Electrochemical Characterization of Porous Membranes with Adsorbed Charges from Convective Diffusion and Counter-Current Electrolysis Experiments[1]

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Received January 18, 1995

Abstract—Experimental methods for the electrochemical characterization of porous membranes with adsorbed charges are described. Convective diffusion and counter-current electrolysis experiments permit the determination of the membrane constant (effective membrane area/membrane thickness) and the ion transport numbers, respectively. The first one is a key parameter in electrokinetic experiments, while the latter provides information on the membrane selectivity. A simple, theoretical model based on the Nernst–Planck equation and the Langmuir isotherm can be used to describe the coupling between ion adsorption and transport.

INTRODUCTION

Counter-current electrolysis in a porous membrane is based on the simultaneous effects of diffusion, migration, and convection on the transport of ions. The convective flow opposes electrical migration and diffusion. This approach is not suitable for any reasonable, industrial-scale application yet. However, in the last 15 years, some important new developments have occurred which have opened the way to exploiting these ideas. Porous membranes with well defined characteristics have become available, and the solution of the Nernst–Planck equations with convective terms has been thoroughly studied [1, 2].

Counter-current electrolysis has been extensively studied for separating small cations [3], but recent studies have shown that it can also be effectively applied in the separation of proteins [4]. The electrophoretic movement of a charged particle against a moving reference frame (the forced convection through the porous membrane) results in a separation according to the charge and viscous drag. Furthermore, the technique has proved to be useful in the determination of the diffusion coefficients and the effective charge numbers of a polydisperse polyelectrolyte [5]. In all these studies, the porous membrane was considered non-charged. However, the important effects caused by the adsorption of ions on the surface of the polymer membrane matrix in the limit of low electrolyte concentration have been emphasized recently [6–9].

In this paper we aim to review the currently available methods for the electrochemical characterization of porous membranes which make use of counter-current electrolysis [10, 11]. However, other, classical methods will also be mentioned [12]. Though studies dealing with the electrochemical characterization of ion-exchange membranes are quite abundant in the literature [13, 14], there appears to be very few that focus on porous membranes. Even though the industrial use of ion-exchange membranes could justify this situation, it must be emphasized that the characterization of porous membranes is also relevant, both from the fundamental point of view (the coupling of ion adsorption and transport leads to interesting phenomena) and from the practical one (the adsorbed charge can affect ion transport in the limit of low electrolyte concentration).

Our first step is the study of the membrane constant A/d (effective membrane area/membrane thickness). This is a key parameter in electrokinetic measurements [15]. If an electrokinetic phenomenon is studied by measuring a force with respect to a flux or vice versa, the ratio of pore area to pore length A/L must be known. In practice, this means that the membrane constant is to be determined in a separate measurement. However, if the electrokinetic phenomenon is investigated by measuring one force (flux) with respect to another force (flux), the membrane constant does not appear in the equation. Thus, A/d must be known when electrokinetic phenomenon such as second streaming current ($I/\Delta p$, $\Delta V = 0$), second electro-osmotic flow ($J_m/\Delta V$, $\Delta p = 0$), second streaming potential ($\Delta V/J_m$, $I = 0$) or second osmotic pressure ($\Delta p/I$, $J_m = 0$) are dealt with. However, the membrane constant needs not to be known, e.g., in the case of streaming potential ($\Delta V/\Delta p$, $I = 0$), electro-osmotic pressure ($\Delta V/\Delta p$, $J_m = 0$) and electro-osmotic flow (J_m/I, $\Delta p = 0$).

Here, the membrane constant will be determined from convective diffusion experiments [10]. Under open-circuit conditions, a convective flow will be forced through the membrane. This convective flow is

imposed by introducing water into one of the compartments (the small one), which, in turn, decreases the solution concentration in that compartment. The associated salt diffusion will eventually lead to a steady state in which the salt flux is zero. Then, a plot of logarithm of the bulk concentrations ratio vs. convective flow through the membrane will allow us to determine the membrane constant from the obtained slope. However, we will see here that the charges adsorbed on the walls of the membrane pores can have important effects on this determination at low concentrations.

