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# Cation Membrane Transport: Evidence for Local Validity of Nernst-Planck Equations

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*Diffusion / Electrochemistry / Membranes / Nonequilibrium Phenomena / Transport Properties*

Local transport coefficients have been experimentally determined for transport of  $H^+$ ,  $Na^+$ ,  $H_2O$  and current, and for transport of  $K^+$ ,  $Sr^{2+}$ ,  $H_2O$  and current in a cation exchange membrane. Adjacent electrolytes contained 0.03 N solution mixtures of HCl and NaCl, or 0.03 N or 0.01 N solution mixtures of KCl and  $SrCl_2$ . The fluxes and forces used in the presentation are based on a choice of neutral and independent components of the system. — The concentration dependence of the membrane conductivity and the electric mobility of ions has been described by a model which relates the reduction of one cation mobility to the equivalent fraction of the other cation. The mobility ratio varies between 4 and 15 for  $u_H/u_{Na^+}$  and 3 and 6 for  $u_K/u_{Sr^{2+}}$ . The transference numbers for the monovalent salt system can be predicted within experimental uncertainty limits from this model. Local diffusion coefficients are derived and compared to electric mobilities. The result is that the Nernst-Planck equation using equal electric and diffusional mobility is valid for all concentrations within  $\pm 10\%$  on the average for both systems. Water transport will modify the Nernst-Planck flux equations when gradients in chemical potential of water becomes about  $10^{-5}$  times the gradients in chemical potential of salts. Calculations predict a negligible contribution to the chemical potential gradient of salts from pressure variations in the membrane during interdiffusion. — In total these results make possible a continuous description of membrane transport processes.

## 1. Introduction

The aim of the present investigation is to develop continuous descriptions of membrane transport phenomena. In order to do so the concentration dependency of the phenomenological coefficients and local concentration profiles must be determined.

We present here a complete determination of electrical and diffusional transport data for the systems NaM—HM and KM— $SrM_2$ . M means cation site in a cation exchange membrane. A complete determination of the phenomenological coefficients is valuable because essential and less essential effects can be sorted out from an overall picture of the coupled transport processes. The determination allows for a control of the assumptions behind the Nernst-Planck flux equations.

A determination of all phenomenological coefficients in a three component system has been carried out by Chu et al. [1]. The work concerns *average* coefficient determinations. To our knowledge *local* coefficients are not available for a cation membrane with two salts and water.

In his review article Teorell [2] describes conceptual developments in the field of membrane transport. The present investigation uses irreversible thermodynamics to describe the transport of salts, water and current across an ion exchange membrane. It represents an extension of two pre-

vious articles [3,4]. New concepts are not introduced. Our presentation does however differ from most other presentations dealing with the same topic (see e.g. Ref. [5]). The reason is that we have chosen as basic component variables, the independent and neutral components of the system in accordance with Gibbs definition of components [6]. This ensures well defined, measurable partial molar quantities (i.e. chemical potentials) for electrolyte solutions. The consequence is that electrochemical potentials are avoided. Reasons for doing this have been given by Førland et al. [7–10] and Grjotheim [11].

In their extensive analysis of membrane transport processes, Kedem and Katchalsky [12] presented a so-called practical set of flux equations which are fitted for experimental situations. The practical flux equations bear a resemblance to ours in the emphasize placed on measurable quantities. Kedem and Katchalsky do, however, introduce the concept of local electrostatic potentials in their further interpretation of measurements. We shall see here, how ionic models for transport can be introduced in an alternative manner.

## II. Theory

### a) The Transport of Two Salts, Water and Electric Charge Across a Cation Exchange Membrane

The coupled transport of three components; two salts, water and electric charge can be written in terms of the following flux equations [3].

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$$J_1 = -L_{11} \nabla \mu_1 - L_{12} \nabla \mu_2 - L_{13} \nabla \mu_3 - L_{14} \nabla \phi \quad (1)$$

$$J_2 = -L_{21} \nabla \mu_1 - L_{22} \nabla \mu_2 - L_{23} \nabla \mu_3 - L_{24} \nabla \phi \quad (2)$$

$$J_3 = -L_{31} \nabla \mu_1 - L_{32} \nabla \mu_2 - L_{33} \nabla \mu_3 - L_{34} \nabla \phi \quad (3)$$

$$j = -L_{41} \nabla \mu_1 - L_{42} \nabla \mu_2 - L_{43} \nabla \mu_3 - L_{44} \nabla \phi. \quad (4)$$

The membrane components are either HM(1), NaM(2) and H<sub>2</sub>O(3), or KM(1), SrM<sub>2</sub>(2) and H<sub>2</sub>O(3). The membrane surfaces are in contact with aqueous solutions of HCl and NaCl or KCl and SrCl<sub>2</sub> respectively. The concentration of Cl<sup>-</sup> in the aqueous solution is such that coions do not enter the membrane. XM denotes a cation site for X<sup>+</sup> in the matrix of the membrane. The current density,  $j$ , is controlled through the external circuit. The fluxes,  $J_i$ , phenomenological coefficients,  $L_{ij}$ , and chemical potential gradients  $\nabla \mu_j$  are numbered according to the numbering of the components. The electric potential gradient  $\nabla \phi$  is defined by potential measurements with auxiliary electrodes. In Eqs. (1)–(4)  $\nabla \phi$  is given in units of J F<sup>-1</sup> m<sup>-1</sup>. The frame of reference for the fluxes is the membrane.

