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Counterion transport numbers of poly(acrylic acid)-grafted porous ion-exchange membranes as determined from current step measurements

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Abstract—The effect of an electric current on the concentration polarization of the external bathing solutions and the permselectivity of poly(acrylic acid)-grafted porous ion-exchange membranes has been studied. The experimental approach is based on the transient behavior of the total electric potential drop through the membrane cell when a current step is imposed from external nonpolarizable electrodes. When this voltage drop is recorded as a function of time, a transition time characteristic of each membrane system is obtained. From this time, the counterion transport number for the salt solution ($KCl-H_2O$) in the membrane can be obtained. The theoretical modeling is based on the time-dependent Nernst–Planck equations. It is shown that the transport number, and then the membrane permselectivity, decreases with the electric current. The higher the membrane grafting ratio and the lower the external salt concentration the larger the permselectivity changes. © 1997 Elsevier Science Ltd

Key words: Poly(acrylic acid)-grafted porous ion-exchange membranes, current step measurements, counterion transport number.

INTRODUCTION

Variable permeability membranes (VPM) are polymeric membranes very sensitive to the chemical environment. Their permeability can be controlled by changing the pH and/or the salt concentration or by applying an external electric field [1–6]. This behavior can arise, *eg* from the reversible protonation of suitable groups of a polyacid in the membrane, which in turn leads to the reversible contraction and extension of the polyacid chains with the subsequent opening or closing of pores. Recently [7, 8], we have developed a VPM based on a porous polyvinylidene fluoride (PVDF) filter which was graft modified with poly(acrylic acid) (PAA) chains by radiation-induced grafting utilizing electron beam techniques. The resulting PVDF/PAA membrane is a VPM whose mechanical permeability to an aqueous salt solution changed by several orders of magnitude when varying the pH and/or the salt concentration of the external solution. In addition, the VPM is able to show permselectivity properties, as determined from the measurements of the potential of a cell with transference [7]. In order to employ this porous ion-exchange membrane in practical applications, however, it is necessary to consider also its permselectivity in current-driven processes. In particular, we wish to determine the effect of an electric current on the concentration polarization of the external bathing solutions and the permselectivity of poly(acrylic acid)-grafted porous ion-exchange membrane. We consider the counterion transport number, since this membrane parameter is the basis of any definition of membrane permselectivity. Although there is an increasing interest in VPM, basic studies on the ion permselectivity of VPM in current-driven processes are lacking [1].

The experimental approach followed is based on the transient behavior of the total electric potential drop through the membrane cell when a current step is imposed. PVDF/PAA membranes with different grafting ratios (percentage increase in weight [7]), $G = 9$, 16, 38 and 85%, are considered. The solution concentrations employed are 10, 50 and 100 mM

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KCl. Steady-state currents in the range 0.4–17 mA are forced through the membrane. It is shown that when the total voltage drop V through the membrane cell is recorded as a function of time t, a transition time τ characteristic of each membrane system is readily obtained from the resulting $V(t)$ curve.

The theoretical modeling is based on the time-dependent Nernst–Planck equations [9]. When an electric current is forced through the charged membrane, concentration polarization effects appear in the diffusion boundary layers (DBL) flanking the membrane [10] and then ion transport must be considered in both regions the membrane and the depleted DBL. The solution of the Nernst–Planck equations gives the ion concentrations in the membrane system as a function of time. Introduction of the experimentally obtained transition times into this solution gives the counterion transport number for each salt concentration as a function of the membrane grafting ratio and the electric current. It is shown that this transport number changes with the electric field, the changes being very marked for the higher grafting ratios and the lower external salt concentrations.

EXPERIMENTAL

A four-electrode potentiostat (Sycopel Scientific Ministat 80) was used in a galvanostatic mode to make electric current steps of selected magnitude. As indicated in Fig. 1, the resulting potential across the membrane was recorded using Luggin capillaries with Ag/AgCl electrodes. The potentiostat was controlled by a computer via 16-bit AD converter card (Quatech DAQ-16). This AD converter was used both for feeding the step into the cell and for acquiring the data. To lower the noise, each point was taken as an average of 10 acquired points.