A second step in the electrochemical characterization of the membrane is the determination of the transport numbers. Transport numbers in membranes have classically been measured either by Hittorf electrolysis or by potentiometric experiments [13]. The Hittorf method, as originally thought, allows for the determination of ion transport numbers in a membrane separating two electrolyte solutions of the same concentration when an external electric field is present. However, concentration polarization always develops in practice, and the measurements obtained from the Hittorf method must then be corrected to take this effect into account. This correction, as well as the generalization of the method to allow for concentration differences between the bulk solutions, requires either an estimation of the salt flux [16], or the solution of the Nernst–Planck equations [17]. Therefore, experimental conditions avoiding the development of concentration gradients are often preferred.

In this paper, the development of concentration differences between the two bulk solutions (occurring in the Hittorf method as previously stated) is avoided by using a convective flow opposed to the electric current [11]. However, ionic concentrations are not uniform throughout the membrane and the local (position-dependent) migrational transport numbers must be computed from the solution of the Nernst–Planck equations. The analysis of the migrational transport numbers as a function of bulk solution concentration poses an additional difficulty in the problem. Since the pore–wall charge in these membranes is due to ion adsorption, the fixed charge concentration must also be determined as a function of bulk solution concentration.

The adsorbed charge concentration can be estimated from both the measurements of the membrane constant at low concentrations and the transport numbers (and Donnan theory). As a final step, we will compare these two estimations with the adsorbed charge calculated from streaming potential measurements. Also, the potentiometric transport numbers determined from emf measurements at zero electric current will be reported and compared with the results of the modified Hittorf method presented here.

Note that our problem involves the simultaneous gradients of three physical magnitudes—concentration, pressure, and electric potential—through the membrane. Then, the interpretation of the experimental results and the modeling of the transport problem are considerably difficult. Analytic and semi-analytic models [18] have usually been concerned with only two of the above gradients and cannot be applied to our problem. This is also the case of the experimental studies; see, e.g., [6–8, 12]. The main objective of the paper is to provide simple equations for the membrane constant and the transport number that can be of interest to the researcher, at least in the particular situation dealt with here. In this context, the Teorell–Meyers–Sievers theory will be preferred, and more refined theories like the capillary space-charge model [6–8] will be used only when necessary (a comparative study of the validity of these two theories can be found in [19]).

EXPERIMENTAL

Apparatus. The membrane cell made of Perspex glass is depicted in Fig. 1. The exposed membrane area was a circle of ca. 0.28 cm^2. The volume of the α-compartment was small (1.2 ml) compared to that of the β-compartment (1000 ml). The convective flow V^c was controlled by a peristaltic pump P_2 (Ismatec IPN). The solution in the α-compartment was circulated through a conductivity cell K (Radiometer CDC 114) by a pump P_1 with circulation rate $15V^c$. The volume of the conductivity cell, together with its tubing, was ca. 175 ml. The conductivity was measured with a Philips PW 9527 conductivity meter and monitored continuously by an x–t recorder (BBC Goerz Metrawatt SE120). The conductivity cell was maintained at 25°C temperature by mounting it in the thermostated bath (Haake FE2). The temperature of the membrane cell was controlled with a heat exchanger in the β-compartment. As a current supply, we used Amel 549 potentiostat for low currents and LAB 522 regulated power supply for large currents. The current was measured with an auxiliary current meter in both cases (Keithley 485 picoammeter for currents below 2 mA and Fluke 8012A Digital multimeter above it.)