Six independent relations exist among the coefficients according to Onsager [13]:

$$L_{ij} = L_{ji} \quad i, j = 1, \dots, 4. \quad (5)$$

Furthermore, since current is carried by the two cations,

$$z_1 J_1 + z_2 J_2 = j \quad (6)$$

the following four relations can be derived [3]:

$$z_1 L_{1i} + z_2 L_{2i} = L_{4i} \quad (7)$$

where  $z_1 = z_2 = 1$  for the system HM–NaM–H<sub>2</sub>O and  $z_1 = 1$  and  $z_2 = 2$  for the system KM–SrM<sub>2</sub>–H<sub>2</sub>O. We are then left with six unknown coefficients in the matrix (1)–(4). It is practical to eliminate  $\nabla \phi$  in Eqs. (1)–(3), to see the relation between coupled transport of mass and charge and the case of pure diffusion. By introducing  $\nabla \phi$  from Eq. (4) into the first three equations, we have:

$$J_1 = -l_{11} \nabla \mu_1 - l_{12} \nabla \mu_2 - l_{13} \nabla \mu_3 - t_1 j \quad (8)$$

$$J_2 = -l_{21} \nabla \mu_1 - l_{22} \nabla \mu_2 - l_{23} \nabla \mu_3 - t_2 j \quad (9)$$

$$J_3 = -l_{31} \nabla \mu_1 - l_{32} \nabla \mu_2 - l_{33} \nabla \mu_3 - t_3 j \quad (10)$$

where

$$l_{ij} = L_{ij} - \frac{L_{i4} L_{4j}}{L_{44}} \quad (i = 1, 2, 3) \quad (11)$$

$$t_i = \frac{L_{i4}}{L_{44}} = \left( \frac{J_i}{j} \right) \nabla \mu_j = 0 \quad (i = 1, 2, 3) \quad (12)$$

$l_{ij}$  are called phenomenological diffusion coefficients. These are electrode independent contrary to the  $L_{ij}$ 's. From Eq. (11) it is clear that the Onsager reciprocal relations are also valid for the  $l_{ij}$ 's.

The  $t_i$ 's are transference coefficients, defined as moles of component  $i$  transferred per equivalent of charge transferred. They do not necessarily sum up to unity. Ionic transference numbers, defined as fraction of electric current carried by an ion, always sum up to unity. With Cl<sup>-</sup> reversible electrodes, Ag/AgCl, the transference coefficients and ion transference numbers are related by:

$$t_1 = t_{H^+} \quad \text{and} \quad t_2 = t_{Na^+} \quad (13)$$

for the system HM–NaM–H<sub>2</sub>O and

$$t_1 = t_{K^+} \quad \text{and} \quad t_2 = \frac{1}{2} t_{Sr^{2+}} \quad (14)$$

for the system KM–SrM<sub>2</sub>–H<sub>2</sub>O.

For pure diffusion ( $j = 0$ ), it follows from Eqs. (7)–(10) that

$$z_1 l_{1i} + z_2 l_{2i} = 0 \quad i = 1, 2, 3. \quad (15)$$

The above equations form the basis from which the expressions in this paper will be derived. The condition for their validity is local equilibrium and no bulk transport of solutions.

## b) Controls for the Nernst-Planck Equation

The Nernst-Planck equation for an ion is valid if the electric and diffusive mobilities of the ion are equal (the Nernst-Einstein assumption). Nernst-Planck equations are obtained from Eqs. (1)–(6), by introducing the conditions  $L_{12} = 0$  and  $\nabla \mu_3 = 0$  [3]:

$$\text{HM–NaM membrane: } J_{HM} = -L_{14}(\nabla \mu_{HM} + \nabla \phi) \quad (16a)$$

$$J_{NaM} = -L_{24}(\nabla \mu_{NaM} + \nabla \phi) \quad (16b)$$

$$\text{KM–SrM}_2 \text{ membrane: } J_{KM} = -L_{14}(\nabla \mu_{KM} + \nabla \phi) \quad (17a)$$

$$J_{SrM_2} = -\frac{1}{2} L_{24}(\nabla \mu_{SrM_2} + 2\nabla \phi). \quad (17b)$$

We see from Eqs. (16) and (17) that the electric and chemical force have the same effect per equivalent charge transferred. Since the membrane is perfectly cation selective,

$$J_{HM} = J_{H^+}, J_{NaM} = J_{Na^+} \quad \text{and} \quad J_{KM} = J_{K^+}, J_{SrM_2} = J_{Sr^{2+}}. \quad (18)$$

By independent determination of  $L_{11}$  and  $L_{14}$ , the assumption  $L_{12} = 0$  can be checked using Eq. (7). Holt et al. [4] have given a procedure which we shall use to calculate  $L_{11}$  from diffusion experiments. The coefficient  $L_{14}$  shall be calculated from  $L_{44}$  and  $t_1$ .

The membrane conductivity  $\kappa = L_{44}/F^2$  shall be calculated from the membrane resistance  $R$  by  $\kappa = \Delta x/AR$  where  $A$  is the membrane area and  $\Delta x$  is the membrane thickness. The ion exchange capacity is constant and equal to  $c$ . The membrane conductivity can be expressed by membrane mobilities  $u_i$  and membrane equivalent fractions,  $X_{iM}$ , through

$$\kappa = cF(X_{HM} u_{H^+} + X_{NaM} u_{Na^+}) \quad (19)$$

and

$$\kappa = cF(X_{KM} u_{K^+} + X_{SrM_2} u_{Sr^{2+}}). \quad (20)$$

Transference numbers are equal to:

$$t_{H^+} = \frac{X_{HM} u_{H^+}}{X_{HM} u_{H^+} + X_{NaM} u_{Na^+}} \quad (21a)$$

$$t_{Na^+} = \frac{X_{NaM} u_{Na^+}}{X_{HM} u_{H^+} + X_{NaM} u_{Na^+}} \quad (21b)$$

and

$$t_{K^+} = \frac{X_{KM} u_{K^+}}{X_{KM} u_{K^+} + X_{SrM_2} u_{Sr^{2+}}} \quad (22a)$$

$$t_{Sr^{2+}} = \frac{X_{SrM_2} u_{Sr^{2+}}}{X_{KM} u_{K^+} + X_{SrM_2} u_{Sr^{2+}}} \quad (22b)$$

The expression for emf,  $E$ , of the cell is from Eq. (4)

$$EF = - \int_1^3 \sum_{i=1}^3 t_i d\mu_i \quad (23)$$

where  $t_i$  are transference coefficients.  $E$  is the electromotive force of the cell in volts. Emf measurements shall be used as a consistency check for transference numbers.

### c) Interdiffusion Coefficient

When Nernst-Planck equation is valid, Eq. (11) can be reduced to give

$$l_{11} = t_1(1 - t_1) L_{44}. \quad (24)$$

This means that  $l_{11}$  can be determined approximately from measurements of the membrane conductivity and transference coefficients.