The cell described in Fig. 1 was made of perspex and consisted of two equally sized compartments (28 cm^3), which were in contact through the membrane to be studied. The exposed membrane area was 0.071 cm^2. The current electrodes were Ag/AgCl electrodes made by electrolyzing a silver plate as an anode in 0.1 M HCl solution with an electric current density of 0.4 mA cm^{-2}. To avoid the precipitation of colloidal silver chloride possibly formed at current electrodes onto the studied membrane, the actual electrode compartments were separated from the membrane compartments with the aid of porous microfiltration membranes (Millipore DV) with 0.65 μm nominal pore size.

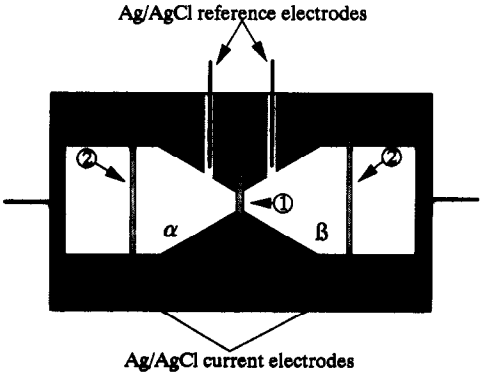

Fig. 1. Experimental set-up of the cell used for the current step measurements. The numbers denote the VPM (1) and the porous membranes (2) separating the electrode chambers from the membrane cell.

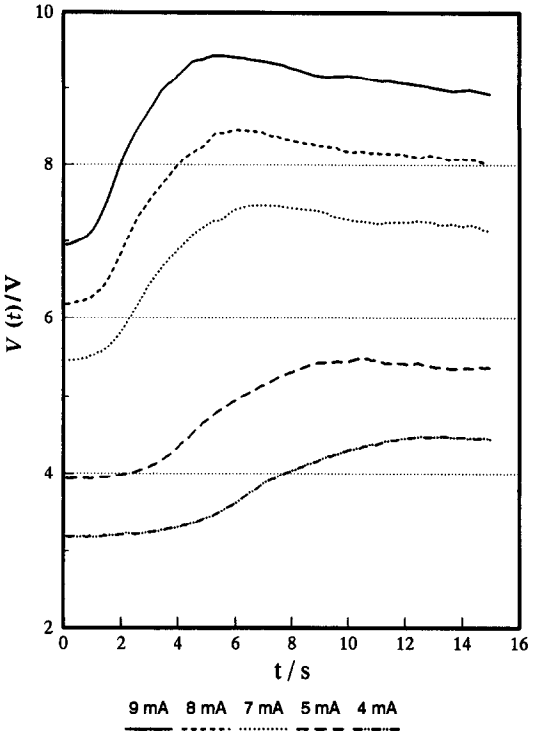

Fig. 2. Electric potential curves $V(t)$ for $G = 9\%$, $c_{0,DBL} = 50$ mM KCl and currents steps $I = 4$, 5, 7, 8 and 9 mA.

The VPM used was a hydrophobic PVDF porous filter (Millipore) of 5.0 μm nominal pore size graft modified with PAA chains by radiation induced grafting. Experimental information on membrane structure and characterization can be found elsewhere [7].

RESULTS

Figure 2 shows a typical set of the curves $V(t)$ *vs* t obtained for the grafted membranes. It corresponds to a membrane with $G = 9\%$, $c_{0,DBL} = 50$ mM KCl and current steps giving the steady state currents 4, 5, 7, 8 and 9 mA. Note that all curves show an electrical resistance at initial times $t \ll \tau$ of some 800 Ω, where τ is the inflection point in the curves. This resistance should be ascribed to the unpolarized (membrane + adjacent solution layers) system.

