

A new method for determining transport numbers of charged membranes from convective diffusion experiments ^{*}

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Abstract

We present a new method for determining transport numbers of charged membranes from convective diffusion experiments. The development of concentration differences in the two bulk solutions due to the passage of an electric current (which is characteristic of conventional Hittorf methods in membrane systems) is avoided by using a convective flow opposed to the electric current. A theoretical modelling based on the Nernst–Planck equations gives both the membrane charge density and the transport number from the experimental data. The proposed method is suited for membranes porous enough to allow a hydrodynamic flow through and avoids the need for an accurate chemical analysis, since only conductometric determinations are required.

1. Introduction

Transport numbers of ions in charged membranes have been measured classically either by the Hittorf method or by a potentiometric method based on the analysis of a cell with transference [1]. In fact, the Hittorf method is a definition of the transport number in electrolyte solutions, but in a membrane system its application depends on the possibility of estimating the diffusional contribution due to the concentration polarization [2]. One method presented utilizing a stack of membranes avoids the problem of concentration polarization, but it is tedious to use in practice [3].

The fact that the Hittorf method is based on the effect of an external electric field while the potentiometric method involves a concentration difference makes the Hittorf method more interesting, e.g. for the case of electrically modulated variable permeability membranes [4]. This kind of membrane changes its transport properties in the presence of external electric fields, usually because of the changes in membrane

porosity. This naturally means that the determination of the transport number for these membranes must be based on the Hittorf method instead of the potentiometric method.

In this article we present a new method where the development of concentration differences between the two bulk solutions (occurring when the conventional Hittorf method is applied to a membrane system) is avoided by using a convective flow opposed to the electric current. This method is suitable for the determination of transport numbers provided that the membrane is porous enough to allow a hydrodynamic flow through. Since the ionic concentrations are not uniform throughout the membrane system, the local transport numbers must be computed from a numerical solution of the Nernst–Planck equations.

We verify the feasibility of the method developed for the case of a charged porous microfiltration membrane whose charges are due to the adsorption of anions on the membrane pore wall. This adds to the difficulty of the problem because the charge density on the pore walls is concentration dependent, which results in changes in the transport numbers. It will be shown that both the charge density and the transport number can be evaluated from the experimental data by means of the present method.

^{*} Dedicated to Professor Richard P. Buck on occasion of his 65th birthday.

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2. Experimental

2.1. Apparatus

Figure 1 depicts the membrane cell made of Perspex used in this work. The exposed membrane area was ca. 0.28 cm^2 . The volume of the α compartment was small (1.2 ml) compared with that of the β compartment (1000 ml). The convective flow \dot{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 $15\dot{V}^c$. The volume of the conductivity cell together with its tubing was ca. 1.5 ml. The conductivity was measured with a Philips PW9527 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 thermostatted bath (Haake FE2). The temperature of the membrane cell was controlled using a heat exchanger made of glass in the β compartment. As a current supply we used an Amel 549 potentiostat for low currents and LAB522 regulated power supply for large currents. The current was measured with auxiliary current meters in both cases (Keithley 485 picoammeter for currents smaller than 2 mA and Fluke 8012A digital multimeter for currents greater than 2 mA).

The porous Ag/AgCl cathode with a large surface area was prepared using the following thermal-electrolytic method [5]. A perforated silver plate ($30 \text{ mm} \times 30 \text{ mm} \times 0.5 \text{ mm}$) was covered with a 1 mm thick layer of Ag_2O . The coverage was dried in 90°C and reduced by raising the temperature at a slow rate (over 4 h) to

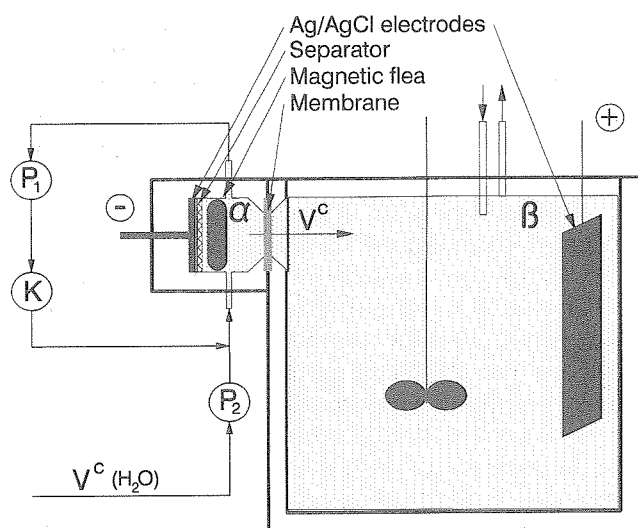


Fig. 1. Schematic drawing of the experimental cell.