The phenomenological coefficient  $l_{11}$  express interdiffusion of ions because  $l_{11} = l_{12} z_2/z_1$  from Eq. (15). From Eqs. (8) and (15) a flux equation for interdiffusion is given for  $z_1 = z_2 = 1$  (assuming  $\nabla\mu_3 = 0$ )

$$J_1 = -l_{11}(\nabla\mu_1 - \nabla\mu_2). \quad (25)$$

Fick's first law for interdiffusion in the membrane can be formulated for two monovalent ions:

$$J_1 = -D_{12}(\nabla X_{1M} - \nabla X_{2M}) \quad (26)$$

where  $D_{12}$  is Fick's interdiffusion coefficient, of ions 1 and 2,  $X_{iM}$  is the equivalent fraction of the ion  $i$  in the membrane. Eqs. (26) and (25) relate Fick's interdiffusion  $D_{12}$  to the phenomenological diffusion coefficient  $l_{11}$  by

$$D_{12} = l_{11} RT/2X_{1M} X_{2M} \quad (27a)$$

or

$$D_{12} = t_1(1 - t_1) \kappa F^2 RT/2X_{1M} X_{2M} \quad (27b)$$

if Eq. (24) is valid. A similar expression can be found for divalent ions.

### d) Pressure Gradients During Interdiffusion

In stationary state a balance is created between water transport due to charge transport and water transport by diffusion. A pressure gradient across the membrane may result [4], and may influence the salt transport. The size of the pressure and the variation of  $P$  with the membrane coordinate  $x$ , is then of interest. This has been discussed previously [4]. In the present article we shall calculate  $dP/dx$  and  $P(x)$  by a different procedure.

We may solve the local value of the pressure gradient from Eqs. (8) and (10) for  $j = 0$ .

$$J_3 = \frac{l_{13}}{l_{11}} J_1 - \left( l_{33} - \frac{l_{13} l_{31}}{l_{11}} \right) \nabla\mu_3. \quad (28)$$

The gradient in chemical potential of water is next replaced by  $\nabla\mu_3(c)$  and  $V_3 \nabla P$ . The simplification  $l_{33} = \text{const} \gg l_{13} l_{31}/l_{11}$  is introduced. In the stationary state, the divergence of the fluxes are zero. This condition is applied to Eq. (28). Then the equation is integrated twice. With the boundary conditions  $P = 0$  at  $x = 0$ , and  $P = 0$  at  $x = 1$ , the following equations are obtained:

$$\frac{dP}{dx} = \frac{\Delta x}{l_{33} V_3} \left( \frac{l_{13}}{l_{11}} J_1 \right) - \frac{d\mu_3(c)}{V_3 dx} + C \quad (29)$$

$$P(x) = \int_0^x \left[ \frac{\Delta x}{l_{33} V_3} \left( \frac{l_{13}}{l_{11}} J_1 \right) - \frac{d\mu_3(c)}{V_3 dx} + C \right] dx. \quad (30)$$

In these equations  $C$  is a constant given by the integral of Eq. (30) from one to zero. Pressures calculated by Eq. (29) are not absolute, but pressures above the value of the external solutions. The ratio  $l_{13}/l_{11}$  can be determined experimentally from water flux and diffusion experiments, assuming the condition  $\nabla\mu_3 \approx 0$ , and  $\nabla P \approx 0$ . Through Eq. (29) and the parameters  $l_{33}$  and  $l_{13}$ , we are able to control the influence of  $\nabla\mu_3$  in Eqs. (8)–(10) during charge transfer and diffusion.

## III. Experimental

For the HCl–NaCl-membrane system the total concentration of  $\text{Cl}^-$  in adjacent electrolyte solutions was 0.03 N. The mixtures of HCl and NaCl had mol fractions 0, 1/8, ..., 7/8, 1.

For the system KCl– $\text{SrCl}_2$ -membrane two total concentrations of  $\text{Cl}^-$  in adjacent electrolyte solutions were investigated; 0.01 N and 0.03 N. Between eight and ten mixtures of KCl and  $\text{SrCl}_2$  were used. Data on transference coefficients, interdiffusion and conductivity have partly been reported before for 0.03 N solutions [4].

Both systems were checked for coion sorption in the membrane, by equilibrating the membrane pieces first in chloride solutions and then putting them into  $\text{NaNO}_3$ , 0.1 N. It was not possible to detect any  $\text{Cl}^-$  in the  $\text{NO}_3^-$  solution within the sensitivity of the potentiometric method in use,  $10^{-8}$  N. Therefore it can be concluded that there is no coion sorption in the membrane for the concentrations in question.

The membrane studied was of the type CR 61 AZL 386 from Ionics Inc., Watertown, Mass. (USA). This is made of cross-linked sulfonated copolymers of vinyl, reinforced with a glass fiber fabric. The conductivity of the HM–NaM– $\text{H}_2\text{O}$  system was measured using a Philips conductivity meter, type PW 9509 at frequency 2 kHz. The membrane was mounted directly between two Pt-black

electrodes. The conductivity was measured both with and without membrane. Constant geometry of the measuring unit was obtained by mounting the Pt-black electrodes to a micro-screw. A constant value of the conductivity was obtained before readings were done. The temperature was  $25.00 \pm 0.02^\circ\text{C}$ . Before measurements, the membranes were kept in equilibrium solutions for minimum two weeks.

The interdiffusion cell for the HCl–NaCl-membrane system was stirred by circulating solutions parallel to the membrane surface. A precision gear pump from Ismatec SA, type P 142 with speed regulation was used. A flow rate of about  $3 \text{ dm}^3 \text{ min}^{-1}$  was used. The temperature was  $25.0^\circ\text{C}$ . Further experimental details on interdiffusion measurements, volumetric measurements and the determinations of the transference coefficients, have been described elsewhere. Glass and metal were used as construction materials for the cell for volumetric measurements in order to avoid absorption of solvent [15].