The porous Ag/AgCl cathode with large surface area was prepared using the thermal-electrolytic method described in [20]. The electrode was assembled in the end of α-compartment. It was separated from the rest of the compartment using a microfiltration membrane and a nylon net to shield the electrode against the rotating magnetic flea, and to avoid adsorption of colloidal AgCl on the membrane under study. A silver wire with a 2 mm diameter was used as an anode in the β-compartment. The AgCl layer was removed from the anode surface mechanically when needed.

Materials. Durapore WLP (Millipore) filters with a mean pore diameter of 0.1 μm and porosity of ca. 70% were used as porous membranes. The same type of membrane was also used as a separator for the cathode. The membranes were soaked for 24 h in the electrolyte solution before measurements. The solutions were prepared by weighting using pro analysis grade KCl (Merck) and Milli-Q water (Waters).

Membrane constant measurements. The porous membrane was soaked in Milli-Q water for at least 48 h

before use. Once the cell was assembled, the α-compartment was carefully filled by feeding Milli-Q water. The β-compartment was then filled with the working solution already thermostated to 25°C. The experiment was started by selecting the pumping rate and starting the monitoring of the conductivity. The system was in a steady state when the conductivity of the α-compartment had reached a constant value. This value was also used to calculate the steady state concentration of the α-side. The next pumping rate was then selected. The pumping rates varied from 8.4 to 0.39 ml/h. The conductivity measurement was calibrated after each experiment by feeding standard solutions to the α-compartment. The β-compartment was empty in these experiments. Fresh solutions were changed to the β-compartment twice a day. For each combination of membrane and β-side solution, a new porous membrane was prepared.

Transport number measurements. For a start, the whole cell was filled with KCl solution and all air was removed from the tubing. The initial conductivity was recorded and the pumping rate was selected before pump P_2 was started. The electric current was controlled manually until the steady state with the initial conductivity in the α-compartment was reached, i.e., the conductivities in the α- and β-compartments remained equal for at least two hours. The convective flow rate V^c was measured in every single experiment by weighting the water reservoir for feeding. The solution in β-compartment was replaced continuously by fresh solution. The conductivity was checked after each experiment by pumping the solution from β-compartment through the conductivity cell to the α-compartment. The next pumping rate was then selected. For each solution concentration, a new piece of membrane was used.

THEORY

Figure 2 shows a sketch of the membrane system under study. Transport is considered in the x direction through a homogeneous membrane that extends from $x = 0$ to d and two diffusion boundary layers (DBLs) lying from $x = -\delta$ to 0 and from $x = d$ to $d + \delta$. The concentration of potassium chloride in the α-compartment is c^α, while that in the β-compartment is c^β. The membrane is negatively charged because of adsorption of chloride ions, and it will be assumed that the concentration X of adsorbed charges is uniform throughout the membrane [7, 8].

The basic equations describing this problem are the steady-state Nernst–Planck equations [21]

$$J_k = -AD_k\left[\frac{dc_k}{dx} + (-1)^{k+1}c_k\frac{d\psi}{dx}\right] + c_kV^c, \quad (1a)$$

$$k = 1, 2, \quad -\delta < x < 0, \quad d < x < d + \delta,$$

$$J_k = -A\overline{D}_k\left[\frac{d\overline{c}_k}{dx} + (-1)^{k+1}\overline{c}_k\frac{d\overline{\psi}}{dx}\right] + \overline{c}_kV^c, \quad (1b)$$
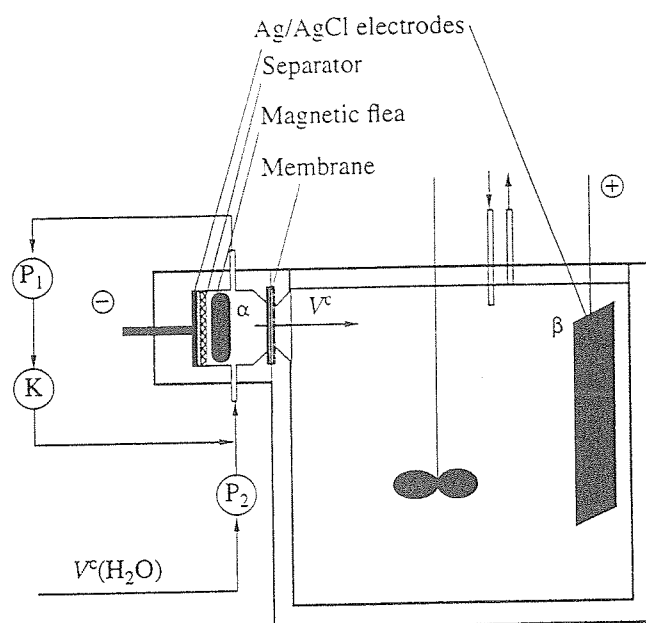
$$k = 1, 2, \quad 0 < x < d,$$