450°C . As a result, a uniform layer of highly porous silver was obtained. Finally, the electrode was anodized with 50 mA current for 2 h in 1 M HCl aqueous solution. Anodizing was repeated afterwards when needed (i.e. after some 30–50 mA h use).

The electrode was assembled in the end of the 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 migration and adsorption of colloidal AgCl on the membrane under study. A 2 mm diameter silver wire was used as an anode in the β compartment. The AgCl layer was removed from the anode surface mechanically when needed. The solution in the β compartment was stirred with a glass propeller.

2.2. Materials

The porous membrane used in this work was Durapore VVLP (Millipore) with mean pore diameter of $0.1 \mu\text{m}$ and porosity of ca. 70%. 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 under study before measurements were carried out. The solutions were prepared by weighing using pro analysis grade KCl (Merck) and Milli-Q water (Millipore). The HCl (p.a. Merck) was used as supplied and Ag_2O (BDH) was thoroughly washed with Milli-Q water to ensure the removal of water-soluble impurities before use.

2.3. Measuring procedure

At the beginning of each experiment, the whole cell was filled with aqueous 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 switched on. 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, resulting in the same concentrations, for at least 2 h. In this situation the convective flow counterbalances the migrational flux, except for some small diffusional contribution. This gives a rough estimate for the transport number simply as a ratio of convective flux and electric current divided by the Faraday constant.

The convective flow rate \dot{V}^c was measured in a single experiment by weighing. The solution in the β compartment was continuously replaced by fresh solution. The conductivity in the β compartment was checked before and after each experiment. The next pumping rate was then selected. For each solution concentration a new piece of membrane was used.

3. Theory

Figure 2 shows a sketch of the membrane system under study. Transport is considered in the x direction through a 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 membrane is bathed by two bulk solutions with the same concentration c_0 of potassium chloride. The membrane is negatively charged owing to adsorption of chloride ions, and it will be assumed that the concentration X of adsorbed charges is uniform throughout the membrane [6–8].

The basic equations describing this problem are the steady state Nernst–Planck equations [9]

$$j_k = -D_k \left[\frac{dc_k}{dx} + (-1)^{k+1} c_k \frac{d\psi}{dx} \right] + c_k v, \quad k = 1, 2 \quad (1)$$

and the assumption of local electroneutrality

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

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

Here j_k , D_k and c_k denote the flux density, diffusion coefficient, and local molar concentration of species k respectively. Subscript 1 refers to cations (counterions) and subscript 2 to anions (coions). Note that the symbol c without subscript is used to denote the ionic concentration in the DBLs. The bulk solution velocity is represented by v , and according to our sign convention this velocity will be positive (see Fig. 2). The electric potential (in RT/F units) is represented by ψ , where F is Faraday's constant, R the gas constant, and T the absolute temperature. The diffusion coefficients are assumed to be constant throughout the whole membrane system because of the high membrane porosity.

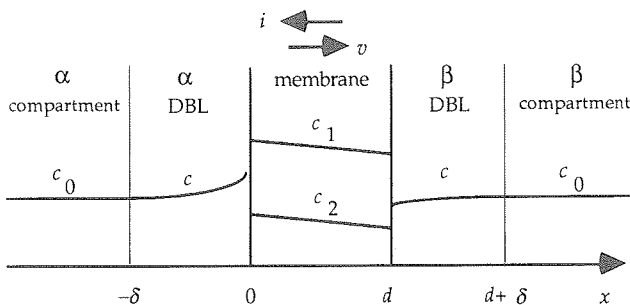


Fig. 2. Sketch of the membrane system showing the concentration profile.

