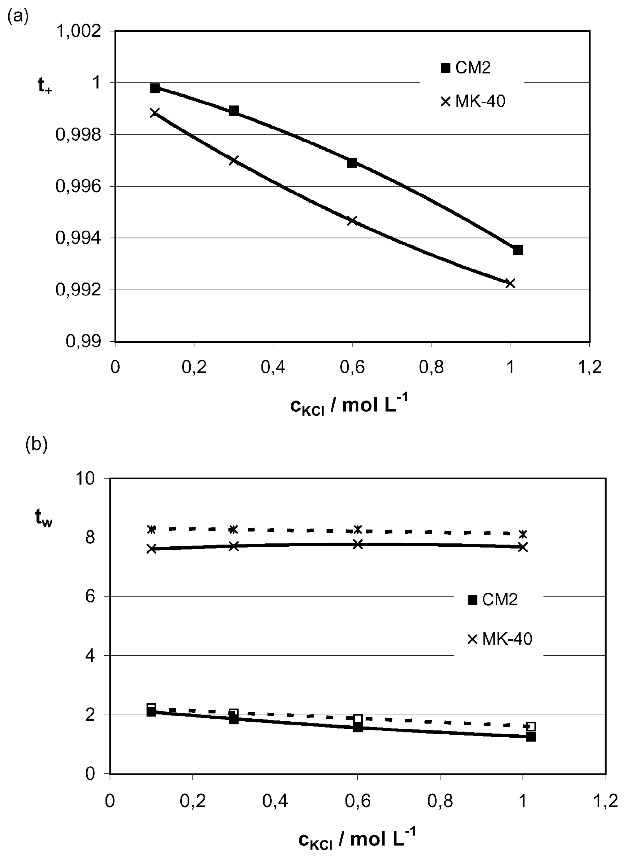

Fig. 4 The K^+ transport number (a) calculated from eqn. (9) and the water transport number (b) calculated from eqn. (1) for CM2 and MK-40 membranes as functions of the KCl equilibrium solution. The measured values of t_{app} for the CM2 and MK-40 membranes are modelled with the polynomials $t_{app} = -0.0097c^2 - 0.0389c + 0.9998$ and $t_{app} = -0.1487c + 1$, respectively [the corresponding curves are shown in Fig. 3(b)]. The dotted lines in (b) show the results of the t_w calculation when assuming that $t_+ = 1$.

exchange capacity. The nature of the polymer matrix and the membrane structure play an important role: the *n* value is only slightly higher for the MK-40 membrane in comparison with MF-4SK, but the exchange capacity is distinctly higher. Nevertheless, the permselectivity of MK-40 is practically the same as that of MF-4SK at 1.0 M NaCl, and it is less than that for MF-4SK in the range of higher concentrations.[22] The explanation is that MK-40 is a heterogeneous membrane and the distribution of the charged sites is less uniform in comparison with MF-4SK: most of the sites are concentrated in regions that can be called "charged gel",[17,19] the "inter-gel" spaces being devoid of them. The more hydrophobic matrix of MF-4SK leads to a lower water transport in comparison with MK-40.

The obtained results show that the proposed method allows the counter-ion and the water transport numbers to be evaluated from measurements of a reduced number of membrane transport properties.

III.3. Application for the membrane characterisation procedure

Consider now the application of the proposed procedure for membrane characterisation. Four membrane systems were studied: a MK-40 membrane in KCl solutions and a CM2 membrane in LiCl, NaCl and KCl solutions. The main membrane characteristics are given in Table 1. Three transport properties were measured in the case of MK-40/KCl and CM2/KCl systems: the specific conductivity under alternating current κ, the diffusion flux from a solution with a concentration c_s into deionised water and the apparent transport number t_{+app} by Prigent's method.[21] In the case of the CM2/LiCl and CM2/NaCl systems, κ and t_{+app} only were measured. The results of the measurements are presented in Fig. 3. The membrane integral permeability is calculated by using eqn. (2).