Fig. 1. Schematic drawing of the experimental cell.

and the assumption of local electroneutrality

$$c_1(x) = c_2(x) \equiv c(x), \quad -\delta < x < 0, \quad d < x < d + \delta, (2a)$$

$$\overline{c_1(x)} = \overline{c_2(x)} + X, \quad 0 < x < d. \quad (2b)$$

Here J_k, D_k, and c_k denote the flux, diffusion coefficient, and local molar concentration of species k, respectively. The effective membrane area is denoted by A. Subscript 1 refers to cations (counterions) and subscript 2 to anions (coions). Overbars denote magnitudes corresponding to membrane phase. The symbol c without subscript is used to denote the ionic concentration in the DBLs. The (convective) solvent flow is represented by V^c, and according to our sign convention, this flow will be positive (Fig. 2). The electric potential in RT/F units is represented by ψ, where F is Faraday constant, R the gas constant, and T the absolute temperature.

The experimental conditions impose a zero cation flux

$$J_1 = 0, \quad (3a)$$

and therefore, the anion flux accounts for the electric current

$$I = -FJ_2. \quad (3b)$$

Since the electric current is opposed to the convective flow (see Fig. 2), I is negative.

The concentration profiles in the DBLs can be easily computed by eliminating the migration terms from (2) and making use of (3). In particular, at the DBL side of the membrane–DBL interfaces, we have [2, 11]

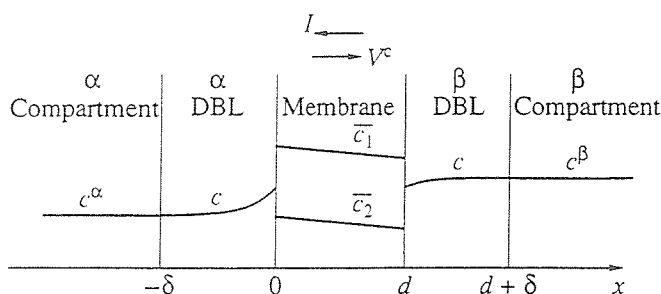$$c(0) = c^\alpha e^{Pe} + c_I(1 - e^{Pe}) \quad (4a)$$

Fig. 2. Sketch of the membrane system showing the concentration profile.

and

$$c(d) = c^{\beta}e^{-Pe} + c_I(1 - e^{-Pe}), \qquad (4b)$$

where $Pe = \dot{V}^c \delta / AD$ is the Peclet number, $D \equiv 2D_1D_2/(D_1 + D_2)$ is the salt diffusion coefficient, $c_I \equiv -t_1^b I/F\dot{V}^c$, and $t_1^b \equiv D_1/(D_1 + D_2)$ is the migrational transport number of the cation in the bulk solutions. In (4) we have imposed the boundary conditions $c(-\delta) = c^{\alpha}$ and $c(d + \delta) = c^{\beta}$ (see Fig. 2).

