

The Effect of an Intermediate Layer on the Determination of Transport Numbers in Ion Exchange Membrane

P. FORSELL, K. KONTTURI and A. EKMAN

Helsinki University of Technology, Department of Chemistry, SF-02150 Espoo, Finland

When transport numbers of ions in ion exchange membranes are simultaneously measured, a compound membrane – a stack of closely packed membranes – is used. The effect of a boundary layer between identical membranes is considered. This boundary layer is a source of inhomogeneity but it is both theoretically and experimentally shown that it adapts itself to the transport in the ion exchange membrane provided that the layer is thin enough and the electric current does not exceed the limiting current.

When measuring transport across ion exchange membranes the effect of adjacent boundary layers must be considered. This is of special importance in the boundary between bulk solution and the membrane, but also the boundary layers between two identical membranes is a source of inhomogeneity and it can be regarded as a membrane itself. In a compound membrane¹ this boundary layer may have an effect on the transport. The purpose of this paper is to show that this effect becomes negligible provided that the thickness of this layer is small compared with the thickness of the ion exchange membranes and that the diffusion coefficients in these layers are at least of the same order of magnitude as in the membrane.

THEORY

Consider a stack of identical, closely packed ion exchange membranes. In practice the stack consists of several pairs of two kinds of layers M and W; layer M denotes an ion exchange membrane and layer W denotes the thin water layer between two layers M. Both kinds of layers contain ions which can be transported by diffusion and electric migration. Diffusion coefficients and transport numbers are different in these two different kinds of layers. Without electric current the state of equilibrium will be established and no gradients exist inside the layers. If constant electric current is applied the stationary state for all fluxes is reached. However, there will be concentration gradients inside the layers due to the differences in transport numbers.

Transport Equations

The transport of two counterions (1 and 2) and water in an ion exchange membrane can be represented using the membrane as the reference frame by eqns. (1), (2), (3).

$$J_1^M = J_1^{MD} + t_1^M I/z_1 F \quad (1)$$

$$J_2^M = J_2^{MD} + t_2^M I/z_2 F \quad (2)$$

$$J_{H_2O}^M = J_{H_2O}^{MD} + \tau_{H_2O}^M I/F \quad (3)$$

where J_i^M is the total flux of ion i , J_i^{MD} the diffusional flux of ion i , t_i^M the stoichiometric transport number of ion i , $\tau_{H_2O}^M$ is the reduced transport number of water (for the definition of transport numbers *c.f.* Haase²), I electric current density, z_i the charge number of ion i , and F Faraday's constant. The fluxes are related to the membrane and therefore $J_i^M = c_i^M(v_i^M - v_M) = c_i^M v_i^M$ ($v_M = 0$ since the membrane is immobile), where v_i^M is the velocity of ion i in a fixed coordinate system, *i.e.* in the membrane, and v_M is the velocity of the membrane.

The following very reasonable assumptions are made: The diffusion flux of water can be neglected $J_{H_2O}^{MD} = 0$; no co-ions are present in the membrane and that is why no bulk diffusion exists and $z_1 J_1^{MD} = -z_2 J_2^{MD}$; the condition of electroneutrality is valid and the charge density of the membrane is constant resulting in $z_1 dc_1^M/dx = -z_2 dc_2^M/dx$. Using these assumptions eqns. (1), (2) and (3) take the following forms:

$$J_1^M = -D^M \frac{dc_1^M}{dx} + t_1^M I/z_1 F \quad (4)$$

$$J_2^M = -D^M \frac{dc_2^M}{dx} + t_2^M I/z_2 F = +(z_1/z_2) D^M \frac{dc_1^M}{dx} + t_2^M I/z_2 F \quad (5)$$

$$J_{H_2O}^M = c_{H_2O}^M v_{H_2O}^M = \tau_{H_2O}^M I/F \quad (6)$$

where D^M is the interdiffusion coefficient of ions 1 and 2.

From eqns. (4) and (5) it can be clearly seen that there exists no convective water transport term in the equations. This is due to the reference frame which is now selected to be the membrane itself. This fact means that we can now neglect considering the effect of electro-osmotic water transport on transport numbers in the membrane. However, if another reference frames is used, such as the barycentric frame or the frame in which water is the reference substance, one must notice that the membrane will also have a transport number.