In the case of the MK-40/KCl and CM2/KCl systems, it is possible to determine the rest of membrane transport characteristics, which were not measured. Eqn. (9) allows evaluation of the true transport number t_+ from κ, P^* and t_{+app}, where the local permeability P^* is determined by differentiation of the quadratic polynomials modelling the experimental concentration dependencies $\log P - \log c$ [Fig. 3(c)]. The method of computing the activity factor in KCl solutions is described in Appendix 1; the results of this evaluation are presented in Table 2. Then the water transport number can be calculated from eqn. (1). The results of the t_+ and t_w determination are shown in Fig. 4. It can be seen that t_+ is greater for the CM2 membrane and t_w is greater for the MK-40 one. This result is explained by the fact that the exchange capacity is close for these membranes, but the water content is considerably higher for the MK-40 membrane (Table 1).

Very often, some information on the membrane properties is absent. In these cases the use of eqns. (1) and (9) allows the membrane characterisation to be completed. We will consider three common cases.

Case 1: Only the conductivity, diffusion permeability and water transport number are known. In this case, the simultaneous solution of eqns. (1) and (9) gives two supplementary characteristics: t_+ and t_{+app}. Examples of this evaluation for different membranes in 1 M NaCl solution are presented in Table 3. It appears that the calculated value of t_{+app} is sufficiently close to the experimental value. Evidently, these two values would coincide if t_w calculated from κ, P^* and t_{+app} with eqns. (1) and (9) coincided with the experimental t_w value (see Table 1).

The t_+ value found by this method differs more from the Scatchard t_+ value obtained with eqn. (1), in comparison with the other approximate method presented in Section III.1 (see Tables 1 and 3). However, the difference between these two approximate values of t_+ is very small, about 0.1–0.3%, as can be seen from Tables 1 and 3.

Case 2: Only the conductivity and apparent transport number are known. This case is considered for a CM2 membrane in LiCl and NaCl solutions [Fig. 3(a,b)]. Eqn. (1) allows the water transport number t_w to be evaluated. The counter-ion transport number for highly charged membranes such as the CM2 mem-

Table 3 Evaluation of apparent and true counter-ion transport numbers for different membranes in 1.0 M NaCl solution

Membrane	Nafion®120	MF-4SK	MK-40	CM2
t_w (exptal)	6.6[10]	5.0[15]	6.5[13]	3.0[a]
t_{+app} (exptal)	0.85[9]	0.90[15]	0.87[13]	0.943[b]
t_{+app} from κ, P^* and t_w [eqns (1) and (9)]	0.822	0.876	0.856	0.943
t_+ from t_{+app} and t_w [Scatchard's eqn. (1)]	0.97	0.99	0.985	—
t_+ from κ, P^* and t_{+app} [eqn. (9)]	0.945	0.970	0.974	0.996
Case 1: t_+ from κ, P^* and t_w [eqns (1) and (9)]	0.941	0.966	0.973	0.996
Case 3: t_+ from κ and P^* [eqn. (10), $t_w = 0$, $g = 1$]	0.949	0.969	0.976	0.996

[a] Our estimation from κ, P^* and t_{+app} with eqns (1) and (9). [b] Our experimental results.

brane is very close to 1 [Fig. 4(a)] if the solution is not very concentrated. Hence, when using eqn. (1), the difference between t_+ and 1 may be neglected. Fig. 4(b) shows the values of t_w calculated from eqn. (1) with t_+ obtained from eqn. (9) (solid lines) and with $t_+ = 1$ (dotted lines). One can see that the use of the assumption $t_+ = 1$ results in an insignificant overestimation of t_w: the difference between two values of t_w does not exceed 0.33 in the case of CM2 and 0.55 in the case of MK-40. This difference is equal to or less than the measurement error. Hence, when evaluating the water transport number from Scatchard's eqn. (1), the value of t_+ used in the calculation and ranging between its actual value and 1 has very small effect on the result. Note that if one assumes $t_+ = t_{+\mathrm{app}}$, eqn. (1) gives $t_w = 0$, which is obviously too small. Therefore, the evaluation $t_+ = 1$, in the considered case, is better than $t_+ = t_{+\mathrm{app}}$. Thus, when only κ and $t_{+\mathrm{app}}$ are known, the true transport number cannot be evaluated with sufficient precision. It is between $t_{+\mathrm{app}}$ and 1, being more close to 1. At the same time, the calculation of t_w as described above gives satisfactory results.