According to the well-known Donnan equilibrium [13], the coion concentrations at the membrane side of the membrane–DBL interfaces are given by

$$\overline{c_2(0)} = -\frac{X}{2} + \left[\left(\frac{X}{2}\right)^2 + c(0)^2\right]^{1/2} \qquad (5a)$$

and

$$\overline{c_2(d)} = -\frac{X}{2} + \left[\left(\frac{X}{2}\right)^2 + c(d)^2\right]^{1/2}. \qquad (5b)$$

Finally, the integration of (1) to (3) in the membrane leads to

$$\ln\left(\frac{c^{\beta} + c_I(e^{Pe} - 1)}{c^{\alpha} + c_I(e^{-Pe} - 1)}\right) + \left(1 + \frac{2\overline{c_I}}{X}\right)\ln\left(\frac{1 - \overline{c_I}/c_1(d)}{1 - \overline{c_I}/c_2(0)}\right)$$

$$= \frac{\dot{V}^c}{A}\left[\frac{2\delta}{D} + \frac{d}{\overline{D}}\left(1 + \frac{\overline{c_I}}{X}\right)\right], \qquad (6)$$

Table 1. Measured values of parameter $M \equiv A/[(2\delta/D) + (d/\overline{D})]$

c^{β}, mM	M, ml/h
1.00	0.395
10.0	0.372
100	0.363

where $\overline{c_I} \equiv -\overline{D_1}I/F\dot{V}^c(\overline{D_1} + \overline{D_2})$ and $\overline{D} \equiv 2\overline{D_1}\,\overline{D_2}/(\overline{D_1} + \overline{D_2})$.

Note that the above equations cannot be applied to the determination of the potentiometric transport number, because the equations (3) do not hold then. However, the transport equations describing this experimental situation can be solved following the same procedure described above [9, 22].

RESULTS AND DISCUSSION

(a) *Determination of the membrane constant.* According to (6), a plot of $\ln(c^{\beta}/c^{\alpha})$ against convective flow $\dot{V}^c$ under zero electric current conditions (i.e., $c_I = 0$ and $\overline{c_I} = 0$) should be linear and the reciprocal of the slope would be given by

$$M = \frac{A}{(2\delta/D) + (d/\overline{D})}. \qquad (7)$$

Table 1 shows the values obtained. However, since c^{β} is constant in our experimental set-up, (6) implies that c^{α} must be very small at large convective flows (i.e., a few ml/h). This implies, in turn, that the Debye length in the membrane phase increases and can eventually invade a significant part of the pore area. In these cases, the homogeneous membrane model (which is valid only for low pore–wall charge concentrations in the limits of very small and very large values of the ratio (pore radius/Debye length) [19]) should be replaced by the space charge model, where the membrane is modeled as a stack of cylindrical charged pores [6–8, 10, 19, 23].

(b) *Simplified determination of the "Hittorf" transport number.* In the determination of the transport number, $c^{\alpha} = c^{\beta} = c_0$ and thus we can assume that there is no salt diffusion through the membrane system. Furthermore, since convection pushes solution of concentration c_0 into the membrane system and pulls from it solution of this same concentration, the convective flux term could be expressed as $c_0\dot{V}^c$. Finally, migration through the membrane system should take place with an effective transport number t_1^s. Thus, the cation flux can be expressed as

$$J_1 \approx t_1^s\frac{I}{F} + c_0\dot{V}^c = 0, \qquad (8)$$

which gives the definition of the effective cation transport number of the membrane system as