The experimental conditions impose a zero cation flux

$$j_1 = 0 \quad (3a)$$

and therefore the anion flux accounts for the total electric current density

$$i = -Fj_2 \quad (3b)$$

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

The concentration profiles in the DBLs are then given by [10,11]

$$c(x) = -\frac{t_1^b i}{Fv} + \left(c_0 + \frac{t_1^b i}{Fv} \right) \exp \left[\frac{v(x + \delta)}{D} \right], \quad -\delta < x < 0 \quad (4a)$$

and

$$c(x) = -\frac{t_1^b i}{Fv} + \left(c_0 + \frac{t_1^b i}{Fv} \right) \exp \left[-\frac{v(d + \delta - x)}{D} \right], \quad d < x < d + \delta \quad (4b)$$

where $t_1^b \equiv D_1/(D_1 + D_2)$ is the migrational transport number of the cation in the bulk solutions, and $D \equiv 2D_1D_2/(D_1 + D_2)$ is the salt diffusion coefficient. Thus, at the DBL side of the membrane DBL interfaces we have

$$c(0) = c_i + (c_0 - c_i) e^{Pe} \approx c_0 - c_i Pe = c_0 + \frac{i\delta}{2FD_2} \quad (5a) = c_0 \left(1 + \frac{i\delta}{2FD_2 c_0} \right)$$

and

$$c(d) = c_i + (c_0 - c_i) e^{-Pe} \approx c_0 + c_i Pe = c_0 - \frac{i\delta}{2FD_2} \quad (5b) = c_0 \left(1 - \frac{i\delta}{2FD_2 c_0} \right)$$

where $Pe \equiv v\delta/D$ is the Péclet number and $c_i \equiv t_1^b i/Fv$. In eqns. (4) we have imposed the boundary conditions $c(-\delta) = c(d + \delta) = c_0$ (see Fig. 2).

Equations (5a) and (5b) indicate that the salt concentration will become zero at the corresponding membrane surface at high enough current densities. Thus, a limiting current can be defined for this system [10]. However, this limiting current is higher than that without convective flow, and the membrane system will operate in the underlimiting current regime [11].

According to the well-known Donnan equilibrium [1], the ionic concentrations and the electric potential are discontinuous at the membrane|DBL interfaces, and the concentrations $c_2(0)$ and $c_2(d)$ at the membrane side of the membrane|DBL interfaces are related to those at the DBL side through the equations

$$c_1(0)c_2(0) = [c_2(0) + X]c_2(0) = c(0)^2 \quad (6a)$$

and

$$c_1(d)c_2(d) = [c_2(d) + X]c_2(d) = c(d)^2 \quad (6b)$$

Equations (6a) and (6b) are used as boundary conditions for the integration of eqns. (1)–(3) over the membrane. This integration leads to the following relationship between $c(0)$ and $c_2(d)$:

$$\frac{c_2(d) + X \left[\frac{c_2(d) - c_i}{c_2(0) - c_i} \right]^{1+2c_i/X}}{c_2(0) + X \left[\frac{c_2(0) - c_i}{c_2(0) - c_i} \right]} = \exp \left[2 \text{Pe} \frac{d}{\delta} \left(1 + \frac{c_i}{X} \right) \right] \quad (7)$$

Since $c(-\delta) = c(d + \delta) = c_0$, the concentration gradients are expected to be small. There are three possible cases to be considered: (i) absence of concentration gradients, (ii) negative concentration gradients in the DBLs and positive in the membrane, and (iii) positive concentration gradients in the DBLs and negative in the membrane. It is easy to see from Eqs. (1)–(3) that case (i) will occur when $i = 0$ and $v = 0$. Further, Eq. (5a) suggests that c_i must be very similar to c_0 when $\text{Pe} \gg 1$, in order to keep $c(0)$ at a reasonable value. This implies that case (i) will also approximately occur under very large convective flows and electric current densities (since $c_i \equiv -t_1^b i / Fv$ must be kept close to c_0) [11]. However, there will still be non-zero concentration gradients, because eqns. (5a)–(6b) could not be fulfilled otherwise.

It can be seen from eqns. (1)–(3) that case (ii) requires $c_0 < c_i < c_2(x)$, which cannot happen in our system because the membrane has negative charge. On the contrary case (iii) requires $c_0 > c_i > c_2(x)$, which is very plausible, and then we conclude that this is the case of interest here.