The estimation of P^* from eqn. (9) is not effective in this case because t_+ is not known. The approximation $t_+ = 1$ leads to $P^* = 0$. The other limiting assumption, $t_+ = t_{+\mathrm{app}}$, is also very crude when applying eqn. (9); however, it may give an idea of the P^* value, even if it is overestimated by several times.

Case 3: Only the conductivity and the diffusion permeability are known. This is the case where a minimum number of transport properties is to be measured. When assuming $t_{+\mathrm{app}} = t_+$ ($t_w = 0$), eqn. (9) is transformed into a quadratic equation, the solution of which is:

$$t_- = \frac{1}{2} - \sqrt{\frac{1}{4} - \frac{P^* F^2 c}{2RT\kappa g}} = \frac{2Y}{1+\sqrt{1-4Y}}, \text{ where } Y = \frac{P^* F^2 c}{2RT\kappa g} < \frac{1}{4} \qquad (10)$$

For simplified calculations valid at $c \leqslant 2.0$ mol L^{-1} (in the cases considered in ref. 22), the activity factor g may be taken equal to 1 except for LiCl (Table 2).

As Table 3 shows, at $c = 1$ mol L^{-1}, when using these two simplifications, one finds approximated t_+ values closer to the Scatchard values than when using eqn. (9) without simplifications. The explanation is as follows. In the considered cases of relatively hydrophobic membranes the term l_1 is positive and its omission, when deducing eqn. (9), leads to an underestimated value of t_+. When replacing, in eqn. (9), $t_{+\mathrm{app}}$ by t_+, which is higher, a lower value of t_- is found and hence a higher value of t_+. Note also that at $c = 1$ mol L^{-1} the g value is very close to 1. In the range of concentrations from 1.0 to 2.0 mol L^{-1}, g increases weakly and the simplifications $t_{+\mathrm{app}} = t_+$, $g = 1$ remain acceptable. However, if $c > 2.0$ mol L^{-1}, these simplifications become too crude.

IV. Conclusion

A simplified procedure for the determination of IEM transport properties is described. The membrane conductivity, diffusion

Table 4

$a_\pm$	Mean ionic activity of the electrolyte (mol L^{-1})
c_s	Concentration of the "virtual" electroneutral solution (mol L^{-1})
$c_s{}^{\mathrm{I}}$	Interfacial concentration of the left side solution (mol L^{-1})
$c_s{}^{\mathrm{II}}$	Interfacial concentration of the right side solution (mol L^{-1})
c_w	Solvent molarity (water) (mol L^{-1})
d	Membrane thickness (m)
F	Faraday's constant (C mol^{-1})
g	Activity factor of the equilibrium solution [eqn. (8)]
i	Current density (A m^{-2})
J_s	Salt diffusion flux (mol m^{-2} s^{-1})
J_w	Water flux density through the membrane (m s^{-1})
J_v	Volume flux (m s^{-1})
J_+	Cation (counter-ion) flux (mol m^{-2} s^{-1})
l_1	Defined as $L_{+-} - m_s M_w L_{-w}$, term characterising the relative hydrophobicity/hydrophilicity of an IEM
L_{ij}	Coefficients of the Onsager phenomenological equations (mol^2 J^{-1} m^{-1} s^{-1})
m_s	Molality of the salt solution (mol kg^{-1})
M_w	Water molar mass = 0.018 kg mol^{-1}
n	Water content (mole H_2O per mole of charged sites)
P	Salt diffusion permeability coefficient (m^2 s^{-1})
P*	Local diffusion permeability coefficient [eqns. (4) and (5)] (m^2 s^{-1})
Q	Ion-exchange capacity (eq kg^{-1})
R	Molar gas constant (J K^{-1} mol^{-1})
t_w	Water transport number
$t_{+(-)}$	True counter-ion (co-ion) transport number
$t_{+\mathrm{app}}$	Apparent counter-ion transport number
T	Temperature (K)
$\bar{V}_s$	Partial molal volume of the electrolyte (m^3 mol^{-1})
$\bar{V}_w$	Water partial molal volume (m^3 mol^{-1})
w_c	Water content (g H_2O per g of dry IEM)
x	Position in the membrane (m)
$y_\pm$	Mean molar activity coefficient
z_i	Charge of ion i
β	Electroosmotic permeability coefficient (m A^{-1} s^{-1})
β_s	Coefficient = 1 + d(log$P$)/d(logc_s)
κ	Electrical conductivity (S m^{-1})
ν_i	Stoichiometric number of ion i
σ	Staverman's reflection coefficient
ED	Electrodialysis
IEM	Ion-exchange membrane