Table 1  
Transference numbers of  $\text{H}^+$  as function of equivalent fraction,  $X_{\text{HM}}$ , in membrane. Temperature is  $25^\circ\text{C}$

| $X_{\text{HM}}$ | $t_{\text{H}^+}$<br>calculated from<br>Eq. (31) | $t_{\text{H}^+}$<br>(measured) |
|-----------------|---|--------------------------------|
| 0               | 0   | —                              |
| 0.161           | $0.48 \pm 0.03$                                 | $0.48 \pm 0.03$                |
| 0.312           | $0.72 \pm 0.05$                                 | $0.67 \pm 0.03$                |
| 0.452           | $0.84 \pm 0.06$                                 | $0.78 \pm 0.03$                |
| 0.582           | $0.92 \pm 0.07$                                 | $0.87 \pm 0.03$                |
| 0.702           | $0.96 \pm 0.07$                                 | $0.93 \pm 0.03$                |
| 0.812           | $0.98 \pm 0.07$                                 | $0.97 \pm 0.03$                |
| 0.911           | $0.99 \pm 0.07$                                 | $0.99 \pm 0.03$                |
| 1               | 1   | —                              |

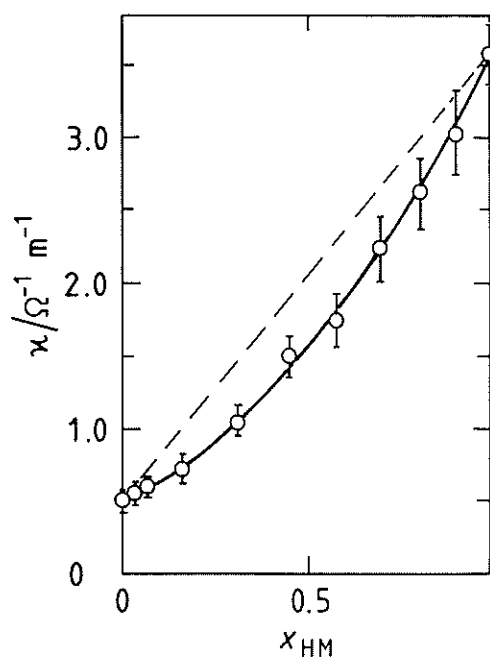


Fig. 1

Membrane conductivity,  $\kappa$ , as a function of equivalent fraction of HM in the membrane,  $X_{\text{HM}}$ , for the system HM–NaM– $\text{H}_2\text{O}$ . Experimental points with uncertainties are denoted. The curved line is derived from the functions in Eq. (31). The stipled curve represent values assuming a constant mobility ratio. Temperature is  $25^\circ\text{C}$

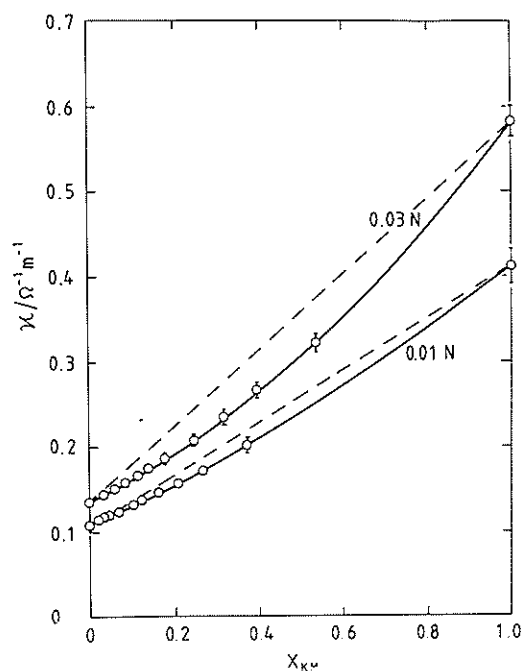


Fig. 2

Membrane conductivity,  $\kappa$ , as a function of equivalent fraction of KM in the membrane,  $X_{\text{KM}}$ , for the system KM– $\text{SrM}_2$ – $\text{H}_2\text{O}$ . Experimental points with uncertainties are denoted. The curved line is derived from the functions in Eq. (31). The stipled curve represent values assuming a constant mobility ratio. Temperature is  $25^\circ\text{C}$

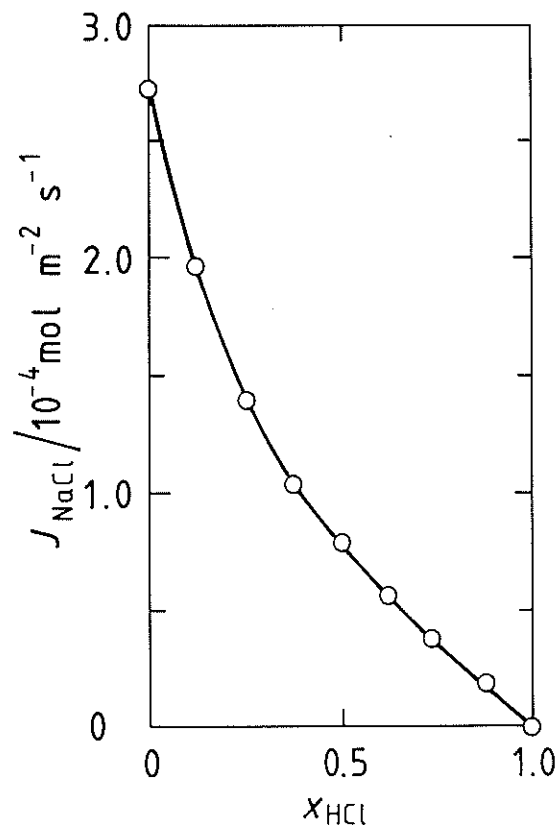


Fig. 3

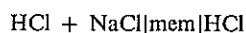
The interdiffusion flux,  $J_{\text{NaCl}}$ , as a function of composition of the left hand side of the cell, HCl + NaCl|mem|HCl. Total concentration of  $\text{Cl}^-$  is 0.03 N. Temperature is  $25^\circ\text{C}$

## IV. Results

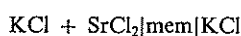
## a) Measurements

The electric conductivity is plotted as a function of  $X_{\text{HM}}$  in Figs. 1 and 2 for the two systems HM—NaM—H<sub>2</sub>O and KM—SrM<sub>2</sub>—H<sub>2</sub>O respectively. The ionic transference numbers for the HM—NaM—H<sub>2</sub>O system, are given as a function of  $X_{\text{HM}}$  in Table 1.