Table 1.
Transition time τ for different current steps I, grafting ratios G and concentrations $c_{0,DBL}$

	10 mM			50 mM			100 mM		
G (%)	I (mA)	τ (s)	$I\tau^{1/2}$	I (mA)	τ (s)	$I\tau^{1/2}$	I (mA)	τ (s)	$I\tau^{1/2}$
9	0.40	6.05	0.98	4.00	6.40	10.1	10.0	7.40	27.2
	0.50	4.10	1.01	5.00	4.30	10.4	15.0	3.65	28.7
	1.00	0.98	0.99	7.00	2.40	10.8	17.0	2.60	27.4
	1.30	0.65	1.05	8.00	1.85	10.9	20.0	2.05	28.6
	1.80	0.43	1.18	9.00	1.65	11.6			
16	0.50	3.25	0.90	2.00	11.8	6.87	5.00	8.85	14.9
	0.70	1.83	0.95	3.00	5.10	6.77	7.00	5.25	16.0
	0.90	1.18	0.98	4.00	3.25	7.21	10.0	2.90	17.0
	1.00	1.00	1.00	5.00	2.15	7.33	15.0	1.55	18.7
	1.10	0.98	1.09	7.00	1.40	8.28			
	1.20	0.81	1.08						
	1.30	0.69	1.08						
38	0.25	9.80	0.78	2.00	7.20	5.37	4.00	11.5	13.6
	0.30	6.55	0.77	3.00	3.15	5.32	7.00	4.50	14.8
	0.40	3.95	0.79	5.00	1.35	5.81	10.0	2.20	14.8
	0.60	2.00	0.85	7.00	0.80	6.26	12.0	1.65	15.4
	0.70	1.65	0.90	9.00	0.50	6.36	17.0	0.90	16.1
	1.00	0.95	0.95						
85	0.20	11.5	0.68	2.00	7.95	5.64	4.00	9.75	12.5
	0.30	5.70	0.72	3.00	3.90	5.92	7.00	3.55	13.2
	0.40	3.50	0.75	5.00	1.70	6.52	10.0	2.10	14.5
	0.60	1.80	0.80	7.00	1.00	7.00	12.0	1.75	15.9
	0.80	1.10	0.84	9.00	0.65	7.25	17.0	1.00	17.0

Table 1 gives the electric current I (steady-state value) vs time τ (average value for two experiments with current flowing in opposite directions) when $G = 9$, 16, 38 and 85% for each concentration 10, 50 and 100 mM KCl. Table 2 presents the transport numbers obtained from quasiequilibrium emf measurements in a cell with transference using a rotating diffusion cell [7]. Finally, Table 3 gives I vs time τ when a Nafion® 117 membrane is placed instead of the VPM in the cell of Fig. 1.

THEORY

Figure 3 shows a schematic view of the membrane system. Transport is assumed to occur along the axial direction, so that the ion concentrations c_+ and c_- are functions of position x and time t. Subscripts + and − indicate potassium and chloride ions. Activity coefficient effects are ignored. The membrane extends from $x = 0$ to $x = d$ and is flanked by two diffusion boundary layers of thickness δ [10–14]. The electric current I flows in the positive x direction. The fixed charge concentration in the membrane is denoted by c_M.

Table 2.
Counterion transport numbers $t_{+,M}$ obtained from the measurement of potential in a cell with transference [7] for different concentrations $c_{0,DBL}$

	10 mM	50 mM	100 mM
G (%)	$t_{+,M}$	$t_{+,M}$	$t_{+,M}$
8	0.88	0.71	0.65
12	0.90	0.75	0.71
36	0.96	0.87	0.80
93	0.91	0.88	0.82

The theory aims at obtaining the counterion (potassium) transport number of the VPM from the experimental V vs t curves. The inflection point in these curves (see Fig. 2) is interpreted as the time τ required to polarize the membrane system (membrane plus DBLs) so that the concentration in the DBL side of the DBL/membrane interface at $x = 0$ is practically zero [13, 14]. First, we present a simplified theory to evaluate τ [13]. Second, we relate the counterion transport numbers in the membrane phase and in the bathing solution to this time. Finally, the transport number in the membrane is calculated from the comparison between the theoretical expression for τ and the measured values.