$$t_1^s \equiv -\frac{Fc_0\dot{V}^c}{I} = t_1^b\frac{c_0}{c_I}. \qquad (9)$$

Now, integration of the Nernst–Planck equations over the membrane system [after elimination of the electric field term by adding J_1 times c_2 and J_2 times c_1, and making use of (3)] allow us to obtain the parameter c_I
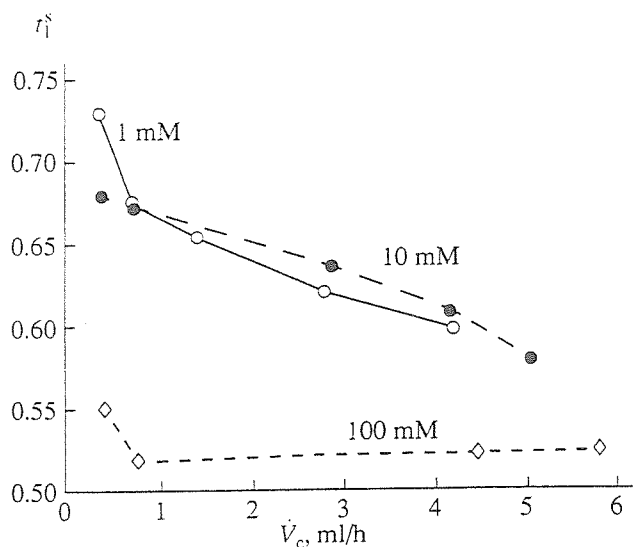
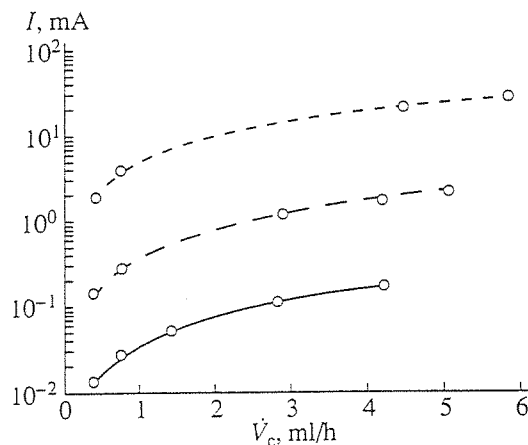Fig. 3. Effective transport number of the membrane system t_1^s vs. the convective flow $\dot{V}^c$.

Fig. 4. Logarithm plot of the electric current I vs. the convective flow $\dot{V}^c$ for different values of the bulk solution concentration c_0 : (—) 1.00 mM, (– – –) 10.0 mM and (- - -) 100 mM. The circles are experimental values and the curves have been obtained from (6) with $X = 1$, 10, and 15 mM, respectively. Other parameters are $d/\delta = 8$ and $t_1^b = 0.51$.

in terms of average ion concentrations, and then (9) transforms to

$$t_1^s = t_1^b \frac{c_0}{\bar{c}_1} = t_1^b \frac{\displaystyle c_0 \int_{-\delta}^{d+\delta} c_1 dx}{\displaystyle \int_{-\delta}^{d+\delta} c_1 c_2 dx}. \qquad (10)$$

Figure 3 shows the transport numbers obtained from (9). The marked dependence of t_1^s on the convective flow is likely to come from the diffusional contribution to the cation flux, which was neglected in (8), and therefore a more accurate determination procedure should be considered.

(c) *Determination of the "Hittorf" transport number.* In order to compare theory and experiment, we need to know several parameters. The diffusion coefficients in the solution phase are taken from the literature. [Note that t_1^b can also be obtained from experiments with large convective flow and electric current, since we know from theory that $c_1 \simeq c_0$ in this case; see (9).] The diffusion coefficients in the membrane phase are assumed to be the same as in solution phase because the membrane porosity is high and the adsorbed charge concentration is small. The membrane constant is determined as described in Section (a).

The experimental results can now be fitted to (6) with the adsorbed charge concentration X and the ratio $\delta/(d + 2\delta)$ as fitting parameters. [Note that the concentrations $\overline{c_2(0)}$ and $\overline{c_2(d)}$ are obtained from (5).] Figure 4 shows the experimental results for $c_0 = 1$, 10, and

100 mM together with the theoretical fitting curves. The values used for X are 1, 10, and 15 mM, respectively, and the value 0.1 has been taken for the ratio $\delta/(d + 2\delta)$. The value of t_1^b is estimated as 0.51 from the data corresponding to $c_0 = 100$ mM and higher convective flows. It must be said, however, that the fitting curve is not very sensitive to the values of $\delta/(d + 2\delta)$ and X. Figure 4 shows excellent agreement between theory and experiment, but a similar agreement can be obtained even when $\delta/(d + 2\delta)$ and X differ in 10–20% from the above values.