In the aqueous solution (W) the transport equations for ions 1 and 2 are

$$J_1^W = -r_{1c} \left(D_{11}^W \frac{dc_1^W}{dx} + D_{12}^W \frac{dc_2^W}{dx} \right) + t_1^W \frac{I}{z_1 F} + c_1 v_{H_2O}^W \quad (7)$$

$$J_2^W = -r_{2c} \left(D_{21}^W \frac{dc_1^W}{dx} + D_{22}^W \frac{dc_2^W}{dx} \right) + t_2^W \frac{I}{z_2 F} + c_2 v_{H_2O}^W \quad (8)$$

where the total flux of ion i , J_i^W , as well as the velocity of water $v_{H_2O}^W$ is in reference to a fixed coordinate system. D_{ij}^W is the diffusion coefficient, c_i^W the concentration of ion i , r_{ic} the stoichiometric coefficient of ion i , and t_i^W the transport number of ion i in water.

In many cases (*e.g.* in NaCl-KCl-H₂O system) we may assume as a first approximation that the cross-diffusion coefficients are small, *i.e.* D_{12} , $D_{21} < D_{11}$, D_{22} . As a second approximation we can assume that the convective terms in eqns. (7) and (8) are small; note

that in stationary state $J_{\text{H}_2\text{O}}^{\text{W}} = J_{\text{H}_2\text{O}}^{\text{M}} = c_{\text{H}_2\text{O}}^{\text{W}} v_{\text{H}_2\text{O}}^{\text{W}}$, and because $c_{\text{H}_2\text{O}}^{\text{W}}$ in the water phase is much greater than $c_{\text{H}_2\text{O}}$ in the membrane phase, $v_{\text{H}_2\text{O}}^{\text{W}}$ becomes relatively small. Thus we obtain eqns. (7) and (8) in the forms:

$$J_1^{\text{W}} = -r_{1c} D_1^{\text{W}} \frac{d c_1^{\text{W}}}{dx} + t_1^{\text{W}} \frac{I}{z_1 F} \quad (9)$$

$$J_2^{\text{W}} = -r_{2c} D_2^{\text{W}} \frac{d c_2^{\text{W}}}{dx} + t_2^{\text{W}} \frac{I}{z_2 F} \quad (10)$$

where D_1^{W} and D_2^{W} are the main diffusion coefficients. One must take into account that the above-mentioned assumptions are not necessary but they simplify the treatment.

Experimental Transport Number

In stationary state

$$J_i^{\text{M}} = J_i^{\text{W}} = \text{constant}; i=1, 2 \quad (11)$$

but concentration gradients and transport numbers may vary with respect to spacial coordinate. We designate the ratio of the gradients of ion i at certain points in layers M and W by α_i .

$$\alpha_i = \frac{d c_i^{\text{M}}}{dx} / \frac{d c_i^{\text{W}}}{dx}; i=1, 2 \quad (12)$$

The gradients in the membrane can be solved from eqns. (4), (5), (9) and (10) giving:

$$\frac{d c_i^{\text{M}}}{dx} = \frac{(t_i^{\text{W}} - t_i^{\text{M}})}{(D^{\text{M}} - \frac{r_{ic}}{\alpha_i} D_i^{\text{W}})} \cdot \frac{I}{z_i F}; i=1, 2 \quad (13)$$

By substituting eqn. (13) into eqns. (4), (5) we obtain

$$J_i^{\text{M}} = D^{\text{M}} \frac{(t_i^{\text{W}} - t_i^{\text{M}})}{(D^{\text{M}} - \frac{r_{ic}}{\alpha_i} D_i^{\text{W}})} \cdot \frac{I}{z_i F} + t_i^{\text{M}} \frac{I}{z_i F}; i=1, 2 \quad (14)$$

We define the experimental transport number in the membrane (θ_i^{M}) by

$$\theta_i^{\text{M}} = \frac{z_i F J_i^{\text{M}}}{I}; i=1, 2 \quad (15)$$

From eqn. (14) we obtain

$$\theta_i^{\text{M}} = \frac{\alpha_i D^{\text{M}}}{\alpha_i D^{\text{M}} - r_{ic} D_i^{\text{W}}} \cdot t_i^{\text{W}} + \frac{r_{ic} D_i^{\text{W}}}{r_{ic} D_i^{\text{W}} - \alpha_i D^{\text{M}}} \cdot t_i^{\text{M}}; i=1, 2 \quad (16)$$