For the sake of simplicity, we consider an ideal system where the DBL extends from $x = 0-$ to $x \to -\infty$, and the membrane extends from $x = 0+$ to $x \to +\infty$. We ignore the other membrane/solution interface (see Fig. 3), because we assume that the transient behavior in Fig. 2 is dictated by the low salt concentration values reached at $x = 0$ when the electric current flows through the system [12–14]. The severe concentration polarization effects which occur in the DBLs in current-driven processes with ion-exchange membranes are well documented in

Table 3.
Transition time τ of the Nafion® 117 membrane for different current steps I and concentrations $c_{0,DBL}$

Membrane	10 mM			50 mM			100 mM		
	I (mA)	τ (s)	$I\tau^{1/2}$	I (mA)	τ (s)	$I\tau^{1/2}$	I (mA)	τ (s)	$I\tau^{1/2}$
Nafion® 117	0.20	7.65	0.55	1.00	7.80	2.8	2.00	7.80	5.6
	0.30	3.45	0.56	3.00	1.00	3.0	3.00	3.45	5.6
	0.40	1.95	0.56	4.00	0.50	2.8	5.00	1.25	5.6
	0.80	0.50	0.56	5.00	0.40	3.2	10.0	0.31	5.6
	1.20	0.23	0.58				12.0	0.24	5.9
	1.80	0.10	0.57						

Lakshminarayanaiah's [13] and Hellfferich's [14] books.

The basic equations ruling the problem are the local electroneutrality assumption:

$$c_+(x,t) = c_-(x,t) + c_M \quad x > 0 \tag{1}$$

$$c_+(x,t) = c_-(x,t) \quad x < 0 \tag{2}$$

the Nernst–Planck equations for the ion fluxes written in the form [11]:

$$J_+(x,t) = -A_\alpha D_{\pm,\alpha}\frac{\partial c_+}{\partial x} + t_{+,\alpha} \times \frac{I}{F}, \quad \alpha = \text{DBL, M} \tag{3.a}$$

$$J_-(x,t) = -A_\alpha D_{\pm,\alpha}\frac{\partial c_-}{\partial x} - t_{-,\alpha}\frac{I}{F}, \quad \alpha = \text{DBL, M} \tag{3.b}$$

and the continuity equations

$$\frac{\partial c_i}{\partial t} \approx D_{\pm,\alpha}\frac{\partial^2 c_i}{\partial x^2}, \quad i = +,-, \tag{4}$$

where the phase subscript $\alpha(\alpha = \text{DBL, M})$ takes into account that the effective area for ion transport, A, the salt diffusion coefficients $D_\pm$ (defined as in [11]) and the transport numbers t_+ and t_- take different values in the DBL and in the membrane. Note that in order to obtain equation (4) from equation (3), the diffusion coefficients and the transport numbers are assumed to be approximately independent of position in both phases.

At the membrane/solution interface, we impose the conditions of the Donnan equilibrium [9, 13, 14]:

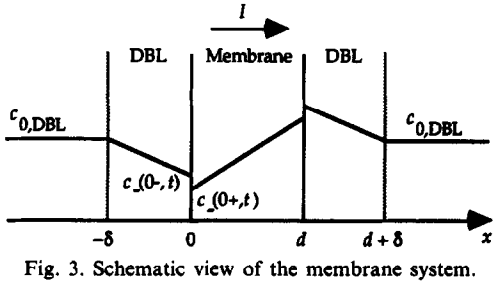

Fig. 3. Schematic view of the membrane system.

$$\frac{c_-(0+,t)}{c_-(0-,t)} = \frac{c_+(0-,t)}{c_+(0-,t)} \tag{5}$$

and the continuity of the coion flux:

$$-A_{DBL}D_{\pm,DBL}\left(\frac{\partial c_-}{\partial x}\right)_{x=0-} - t_{-,DBL} \times \frac{I}{F} = -t_{-,M}\frac{I}{F} \tag{6}$$