4. Results and discussion

In order to compare theory and experiment, we need to relate the convective flow \dot{V}^c and the electric current I to the bulk solution velocity v and the electric current density i respectively. If A denotes the effective membrane area, these relationships are simply $\dot{V}^c = Av$ and $I = Ai$. Thus, the theoretical parameter c_i is obtained as

$$c_i = -\frac{t_1^b i}{Fv} = -\frac{t_1^b I}{F\dot{V}^c} \quad (8)$$

Table 1. Measured values of the membrane constant $AD/(d + 2\delta)$

c_0/mM	$AD/(d + 2\delta)$ (ml h ⁻¹)
1.00	0.395
10.0	0.378
100	0.349

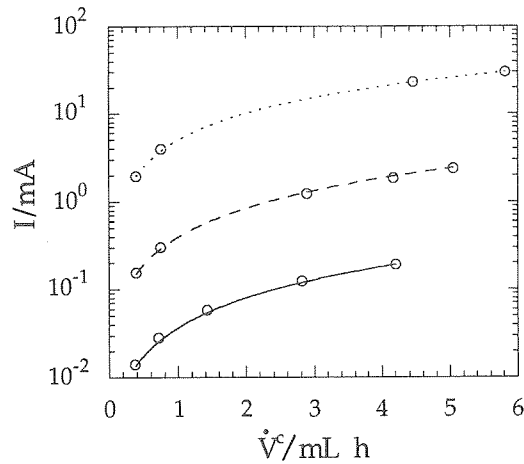


Fig. 3. Logarithmic plot of the electric current I vs. the convective flow \dot{V}^c for different values of the bulk solution concentration c_0 : —, 1.00 mM; ---, 10.0 mM; ·····, 100 mM. \circ , experimental values; the curves have been obtained from Eq. (7) with $X = 1$ mM, 8 mM, and 15 mM respectively. Other parameters are $d/\delta = 8$ and $t_1^b = 0.51$.

where t_1^b can be deduced from experiments with large convective flow and electric currents, since we know from theory that $c_i \approx c_0$ in this case.

The other theoretical parameter is Péclet number $\text{Pe} \equiv v\delta/D$, which now takes the form $\text{Pe} \equiv \dot{V}^c\delta/AD$. The ratio $AD/(d + 2\delta)$ is accessible to experimental determination, but the relation between d and δ is not known either, and then a reasonable value must be introduced for the ratio $\delta/(d + 2\delta)$. In particular, we have estimated Pe as

$$\text{Pe} \equiv \frac{v\delta}{D} = \frac{\delta}{d + 2\delta} \frac{d + 2\delta}{AD} \dot{V}^c \approx 0.1 \frac{d + 2\delta}{AD} \dot{V}^c \quad (9)$$

The ratio $AD/(d + 2\delta)$ is determined in the same membrane cell by measuring the concentration change in the α compartment induced by a convective flow \dot{V}^c (in the absence of electric current and salt flux). Under these particular experimental conditions, the logarithm of the concentration ratio is proportional to the convective flow [12]:

$$\ln \frac{c^\beta}{c^\alpha} = \frac{d + 2\delta}{AD} \dot{V}^c \quad (10)$$

and the membrane parameter $AD/(d + 2\delta)$ can be obtained from the measurement of the concentration ratio. Table 1 shows the values obtained from eqn. (10) at $\dot{V}^c = 0.183$ ml h⁻¹.

The experimental results can now be fitted to eqn. (7) with the adsorbed charge concentration X as the only fitting parameter. (Note that the concentrations, $c_2(0)$ and $c_2(d)$ are obtained from eqns. (5a)–(6b).)

Figure 3 shows the experimental results for $c_0 = 1$ mM, 10 mM, and 100 mM together with the theoretical fitting curve. The values used for X are 1 mM, 8 mM and 15 mM respectively. 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 t_1^b and X . Figure 3 shows an excellent agreement between theory and experiment, but a reasonable agreement could also be obtained even when t_1^b and X differ by ca. 10% from the above values.

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

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

with $X_m = 23$ mM and $k = 0.046$ mM $^{-1}$.