As can be seen from eqn. (16) the experimental transport number is a sort of weighted mean of the two transport numbers t_i^{W} and t_i^{M} . Depending on the value of α_i the experimental

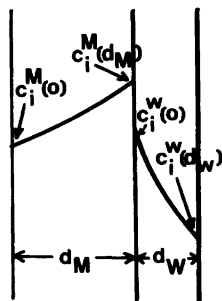


Fig. 1. Schematic concentration profiles of ion i inside the exchange membrane (thickness d_M) and the water layer (thickness d_W) and on the boundaries of these layers.

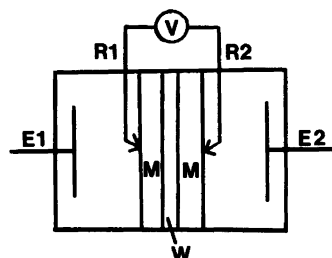


Fig. 2. Schematic description of the cell. M is the ion exchange membrane, W the porous membrane, R 1 and R 2 calomel electrodes, and E 1 and E 2 the electric current carrying electrodes. The bulk solutions consist of the same electrolytes as the equilibrating solutions except that the concentrations of bulk solutions are 0.1 mol dm^{-3} . V is an instrument for measuring the voltage drop.

transport number corresponds more or less closely to the transport number in the membrane t_i^M : the smaller α_i the smaller is the difference between t_i^M and θ_i^M .

Since the experimental transport number (θ_i^M) corresponds to the transport number in the membrane (t_i^M) only in the case where $\alpha_i \rightarrow 0$, we will now consider the value of the coefficient α_i . In Fig. 1 we can see schematical representations of concentration profiles during measurement.

According to the law of the mean for differential calculus there exist points inside the membrane and the water layer where

$$\alpha_i = \frac{d c_i^M}{dx} / \frac{d c_i^W}{dx} = \frac{c_i^M(d_M) - c_i^M(0)}{d_M} / \frac{c_i^W(d_W) - c_i^W(0)}{d_W} \quad (17)$$

The notations in eqn. (17) are clarified in Fig. 1. Assuming distribution equilibrium on the boundaries of the membrane and water layer we have

$$x_i^M(d_M) = \frac{c_i^M(d_M)}{c_1^M(d_M) + c_2^M(d_M)} = k_i \frac{c_i^W(0)}{c_1^W(0) + c_2^W(0)} = k_i x_i^W(0) \quad (18)$$

$$x_i^M(0) = \frac{c_i^M(0)}{c_1^M(0) + c_2^M(0)} = k_i \frac{c_i^W(d_W)}{c_1^W(d_W) + c_2^W(d_W)} = k_i x_i^W(d_W)$$

where k_i is the distribution ratio of ion i . Because the charge density of the membrane is constant, it follows that $c_1^M = c_1^M(d_M) + c_2^M(d_M) = c_1^M(0) + c_2^M(0)$.

Hence we obtain α_i in the form

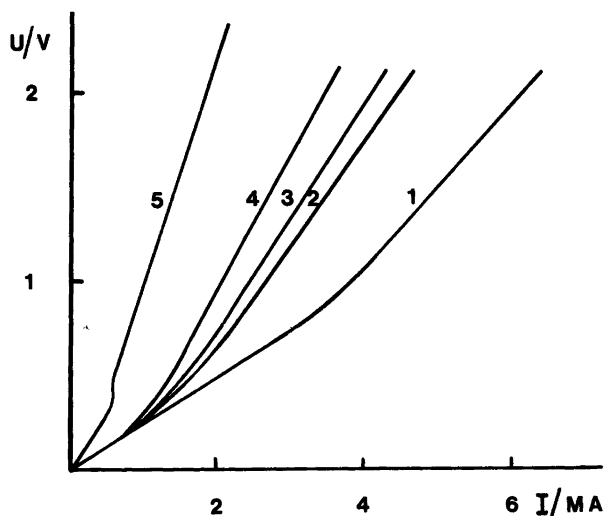


Fig. 3. Current-voltage curves in the system NaCl-H₂O, with one (1), two (2), three (3), four (4) and seven (5) porous membranes.

$$\alpha_i = \frac{[x_i^M(d_M) - x_i^M(0)] c_T^M}{[x_i^M(d_M) c_T^W(d_M) - x_i^M(0) c_T^W(0)] / k_i} \cdot \frac{d_W}{d_M} = \beta_i \frac{d_W}{d_M} \quad (19)$$

where $c_T^W(d_W) = c_1^W(d_W) + c_2^W(d_W)$ and $c_T^W(0) = c_1^W(0) + c_2^W(0)$.