The omission of the diffusional contribution to the coion flux in the membrane phase [see equation (6)] is justified by the following order of magnitude analysis. First, we estimate the migration term as

$$t_{-,M}\frac{I}{F} \approx 2 \times 10^{-8}\ \text{mol s}^{-1}, \tag{7}$$

where we have introduced an average value $t_{-,M} \approx 0.2$ from emf measurements in a cell with transference [7]. Then, we evaluate the membrane diffusional contribution to the coion flux (see Fig. 3) as:

$$A_M D_{-,M}\frac{dc_-}{dx} \approx A_M D_{-,M}\frac{c_-(d-,\tau) - c_-(0+,\tau)}{d} \approx A_M D_{-,M}\frac{-(c_M/2) + [(c_M/2)^2 + (2c_{0,DBL})^2]^{1/2} - 0}{d} \approx 5 \times 10^{-9}\ \text{mol s}^{-1}, \tag{8}$$

where the Donnan equilibrium relationships [13] have been used for the interfacial concentrations. We have estimated $d \approx 10^{-2}$ cm, $A_M \approx A_{DBL}/2$, $c_M \approx 0.1$ M [7] and introduced the upper bound values $D_- \approx 10^{-5}\ \text{cm}^2\ \text{s}^{-1}$ and $c_{0,DBL} \approx 0.1$ M. Comparison of equations (7) and (8) shows that, as a first approximation, the diffusional contribution to the coion flux in the membrane phase can be neglected.

Note that the electroosmotic flow has also been neglected in equation (3). According to the estimations of equations (7) and (8), the migration term is the dominant contribution to the coion flux. The electroosmotic term would be of the same order of magnitude as the migration term if $c_{0,M}V_M \approx 2 \times 10^{-8}$ mol s^{-1}, where V_M is the volume flow through the membrane. Now, the coion concentration in the membrane ($c_{0,M}$) can be calculated by means of the Donnan equation substituting $c_M \approx 10^{-4}\ \text{mol cm}^{-3}$ [8] in equation (11b). This leads to $c_{0,M} \approx 10^{-6}\ \text{mol cm}^{-3}$

for $c_{0,DBL} = 10\ mM = 10^{-5}$ mol cm^{-3} and $c_{0,M} \approx 6 \times 10^{-5}$ mol cm^{-3} for $c_{0,DBL} = 100\ mM = 10^{-4}$ mol cm^{-3}. Therefore, the electroosmotic term might be compared with the migration term only if $V_M \approx (2 \times 10^{-8}\ mol\ s^{-1})/c_{0,M} \approx 2 \times 10^{-3}\ cm^3\ s^{-1} \approx 7\ mL\ h^{-1}$, where we have introduced the intermediate value $c_{0,M} \approx 10^{-5}$ mol cm^{-3}. This volume flow is relatively high for our experimental system and we believe thus that the electroosmotic flow, though not completely negligible at the highest experimental currents, is likely to be smaller than the other contributions to the ionic flux.

Equation (4) is solved by the Laplace transform method [15]. The resulting equation is:

$$s\tilde{c}_- - c_{0,\alpha} = D_{\pm,\alpha} \frac{d^2\tilde{c}_-}{dx^2}, \quad \alpha = DBL, M, \tag{9}$$

whose solution can be written as:

$$\tilde{c}_- = \frac{c_{0,\alpha}}{s} + B_\alpha \exp(-(s/D_{\pm,\alpha})^{1/2}|x|), \quad \alpha = DBL, M, \tag{10}$$

where s is the Laplace variable, B_{DBL} and B_M are undetermined constants and the following boundary and initial conditions have been employed:

$$c_-(-\infty, t) \rightarrow c_{0,DBL} \tag{11.a}$$

$$c_-(+\infty, t) \rightarrow c_{0,M} \equiv -\frac{c_M}{2} + \left[\left(\frac{c_M}{2}\right)^2 + c_{0,DBL}^2\right]^{1/2} \tag{11.b}$$

$$c_-(x,0) = c_{0,DBL}, \quad x < 0 \tag{12.a}$$

$$c_-(x,0) = c_{0,M}, \quad x > 0. \tag{12.b}$$

Here $c_{0,DBL}$ is the electrolyte (KCl) concentration in the bulk solutions.