The interdiffusion flux,  $J_{\text{NaCl}}$ , is shown in Fig. 3 as a function of the electrolyte composition on the left hand side of the cell:



for total concentrations of Cl<sup>−</sup> of 0.03 N on both sides of the membrane. The interdiffusion flux,  $J_{\text{SrCl}_2}$ , is shown in Fig. 4 as a function of the electrolyte composition on the left hand side of the cell:



for the total concentrations of Cl<sup>−</sup> of 0.03 N and 0.01 N on both sides of the membrane.

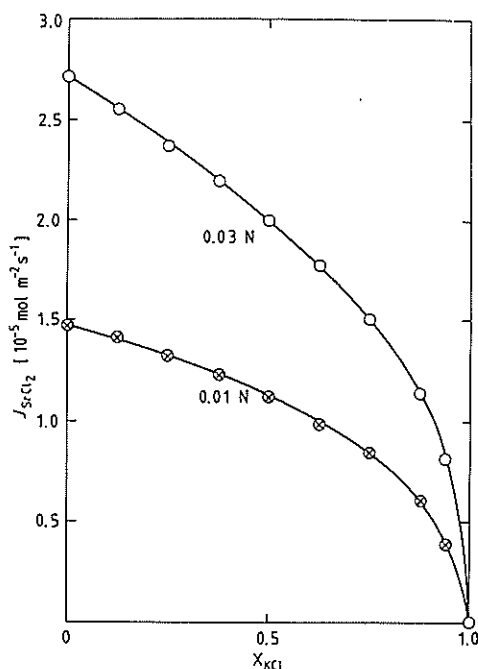


Fig. 4

The interdiffusion flux,  $J_{\text{SrCl}_2}$ , as a function of composition of the left hand side of the cell, KCl + SrCl<sub>2</sub>|mem|KCl. Total concentration of Cl<sup>−</sup> are 0.01 N and 0.03 N. Temperature is 25°C

Table 2

Water permeability coefficients,  $l_{33}$ . Coefficient unit is  $10^{-8} \text{ mol}^2 \text{ s m}^{-3} \text{ kg}^{-1}$ .  $X_{\text{HM}}$  is the membrane fraction of HM,  $X_{\text{HCl}}$  is the mole fraction of HCl in solution. Measured values are marked with an \*

| $X_{\text{HCl}}$ | $X_{\text{HM}}$ | $l_{33}$ |
|------------------|-----------------|----------|
| 0                | 0               | *37.5    |
| 1/8              | 0.161           | 39.0     |
| 2/8              | 0.312           | 40.4     |
| 3/8              | 0.452           | 41.9     |
| 4/8              | 0.582           | *43.4    |
| 5/8              | 0.702           | 44.8     |
| 6/8              | 0.812           | 46.3     |
| 7/8              | 0.911           | 47.7     |
| 1                | 1               | *49.3    |

Values obtained for the osmotic volume flow measured in the pure HM—H<sub>2</sub>O and NaM—H<sub>2</sub>O systems are  $3.87 \cdot 10^{-8} \text{ m}^{-1}$  and  $2.96 \cdot 10^{-8} \text{ ms}^{-1}$  respectively. The water permeability coefficient is shown in Table 2. A linear variation of  $l_{33}$  (Eq. (10)) with composition is assumed. Partial molar volumes used in calculations are  $V_{\text{HCl}} = 18.3$ ,  $V_{\text{NaCl}} = 16.8$  and  $V_{\text{H}_2\text{O}} = 18.0 [10^{-6} \text{ m}^3 \text{ mol}^{-1}]$  [16]. The membrane thickness is  $5.5 \cdot 10^{-4} \text{ m}$ . The water content in the membrane was 40% by volume, and the ion exchange capacity  $C = 1.6 \text{ k eqv. m}^{-3}$  [15].

## b) Calculations

## Mobilities and Transference Numbers

The curves relating the data points of Figs. 1 and 2 represent the functional relations (19) and (20). The mobilities can be expressed as [17]:

$$u_i = u_i^0 (1 - k X_j) \quad (31)$$

where  $u_i^0$  is the mobility of  $i$  in the pure cation membrane,  $k$  is an interaction constant and  $X_j$  is the equivalent fraction of  $j$ . By introducing Eq. (31) into Eq. (19), the following expression for  $k$  is obtained:

$$k = cF \{ X_{\text{NaM}} u_{\text{Na}^+}^0 (1 - k X_{\text{HM}}) + X_{\text{HM}} u_{\text{H}^+}^0 (1 - k X_{\text{NaM}}) \}. \quad (32)$$

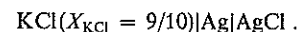
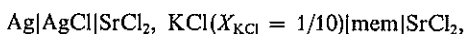
A similar expression is obtained for the system KM—SrM<sub>2</sub>—H<sub>2</sub>O.  $k$  is chosen to give the best least square fit of the curve given by Eq. (32) to the experimental points in Figs. 1 and 2. Results for the parameters  $u_i^0$  and  $k$  are given for the systems HM—NaM—H<sub>2</sub>O and KM—SrM<sub>2</sub>—H<sub>2</sub>O in Table 3.

Table 3  
Ion mobility model parameters for the equation  $u_i = u_i^0 (1 - k X_j)$ 

| Concentration of Cl <sup>−</sup> in solution | Ion pairs $i, j$                   | Membrane mobility, $u_i^0$ [ $10^8 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ] | Interaction constant $k$ |
|--|------------------------------------|---|--------------------------|
| 0.03 N                                       | H <sup>+</sup><br>Na <sup>+</sup>  | 2.3<br>0.3  | 0.50                     |
| 0.03 N                                       | K <sup>+</sup><br>Sr <sup>2+</sup> | 0.38<br>0.09  | 0.28                     |
| 0.01 N                                       | K <sup>+</sup><br>Sr <sup>2+</sup> | 0.27<br>0.07  | 0.19                     |

The mobilities  $u_i$  from Eq. (31) give the transference number for the cations from Eqs. (21) and (22). The calculated — and experimentally determined transference numbers of  $t_{\text{H}^+}$  are given in Table 1. Table 1 shows that the two sets of transference numbers agree within experimental error limits for the HM—NaM—H<sub>2</sub>O system.