permeability and apparent transport numbers should be measured. The true counter-ion transport number and the water transport number, which are more difficult to measure, are then calculated by using the Scatchard relation and a novel relation [eqn. (9)] deduced earlier. This procedure is verified by using the complete characterisation data of several membranes taken from the literature. Some simplification of the procedure is possible. The most interesting is the case when only the conductivity and diffusion permeability are measured. The result of the t_+ calculation in this case differs from that obtained with the full procedure only by few tenths of a per cent. However, the water transport number remains unknown in this case.

An analysis of the experimental data and their treatment show that the true transport number t_+ for studied membranes is very close to 1, at least at concentrations equal or less than 1 M. The difference between the counter-ion apparent transport numbers, $t_{+\mathrm{app}}$, found for different membranes is due, mainly, to the difference in the water transport number t_w, and only after that, to the difference in t_+. Hence, $t_{+\mathrm{app}}$ characterises the water transport through the membrane rather than its permselectivity, which is a function of the true transport numbers in the membrane and solution.

If the transport properties of an unknown membrane are to be characterised, it is recommended to start the measurement from the electrical conductivity κ and diffusion permeability $P(P^*)$ and then apply eqn. (10) to calculate the true transport numbers (the method described in Case 3). Very often this is sufficient to characterise the membrane permselectivity.[36] However, if the true transport number of the counter-ion found by this method is not sufficiently high (<0.95 at 1 M) or/and it is of interest to characterise the membrane at higher concentrations (>2 M), the first method [the measurements of κ, $P(P^*)$ and $t_{+\mathrm{app}}$ and application of eqns. (1) and (9)] should be used. The water transport number can be found in this way. Every time that eqns. (9) and (10) are applied, it should be taken into account that these equations are approximate and valid for ion-exchange membranes of medium water capacity.

Appendix 1

To determine $g = 1 + \mathrm{d}(\ln y_\pm)/\mathrm{d}(\ln c_\mathrm{s})$, the data[7] on $g_\mathrm{m} = 1 + \mathrm{d}(\ln\ y_\pm)/\mathrm{d}(\ln m_\mathrm{s})$ as function of solution concentration were used, here m_s and $\gamma_\pm$ are the molality and the molal activity coefficient, respectively. The relation between g and g_m may be written as follows:[7]

$$g = \frac{g_\mathrm{m}}{1 - c_\mathrm{s}\bar{V}_\mathrm{s}}$$

where $\bar{V}_\mathrm{s}$ is the partial molal volume of the electrolyte.

To evaluate $\bar{V}_\mathrm{s}$, the values 17.42, 19.60 and 22.73 (mL mol^{-1} of NaCl), respectively, for 0.1, 1.0 and 4.0 M NaCl solutions are taken from Stewart and Graydon's paper.[5]

Appendix 2

A list of symbols and acronyms is given in Table 4.

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