The values of the adsorbed charge concentration X can be related to the bulk solution concentration c_0 with a Langmuir-type adsorption isotherm

$$X = X_m \frac{kc_0}{1 + kc_0}, \qquad (11)$$

with maximum adsorbed charge concentration $X_m = 16$ mM and $k = 0.14$ mM^{-1}.

Finally, the migrational transport numbers of the counterion inside the membrane are computed as [24]

$$t_1^m(x) \equiv \frac{D_1 c_1(x)}{D_1 c_1(x) + D_2 c_2(x)} = \frac{t_1^b c_1(x)}{t_1^b c_1(x) + (1 - t_1^b)c_2(x)}. \qquad (12)$$

The migrational transport number in (12) is a position-dependent parameter, and reaches its two extreme values at the two ends of the membrane, $t_1^m(0)$ and $t_1^m(d)$. However, the difference between these two values goes to zero in the limit of $\dot{V}^c \longrightarrow 0$ (and $I \longrightarrow 0$) [11].

Table 2. Effective transport number of the membrane system t_1^s ($\dot{V}^c = 0.39$ ml/h) and transport numbers in the membrane t_1^m ($\dot{V}^c \longrightarrow 0$) at different concentrations

c_0, mM	t_1^s	t_1^m
1.00	0.73	0.73
10.0	0.68	0.69
100	0.55	0.55

Table 3. Potentiometric transport numbers at different concentrations (from [12])

c_0, mM	t_1^m
0.10	0.840
0.51	0.748
2.5	0.600

Table 4. Adsorbed charge concentrations obtained from streaming potential measurements (from [12])

c^β, mM	X, mM
0.10	0.115
1.00	2.58
10.0	5.22
100	14.9

Table 2 shows the comparison of the t_1^s values obtained from the experimental data for $\dot{V}^c = 0.39$ ml/h with the t_1^m values in the limit of $\dot{V}^c \longrightarrow 0$. The agreement observed suggests that the simplified approach in the previous section can be used for the determination of transport numbers. In fact, it can be shown from theory that t_1^s reduces to t_1^m when $X < c_0$ and both the electric current and the convective flow tend to zero. However, when extremely low convective flows are used, the measurements become much more time consuming and considerably less accurate.

(*d*) *Potentiometric transport numbers and adsorbed charge concentration determined from streaming potential measurements.* Finally, it is in order to compare the results of this modified Hittorf method with the potentiometric transport numbers. Table 3 shows the values obtained in [12]. Taking into account the important differences between the two experimental procedures, the agreement obtained is reasonable.

Also, it is interesting to compare the adsorbed charge concentrations obtained here from the fitting of theory to experimental data in Fig. 4 with those result-

ing from streaming potential measurements. Again, Table 4 shows the values of $X = -2q_2/Fr_0$ obtained from the surface charge densities q_2 and pore radius r_0 reported in [12]. The comparison shows that only the order of magnitude of the adsorbed charge concentration can be considered reliable. Similar discrepancies between the values of adsorbed charge concentration obtained from different experimental methods have been reported in the literature [8].

CONCLUSION

The methods currently available (convective diffusion and counter-current electrolysis) for the electrochemical characterization of porous membranes with adsorbed charges have been described. Special emphasis has been put upon the membrane constant and the ion transport numbers. The coupling between ion adsorption and ion transport through the membrane has been described satisfactorily in terms of the Langmuir isotherm and the Nernst–Planck equations.

ACKNOWLEDGMENTS

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