The constant B_{DBL} can now be determined by substitution of equation (10) into the Laplace transform of equation (6):

$$-A_{DBL}\, D_{\pm,DBL} \left(d\tilde{c}_- dx\right)_{x=0-} - t_{-,DBL} \times \frac{I}{F}\frac{1}{s} = -t_{-,M}\frac{I}{F}\frac{1}{s}, \tag{13}$$

with the result

$$B_{DBL} = -\frac{(t_{-,DBL} - t_{-,M})I}{F\, A_{DBL}\, D_{\pm,DBL}^{1/2}} \frac{1}{s^{3/2}}. \tag{14}$$

The concentration at $x = 0-$ obtained from the inverse Laplace transform of equation (10) is:

$$c_-(0-,t) = c_{0,DBL} - \frac{(t_{-,DBL} - t_{-,M})I}{F\, A_{DBL}\, D_{\pm,DBL}^{1/2}} \frac{2}{\pi^{1/2}} t^{1/2}. \tag{15}$$

and the time τ required to reach the condition $c_-(0-,\tau) \approx 0$ is given by:

$$c_{0,DBL} = \frac{(t_{-,DBL} - t_{-,M})I}{F\, A_{DBL}\, D_{\pm,DBL}^{1/2}} \frac{2}{\pi^{1/2}} \tau_2^{1/2}. \tag{16}$$

Lakshminarayanaiah [13] has reviewed the application of chronopotentiometric methods to the determination of transport numbers in membranes. Sand [16] derived as early as 1901 an equation formally similar to equation (16) for the concentration changes in the vicinity of an electrode during electrolysis. Block and Kitchener found that τ varied as $I^{-1/2}$ for a number of membranes [17]. Bobreshova *et al.* [18] have given a similar procedure to that presented here to obtain transport numbers from chronopotentiometric measurements.

From equation (16), the counterion transport number can be written as:

$$t_{+,M} = t_{+,DBL} + \frac{1}{2} F\, A_{DBL}\, (\pi\, D_{\pm,DBL})^{1/2} \frac{c_{0,DBL}}{I\, \tau^{1/2}}. \tag{17}$$

In our case, $t_{+,DBL} \approx 0.49$ and $D_{\pm,DBL} \approx 2 \times 10^{-5}$ cm^2 s^{-1} (infinite dilution values for an aqueous KCl solution [19]) and $A_{DBL} \approx 0.071$ cm^2. Equation (17) gives the changes of $t_{+,M}$ with the electric current I for each concentration $c_{0,DBL}$.

The assumption of infinite DBL should not influence very much the calculated counterion transport numbers: the inverse Laplace transform of equation (10) gives exponential and error functions whose characteristic decay length is $\delta = 2(D_{\pm,DBL}t)^{1/2}$. For $t = \tau \approx 5$ s, then $\delta = 2 \times 10^{-2}$ cm, which is much smaller than the typical cell dimensions. Therefore, we see that (i) the theoretical model incorporates implicitly the characteristic length of the problem and (ii) this length is negligible when compared with the axial dimensions of the bathing solution. A previous study [17] has shown that the assumption of infinite DBL led to transient times in rough agreement with experiments.

RESULTS AND DISCUSSION

Table 1 gives the values of I and τ for each concentration and grafting ratio. From these values and equation (17), the counterion transport numbers are readily obtained. Three sets of experimental data corresponding to concentrations 10, 50 and 100 mM KCl are reported in Fig. 4. The abscissa value is taken as $I/c_{0,DBL}$, a term proportional to the electric field within the membrane.

The membrane with $G = 9\%$ exhibits some selectivity, since $t_{+,M} \approx 0.75$ for $c_{0,DBL} = 10$ mM. The membrane with G = 85% is clearly selective to the counterion, with $t_{+,M}$ decreasing from 0.85 for $c_{0,DBL} = 10$ mM to 0.65 for $c_{0,DBL} = 100$ mM. We see that the counterion transport number decreases significantly with the electric current. It should also be observed that the transport numbers measured in the presence of an electric current are systematically