For the KM—SrM<sub>2</sub>—H<sub>2</sub>O system, the two sets of transference numbers did not give a similar good agreement. In order to be able to choose between the sets, emf was measured for the following cell:



Temperature was 25°C and the total concentration of Cl<sup>−</sup> was 0.03 N. The result was 1.4 mV. A calculation of emf using Eq. (23) gave values of −16.1 mV and 8.7 mV for the measured and calculated transference numbers, respectively. A change in the transference numbers of about  $\pm 0.03$  units, will cause a change in the calculated emf of about 4 mV. The contribution of the term  $t_{\text{H}_2\text{O}} d\mu_{\text{H}_2\text{O}}$  to the emf is less than 0.1 mV.

The experimentally determined transference numbers give too great values for  $t_{\text{K}^+}$ . This may be explained by the big difference between  $t_{\text{K}^+}$  in the solution and in the membrane. The ratio of



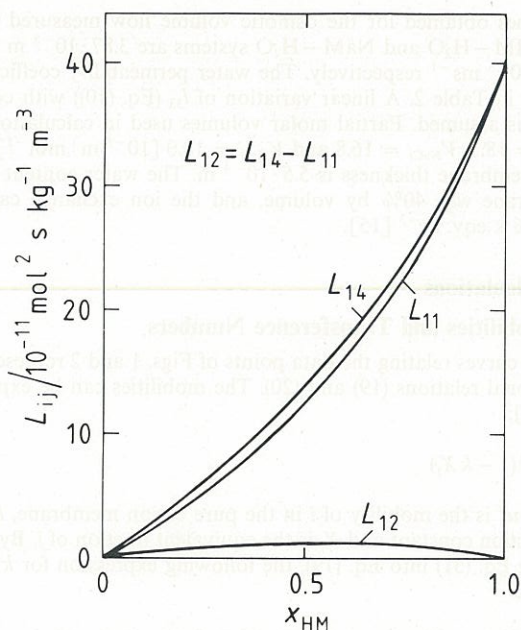


Fig. 5

Variations in the coefficients  $L_{12}$ ,  $L_{11}$  and  $L_{14}$  with composition of HM in the membrane,  $x_{HM}$ , for the system HM–NaM–H<sub>2</sub>O. Total concentration of Cl<sup>−</sup> in external solutions is 0.03 N. Temperature is 25°C

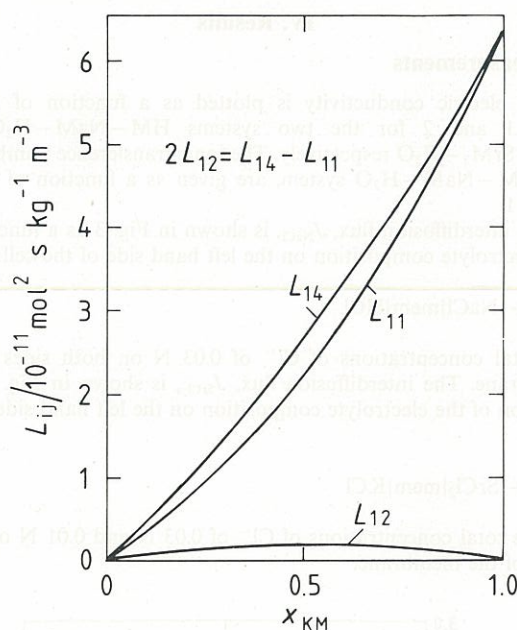


Fig. 6

Variations in the coefficients  $L_{12}$ ,  $L_{11}$  and  $L_{14}$  with composition of KM in the membrane,  $x_{KM}$ , for the system KM–SrM<sub>2</sub>–H<sub>2</sub>O. Total concentration of Cl<sup>−</sup> in adjacent solutions is 0.03 N. Temperature is 25°C

electrical current conducted by K<sup>+</sup> and Sr<sup>2+</sup> is significantly less in the membrane than in the solutions outside the membrane, as given by the mobility ratios. Because of this, KCl will accumulate on the membrane surface in the ion donating half cell. The equilibrium is shifted to greater K<sup>+</sup> contents in the membrane. The value of  $t_{K^+}$  is thereby increased compared to a value without concentration polarization.

The calculated set of transference numbers are preferred for a calculation of the coefficients  $L_{14}$  and  $L_{24}$  because they predict the emf better than the measured set, however not very well.

### Validity of the Nernst-Planck Equation

The validity of the Nernst-Planck equation was checked according to section IIb after independent determinations of  $L_{11}$  from  $l_{11}$  and  $L_{14}$  from  $t_1$  and  $L_{44}$ . The results of the different calculations are given in Figs. 5 and 6 for the systems, HM–NaM–H<sub>2</sub>O and KM–SrM<sub>2</sub>–H<sub>2</sub>O. The interdiffusion experiments (Figs. 3 and 4) give  $l_{11}$  as well as the concentration profiles inside the membrane, using the membrane equilibrium isotherms [19, 20].

The Fick's interdiffusion coefficient of the membrane,  $D_{12}$ , was determined from  $l_{11}$  using Eqs. (21), (24), (27) and (31) for H<sup>+</sup>–Na<sup>+</sup>, and corresponding equations for K<sup>+</sup>–Sr<sup>2+</sup>. For the HM–NaM–H<sub>2</sub>O system, a typical value for  $l_{11}$  is  $10^{-11}$  mol<sup>2</sup> kg<sup>−1</sup> m<sup>−3</sup>. This corresponds to a Fick's interdiffusion coefficient of about  $1.6 \cdot 10^{-9}$  m<sup>2</sup> s<sup>−1</sup>. For the KM–SrM<sub>2</sub>–H<sub>2</sub>O system, a typical value of  $l_{11}$  is  $10^{-12}$  mol<sup>2</sup> s kg<sup>−1</sup> m<sup>−3</sup> for both total concentrations corresponding to  $D_{12}$  of about  $3 \cdot 10^{-10}$  m<sup>2</sup> s<sup>−1</sup>.