Finally, the migrational transport numbers of the counterion inside the membrane can be computed as [13]

$$\begin{aligned} t_1^m(x) &\equiv \frac{D_1 c_1(x)}{D_1 c_1(x) + D_2 c_2(x)} \\ &= \frac{t_1^b c_1(x)}{t_1^b c_1(x) + (1 - t_1^b) c_2(x)} \end{aligned} \quad (12)$$

since we are assuming that the diffusion coefficients are constant throughout the whole membrane system (which is a good approximation here because of the large porosity and low concentration of adsorbed charges of the membranes employed). Figure 4 shows the values of $t_1^m(0)$ and $t_1^m(d)$ obtained from the con-

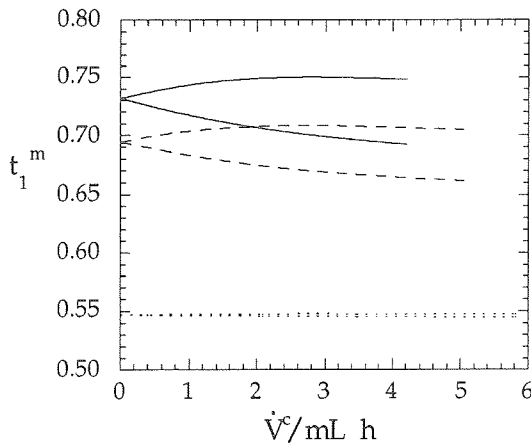


Fig. 4. Transport numbers at $x = 0$ (bottom curves) and $x = d$ (top curves) for the same concentrations and membrane system parameters in Fig. 3.

Table 2. Cation transport numbers at different concentrations determined from eqns. (13) and (15)

c_0 (mM)	t_1^m (eqn. (13))	t_1^m (eqn. (15))
1.00	0.73	0.73
10.0	0.69	0.68
100	0.55	0.55

centration profiles corresponding to the theoretical curves in Fig. 3. When the convective flow goes to zero, these two extreme values of the transport number converge to a value which is characteristic of the membrane charge and bulk solution concentration

$$t_1^m = t_1^b \frac{X/2 + [(X/2)^2 + c_0^2]^{1/2}}{(2t_1^b - 1)X/2 + [(X/2)^2 + c_0^2]^{1/2}} (\dot{V}^c \rightarrow 0) \quad (13)$$

At intermediate convective flows, $t_1^m(0)$ and $t_1^m(d)$ differ by a few hundredths owing to the diffusional contribution to ion transport. At large convective flows (larger than those dealt with here), they tend to converge again to the same value (see the curves corresponding to $c_0 = 100$ mM in Fig. 4).

Since the diffusional contribution is small at low convective flows, we can obtain a rough estimation of the cation transport number through the membrane system by neglecting the corresponding term in the flux equation for the cation and by using an integral transport number characterizing the whole membrane system:

$$j_1 \approx t_1^m \frac{i}{F} + c_0 v \quad (14)$$

Taking into account that $j_1 = 0$, the transport number can be obtained as (note that i is negative)

$$t_1^m \approx -\frac{Fc_0 v}{i} = -\frac{Fc_0 \dot{V}^c}{I} \quad (15)$$

Table 2 shows the transport numbers obtained from eqn. (15) for $\dot{V}^c = 0.39$ ml h $^{-1}$ as well as those resulting from eqn. (13). Agreement is excellent and thus eqn. (15) can be considered as a useful, very simple estimation of the transport number.

5. Conclusions

The advantages of the proposed method are as follows: (i) both the surface charge density of the pores and the transport number can be determined simultaneously; (ii) the transport number can be obtained with reference to a specified concentration, i.e. the bulk electrolyte concentration, by using the extrapolation

procedure based on the theoretical model; (iii) the method can be applied to both very dilute and moderately concentrated solutions; (iv) the need for an accurate chemical analysis is replaced here by a simple conductometric determination (we have only to be able to keep the same conductivity value in both compartments). The last of these is judged to be an important feature of the proposed method.

The shortcomings are that (at least in our experimental case) the model is not very sensitive to the adsorbed charge concentration. Also, the measuring procedure is relatively slow (typically one working day for each measurement) and requires some familiarity with convective flows. Finally, the charged membrane must be porous enough to allow a hydrodynamic flow through.

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