The mole fractions x_i on the boundaries of the membrane and water layer are related by eqn. (18) and since the constant k_i is finite, β_i in eqn. (19) is bounded. Thus α_i approaches zero, when the ratio d_W/d_M approaches zero. Since the diffusion coefficients in water D_i^W are not smaller than the diffusion coefficient in the membrane, D^M , in eqn. (16) the experimental transport number, θ_i^M , approaches the transport number in the membrane, t_i^M , when the ratio $d_W/d_M \rightarrow 0$.

In practice this means that the water layer adapts itself so that the difference in transport numbers $t_i^M - t_i^W$ is compensated for by diffusion in the water layer. Because diffusion depends on the concentration gradients this compensation is possible at a certain value of electric current, which depends on the thickness of the water layer.

The Effect of the Thickness of the Water Layer

The relationship between the electric current and the thickness of the water layer is derived, in the case of monovalent ions using the following assumptions:

1. The flux of the co-ion is zero $\rightarrow J_1^W + J_2^W = I/F$
2. The total amount of ions is constant
3. The convective water flux can be neglected.

With the aid of Nernst-Planck equations the fluxes of the ions are

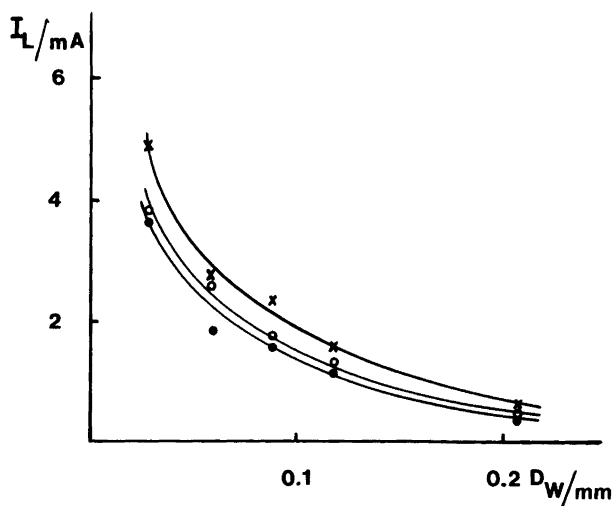


Fig. 4. The limiting current as a function of the thickness of the water layer in NaCl-(●), KCl-(×) and NaCl-KCl-H₂O (○).

$$-J_1^W = d_1^W \frac{dc_1^W}{dx} + c_1^W d_1^W \frac{F}{RT} \frac{d\phi}{dx} \quad (20)$$

$$-J_2^W = d_2^W \frac{dc_2^W}{dx} + c_2^W d_2^W \frac{F}{RT} \frac{d\phi}{dx} \quad (21)$$

$$0 = d_3^W \frac{dc_3^W}{dx} - c_3^W d_3^W \frac{F}{RT} \frac{d\phi}{dx} \quad (22)$$

where d_i^W is the diffusion coefficient of the ion i and ϕ electric potential. Eliminating $d\phi/dx$ from the eqns. (20)–(22) and using the condition of electroneutrality ($c_3 = c_1 + c_2$) integration gives the total concentration

$$c_3 = A - \frac{1}{2} \left(\frac{J_1^W}{d_1^W} + \frac{J_2^W}{d_2^W} \right) x \quad (23)$$

The integration constant A is determined by using the assumption 2 as follows:

$$n_3^W = \int_0^{d_w} A_w c_3(x) dx = V_w c_3^W(E) \quad (24)$$

where n_3^W is the total amount of coions in the water layer ($c_3^W = c_1^W + c_2^W$), A_w the surface area of the water layer, V_w the volume of the water layer, d_w the thickness of the water layer, $c_3^W(E)$ the equilibrium concentrations of the coions. Substituting eqn. (23) into eqn. (24) we obtain

$$A = c_3^W(E) + \frac{d_w}{4} \left(\frac{J_1^W}{d_1^W} + \frac{J_2^W}{d_2^W} \right)$$

and finally

$$c_3^W(x) = c_3^W(E) + \left(\frac{J_1^W}{d_1^W} + \frac{J_2^W}{d_2^W} \right) \left(\frac{d_w}{4} - \frac{x}{2} \right) \quad (25)$$