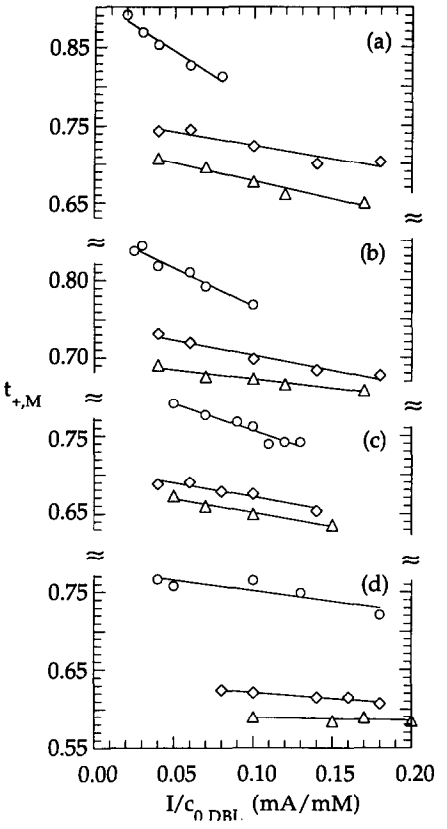

Fig. 4. Counterion transport number $t_{+,M}$ *vs* $I/c_{0,DBL}$ for concentrations $c_{0,DBL} = 10$ mM (○), 50 mM (◇) and 100 mM (△), and grafting ratios $G = 85\%$ (a), 38% (b), 16% (c) and 9% (d).

lower than those resulting from the measurement of potential in a cell with transference [7] (see Table 2). This fact has been previously reported for ungrafted charged membranes [20–22] and is due to the concentration polarization effects in the membrane and the DBLs caused by the passage of the electric current [13, 14, 20, 21]. The existing methods used to measure transport numbers in charged membranes were analyzed theoretically in terms of the Nernst–Planck equations in previous studies [20, 21] and modifications of the Hittorf and emf methods which give approximated relations for the calculation of effective transport numbers were suggested.

In order to compare the changes observed in the permselectivity of the porous ion-exchange membrane with those characteristic of typical ion-exchange membranes, an obvious possibility is to carry out control experiments with ungrafted membranes. This has been done here for a Nafion® 117 membrane and the results obtained are shown in Table 3. Comparison of the experimental results in Table 1 with those in Table 3 shows that the distribution of the $(I\tau^{1/2})$ experimental values appears to be wider for the grafted membranes than for the Nafion® 117 membrane (the only exception corresponds to the case $c_{0,DBL} = 50$ mM, where the above trend is not so clear). This behavior becomes more apparent when high grafting ratios are considered: when $c_{0,DBL} = 10$ mM, the maximum relative change of $(I\tau^{1/2})$ with I is *ca.* 22% for the $G = 85\%$ membrane, but only 4% for the Nafion® 117 membrane. Even though a straightforward application of the theoretical model to the Nafion® 117 membrane is not possible because some of the assumptions introduced here (*eg* membrane homogeneity and Donnan equilibrium) could not be valid [22, 23] for this membrane, the above results seem to indicate that the permselectivity changes with current are very important for the porous ion-exchange membrane.

The physical mechanisms giving rise to the observed permselectivity changes are not completely understood yet. Although these permselectivity changes could be caused by the concentration polarization of the bathing solutions at high currents [13, 14], other mechanisms due to changes in the conformation of the PAA chains of the VPM might also be operative [1, 2, 8]. A significant elastic deformation of the PAA chains along the axial coordinate [24] is not likely to occur for the relatively weak electric fields E within the membrane, which should be of the order of 100 V cm^{-1} from membrane conductivity data [7] and Fig. 2. A more plausible mechanism may be the local changes in the ionic concentrations within the membrane caused by the passage of the electric current [1, 2]. These concentrations dictate both the dissociation equilibrium of the PAA groups and the conformation of the PAA chains along the radial coordinate *via* the electrostatic screening effects [2, 8] and it is well known that the thermodynamic state of the PAA chains influence significantly the membrane selectivity [1, 2, 8].

CONCLUSIONS

We have determined the counterion transport numbers of a poly(acrylic acid)-grafted membrane from current step measurements and applied the time-dependent Nernst–Planck equations to the experimental results. It has been shown that the membrane has permselectivity properties and can thus be considered as a porous ion-exchange membrane. The counterion transport number decreases with the electric current, especially for high membrane grafting ratios and low salt concentrations. These results, together with previous permeability studies [7, 8], show that by selecting the appropriate grafting ratio it is possible to develop membranes which are both porous enough to allow a hydrodynamic flow through in pressure-driven processes and selective enough to exhibit ion-exchange properties in current-driven processes.

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