### Pressure Gradients During Interdiffusion and Net Charge Transfer

In order to determine the pressure gradient during interdiffusion from Eq. (29) it is necessary to make first the approximations that  $\nabla\mu_3$  and  $\nabla P$  give negligible effects on  $l_{13}/l_{11}$  for the experimental conditions  $\Delta\mu_3 = 0$  and  $\Delta P = 0$ . This is next checked through the following procedure. From the value obtained for  $l_{13}/l_{11}$  and  $l_{33}$  from Table 2,  $P$  was estimated from Eqs. (29) and (30). The result was used to control the approximation by checking constancy of the ratio  $l_{13}/l_{11}$  used in Eq. (28). Constancy was obtained for the

system HM–NaM–H<sub>2</sub>O. The calculated pressure gradient and the pressure developed in the equilibrium solutions across the membrane, are shown in Fig. 7 for the system HM–NaM–H<sub>2</sub>O.

Gradients in the concentration dependent part of the chemical potential of water,  $d\mu_3(c)/dx$ , needed for the calculation in Fig. 7 were found from a plot of the water activity as a function of membrane position. The water activities of the HCl–NaCl–H<sub>2</sub>O system were estimated [18].

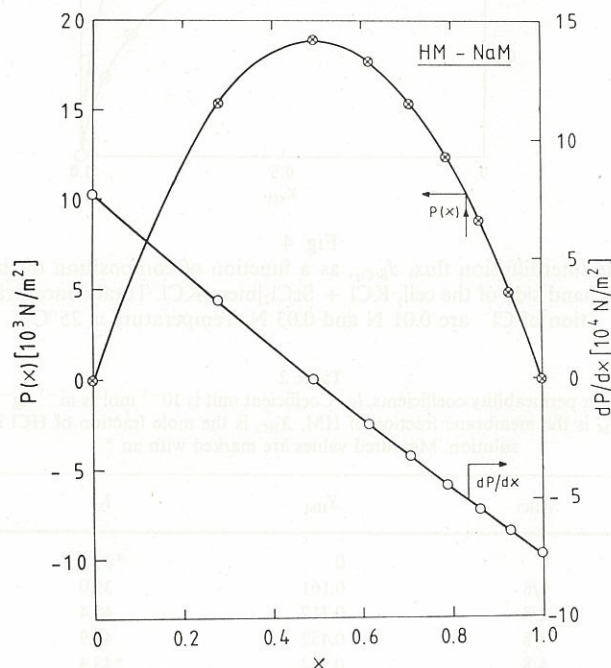


Fig. 7

Pressure gradient,  $dP/dx$ , and pressure  $P(x)$  above external solution pressure as a function of normalized membrane position,  $x$ , for the HM–NaM–H<sub>2</sub>O system

## V. Discussion

### a) A Continuous Description of Ion Transport Across the Membrane

Concentration dependent phenomenological coefficients make possible integrations across ion exchange membranes, in the same manner as integrations across aqueous solutions of varying compositions are performed. The results and calculations of the preceding section have shown one possible way of obtaining parameters for a continuous description.

The results show that the easy starting point to obtain the necessary transport parameters is the membrane conductivity,  $\kappa$ . A complete determination means that ionic mobilities should be obtained from both conductivities and transference numbers. Transference number determinations are, however, much more time consuming than conductivity measurements and the present results indicate that they may be avoided. From  $\kappa$ , ionic mobilities were derived by a simple model. The model for ionic mobility was tested for consistency against data for transference numbers of ions. This model will now be further tested in other systems.

We have further shown in this work that the assumption of equal electrical and diffusional mobility (the Nernst-Einstein assumption) is valid for all membrane compositions within an uncertainty on the average less than  $\pm 10\%$  even for ions of different valency. This result, if general, simplifies the equation set (1–4) dramatically. The diffusional coefficients,  $l_{11}$  and  $l_{22}$ , can then be modelled from the electrical mobility data derived directly from  $\kappa$  (Eq. (24)). An analytical expression for the interdiffusion coefficient as a function of concentration (Eq. (27b)) is the useful result.

The present experimental results are not conclusive, when it comes to include the water transport into a continuous description. This will be a further aim of our investigations. It is, however, clear from Table 2 that the water transport coefficient is so high that Nernst-Planck equations cannot be used in the simplified form (Eqs. (16) and (17)) when the gradient in chemical potential of water is greater than the chemical potential of salt multiplied by a factor of  $10^{-5}$ . Preliminary data in our laboratory as well as published results [21] indicate that the water transport is largely dependent on the presence of external pressure gradients as well as concentration gradients.

The single results shall next be discussed in more detail to bring forward reliability and characteristics.

### b. Ionic Mobility Model

The mobilities were calculated as functions of membrane compositions according to Eq. (6.1). For membranes in equilibrium with 0.03 N solutions, the result is a variation in the mobility ratio  $u_{H^+}/u_{Na^+}$  from 4 in an almost pure Na-membrane to 15 in an almost pure H-membrane. For the ratio  $u_{K^+}/u_{Sr^{2+}}$  the variation is from about 3 in an almost pure Sr-membrane to 6 in an almost pure K-membrane. The limit ratios are 3 and 4 when the membrane is in equilibrium with a 0.01 N solution. Such a change in mobility ratios deviate from the frequently used assumption of constant mobility ratios in the membrane. Constant mobilities can be explained by independent movements of ions. Because of the electroneutrality requirements in the membrane one should

expect obstructions to movement of one ion by the other ions, and thus concentration dependent mobilities. It may be noted that the interaction constant is smaller when the equilibrium solution is more dilute.

Other models for the mobilities were examined. The mobilities calculated according to Eq. (31) were chosen because the ionic transference numbers for the HM–NaM–H<sub>2</sub>O system were modelled quantitatively in this way. Also for the KM–SrM<sub>2</sub>–H<sub>2</sub>O system the corresponding transference numbers were more acceptable, than other results.