With the aid of eqns. (11), (4), and (5) and taking into account the small role of interdiffusion in ion exchange membrane compared with electric migration, eqn. (25) reduces to the form

$$c_3^W(x) = c_3^W(E) + \left(\frac{t_1^M}{d_1^W} + \frac{t_2^M}{d_2^W} \right) \left(\frac{d_w}{4} - \frac{x}{2} \right) \frac{I}{F} \quad (26)$$

When electric current density is increased the profile of the total concentration becomes steeper and, eventually, $c_3^W(dw) = 0$. This implies that the resistivity of the membrane system increases to infinity, and

$$I_L = \frac{4 c_3^W(E) F}{d_w \left(\frac{t_1^M}{d_1^W} + \frac{t_2^M}{d_2^W} \right)} \quad (27)$$

where I_L is called the limiting current. Eqn. (27) shows that the limiting current is inversely proportional to the thickness of the water layer, d_w . If we can show this functional dependence experimentally the assumption that diffusion compensates for the difference $t_1^M - t_1^W$ in the water layer is correct.

EXPERIMENTAL

To verify eqn. (27) experiments were done with the apparatus schematically shown in Fig. 2. Detailed description of the apparatus is presented in paper.³ The ion exchange membranes (Ionics AZL-389) were equilibrated in the following water solutions: 0.01 mol/dm³ NaCl, 0.01 mol/dm³ KCl, and 0.005 + 0.005 mol/dm³ NaCl + KCl. The water layer between the two identical ion exchange membranes consisted of porous membranes (Millipore SC with poresize 8 μm). The ion exchange membranes were packed together with porous membranes as shown in Fig. 2. Porous membranes were wetted with the equilibrating solutions while the total concentration of the bulk solutions was 0.1 mol/dm³ so as to prevent concentration polarization. The experiments were done with one to seven porous membranes.

To control the electric current through the membrane, a PAR 173 potentiostat connected to a PAR 175 universal programmer was used. The electric current was changed linearly as a function of time so slowly that a stationary state was virtually always attained. To obtain the limiting current the voltage drop over the membrane was measured with two identical calomel electrodes (Radiometer K 412). As can be seen from the polarization curve in Figure 3 when limiting current is reached the voltage drop changes rapidly indicating the increase in resistance over the membrane system. In the ideal case the resistance should exceed a very high value after reaching the limiting current. However, in practice, coion leak and stirring effects in the water layer diminish the resistance.

RESULTS

The measured limiting currents as a function of water layer thickness are presented in Fig. 4. It can be clearly seen that the function $I_L=f(1/d_w)$ has a shape of hyperbola as was predicted by eqn. (27).

DISCUSSION

According to Eqn. (9) the concentration gradient in the water layer depends on the electric current providing that the transport number in the membrane and in water are approximately constant. On the other hand, the concentration gradient and the thickness of the water layer determine the concentrations on the boundaries. Because the total amount of the electrolyte in the water layer is constant, there is a limiting value for the gradient and the electric current at the point where the concentration on the boundary becomes zero and the resistance approaches infinity. This limit should be inversely proportional to the thickness of the water layer. From Fig. 3 we can see that the resistance begins to increase at a electric current which is greater the thinner the water layer. However, the resistance does not increase infinitely since the system is not ideal. These experiments verify that the concentration gradients cause the water layer to adapt itself to the transport in the ion exchange membrane. Thus, the effect of the water layer can be neglected provided that layer is thin enough, and the electric current does not exceed the limiting current.

Acknowledgement. This research were financially supported by the Academy of Finland, and the Neste Oy Foundation.

REFERENCES

1. Kontturi, K., Ekman, A. and Forssell, P. *Acta Chem. Scand. A* 39 (1985) 273.
2. Haase, R. *Thermodynamics of Irreversible Processes*, Addison-Wesley, London 1969.
3. Forssell, P. and Kontturi, K. *Sep. Sci.* 18 (1983) 205.

Received September 7, 1984.