### c) Nernst-Planck Equations for Ion Transport

The validity of the Nernst-Planck equations can be studied from Figs. 5 and 6. For the HM–NaM–H<sub>2</sub>O system  $L_{12}$  is always less than 10% the value of  $L_{14}$  for all compositions on the average. The same conclusion is valid for the KM–SrM<sub>2</sub>–H<sub>2</sub>O system of total concentration 0.03 N. The values obtained for the KM–SrM<sub>2</sub>–H<sub>2</sub>O system of total concentration 0.01 N show  $L_{12}$  to be less than 17% the value of  $L_{14}$  for all compositions, except for  $X_{KCl} = 1/8$ , when the deviation is larger. These deviations may be acceptable in some practical applications.

The values for the diffusion coefficients for HCl and NaCl in aqueous solution of concentration 0.03 N, are  $3 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and  $1.5 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  respectively [22]. The corresponding values for KCl and SrCl<sub>2</sub>, are  $1.9 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and  $1.2 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . For the HM–NaM–H<sub>2</sub>O system this indicates small changes between diffusion in aqueous solution and in the membrane phase. For the KM–SrM<sub>2</sub>–H<sub>2</sub>O system the diffusion coefficient is about one order of magnitude smaller than the diffusion coefficient of aqueous solutions. A difference of one order of magnitude is found for other cations too [23].

### d) Membrane Water Transport

The amount of water present in the membrane corresponds to about 17 mol H<sub>2</sub>O per equivalent of membrane ion exchange capacity. This is the amount of water which is available for transport in the membrane. As the composition changes H<sup>+</sup> and Na<sup>+</sup> or K<sup>+</sup> and Sr<sup>2+</sup> may carry varying amounts of water. This can lead to water accumulation and explain the results of Fig. 7. McCallum and Meares [24] found a pressure build-up with a difference in concentrations of one salt between the two sides.

Fig. 7 indicates a symmetrical variation of the pressure. This can be due to the constant ratio of  $l_{13}/l_{11}$ .

The uncertainty of the calculated pressure gradient depends on assumptions behind the determination of the ratio  $l_{13}/l_{11}$ . The order of magnitude and the trend of the variation of pressure with position should be correct. The results of the calculated pressures and pressure gradients (Fig. 7) indicate that the absolute value has a negligible effect on the value of the chemical potential of electrolytes. The importance of this is, as indicated before [3], that emf's of the system can be calculated from an equation like (23) by integration across electrolyte solutions at atmospheric pressure. Scatchard made a similar assumption, but did not consider pressure [25]. It may further be safely assumed that the coefficient of Eqs. (16) and (17) do not vary with pressure.



A pressure gradient of the system  $\text{KM}-\text{SrM}_2-\text{H}_2\text{O}$  has been proposed earlier [4]. A different calculation procedure was then used and  $l_{13}/l_{11} < 0$  was obtained for some compositions. This is unlikely in our system and indicates failure of the method [4].

## VI. Conclusion

The main results of the present study can be summarized as follows:

Conductivity measurements have been used to propose a model for continuous variation of ion mobility in membranes. The model predicts measured ionic transference numbers in the  $\text{HM}-\text{NaM}-\text{H}_2\text{O}$  system within experimental error limits. The model expresses the mobility of one cation,  $u_i$ , as a function of the equivalent fraction in the membrane,  $X_j$ , of the other cation through the equation  $u_i = u_i^0 (1 - kX_j)$ . Other systems should be investigated to establish the membrane mobility model, because several phenomenological coefficients can be derived from it.

The Nernst-Planck equation is locally valid within  $\pm 10\%$  on the average for ion transport through the membrane. Water permeability coefficients indicate that chemical potential gradients in water less than  $10^{-5}$  times salt gradients do not influence salt transport. A further aim will be to include water transport into a continuous description of membrane processes.

The relative value of pressure build-up in the membrane has been recalculated. The magnitude of the pressure indicates a negligible effect on the value of the chemical potential of electrolytes.

The authors thank Einar Johnsen who measured the transference numbers of the  $\text{HM}-\text{NaM}-\text{H}_2\text{O}$  system.

## Symbol List

|          |   |
|----------|---|
| $A$      | membrane area ( $\text{m}^2$ )  |
| $c$      | ion exchange capacity ( $\text{ekv m}^{-3}$ )   |
| $D_{12}$ | interdiffusion coefficient of ions 1 and 2  |
| $E$      | emf (V)   |
| $F$      | Faraday's constant ( $\text{C ekv}^{-1}$ )  |
| $j$      | current density ( $\text{eqv s}^{-1} \text{m}^{-2}$ )   |
| $J_i$    | flux of component $i$ ( $\text{mol s}^{-1} \text{m}^{-2}$ )   |
| $k$      | interaction constant for mobilities   |
| $l_{ij}$ | phenomenological diffusion coefficient for coupled transport of mass ( $\text{mol}^2 \text{s m}^{-3} \text{kg}^{-1}$ )  |
| $L_{ij}$ | phenomenological coefficient for coupled transport of mass and charge ( $\text{mol}^2 \text{s m}^{-3} \text{kg}^{-1}$ ) |
| $P$      | hydrostatic pressure  |
| $R$      | membrane resistance   |
| $t_i$    | transference coefficients of component $i$  |
| $t_j$    | ionic transference number of ion $j$  |
| $u_i$    | membrane mobility of ion $j$ ( $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ )   |

|                |  |
|----------------|--|
| $V_i$          | partial molar volume of component $i$ ( $\text{m}^3 \text{mol}^{-1}$ )                             |
| $x$            | coordinate   |
| $X_{jm}$       | equivalent fraction of ion $j$ in membrane   |
| $z_j$          | charge of ion $j$  |
| $\nabla \mu_i$ | chemical potential gradient of component $i$ ( $\text{J mol}^{-1} \text{m}^{-1}$ )                 |
| $\nabla \phi$  | electric potential gradient measured with auxiliary electrodes ( $\text{J F}^{-1} \text{m}^{-1}$ ) |
| $\kappa$       | membrane conductivity ( $\text{ohm}^{-1} \text{m}^{-1}$ )  |

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