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Conductance Matrix of Amphoteric Ion-Exchange Membrane in Three Ion System

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A conductance matrix describing the ion-transport phenomena in the membrane-three ion system has been determined. It was indicated there that six independent experiments were required in order to determine six independent elements of the conductance matrix. The $NaCl$–$CaCl_2$–amphoteric membrane system was chosen as the three ion system, and three kinds of fluxes, two kinds of transport numbers, and the membrane conductance were measured. Nine elements were experimentally determined on the assumption of Onsager's reciprocal relation. The results showed that the order of elements in conductance matrix was $g_{CaCa}>g_{ClCl}>g_{NaNa}>g_{CaCl}>g_{NaCl}>g_{CaNa}$. In addition, it was pointed out that the interactions among ions can never be ignored when the ion-transport phenomena across membrane are studied.

The transport phenomena of ions through an ion-exchange membrane have been still important subject in spite of many reported papers with respect to the transport properties. The subject appears in processes concentrating the saline water or obtaining the pure water from the saline water.[1] Probably the practical process would be a complicated one because of involving a number of ions. On the other hand, it is also interesting to understand the transport properties of ions through the membrane physicochemically. Generally, according to nonequilibrium thermodynamics, the fluxes transported across the membrane in the electrolyte solution–ion-exchange membrane system can be expressed by a linear combination of the forces generated in the system such as concentration gradient, potential difference and etc. In the previous studies, we have investigated the relationships among the fluxes and the forces in the system consisting of only a single electrolyte.[2–5] If the number of ions in the system increase, the relationships among the fluxes and the forces would become more complex. However, the thermodynamic examination concerning multi-ionic system simulating the realistic subject should be done. We have therefore chosen to study the three ion system which consisted of the mixed electrolytes having common anion, as representing a typical and simple example of multi-ionic system. Moreover, in order to observe simultaneously the detectable ion fluxes due to both cation and anion, use of the ion-exchange membrane having cation- and anion-exchange sites may be preferable from experimental standpoint. Thus, an amphoteric ion-exchange membrane was employed instead of homogeneous ion-exchange membrane.

The purpose of the present study is to clarify the correlation among behaviors of three ions within membrane.

Theory

We consider three ion system which consists of the amphoteric ion-exchange membrane and the mixed electrolyte solution having the common anion. According to the nonequilibrium thermodynamics,[3–5] the relationship between the current densities, i's and the transmembrane potential, V can be given as the following equation,

$$\begin{pmatrix} i_1 \\ i_2 \\ i_3 \end{pmatrix} = -\begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix} \begin{pmatrix} V-V_1 \\ V-V_2 \\ V-V_3 \end{pmatrix}, \tag{1}$$

where subscripts 1—3 refer to the ionic species in the system, V_1—V_3 denote the pseudoequilibrium potentials due to each ionic species, and g_{11}—g_{33}, nine elements of the conductance matrix. In the present system, we assume that Onsager's reciprocal relations are well held among the elements, i.e.,

$$g_{ij} = g_{ji}. \tag{2}$$

With help of Eq. 2, the numbers of elements to be determined are reduced to six from nine. At this point, introducing the contribution due to water, the elements to be determined increase to ten even using Eq. 2. Fortunately, it was pointed out in the previous papers[3–5] that the effect of water on the conductance matrix was negligible when the interaction between ions mainly contribute to the transport phenomena. Therefore, six independent experiments are needed to understand the ion transport phenomena in this system.

The conductance for ions, g_1—g_3 and the membrane conductance, G_m are given as[3]

$$g_k = g_{k1} + g_{k2} + g_{k3} \quad (k=1,2,3), \tag{3}$$

$$G_m = g_1 + g_2 + g_3, \tag{4}$$

where subscript k refers to ionic species.

Taking account of Eqs. 3 and 4, one can obtain the alternative expression of Eq. 1 as follows,

$$\begin{pmatrix} i_1 \\ i_2 \\ I \end{pmatrix} = -\begin{pmatrix} g_{11} & g_{12} & g_1 \\ g_{21} & g_{22} & g_2 \\ g_1 & g_2 & G_m \end{pmatrix} \begin{pmatrix} V_3-V_1 \\ V_3-V_2 \\ V-V_3 \end{pmatrix}. \tag{5}$$

On the other hand, when the supplied current is absent, the membrane current, I and the membrane potential, V_0 are written by

$$I = i_1 + i_2 + i_3, \tag{6}$$

$$V_0 = t_1V_1 + t_2V_2 + t_3V_3, \tag{7}$$

$$t_k = g_k/G_m \quad (k=1,2,3), \tag{8}$$

$$t_1 + t_2 + t_3 = 1, \tag{9}$$

where the subscript o refers to the absence of the supplied membrane current and t_k's are the transport numbers.

Considering the ionic currents in the presence and absence of the membrane currents, we have from Eq. 1,

$$i_k - i_k^0 = g_k(V-V_0) \quad (k=1,2,3), \tag{10}$$

where i_k^0 denotes the ionic current at zero membrane current.

When I=0, we obtain from Eq. 5,

$$\begin{aligned} i_1^0 &= -G_{11}^0(V_3-V_1) - G_{12}^0(V_3-V_2), \\ i_2^0 &= -G_{21}^0(V_3-V_1) - G_{22}^0(V_3-V_2), \end{aligned} \tag{11}$$

where

$$\begin{aligned} G_{11}^0 &= g_{11} - G_m t_1^2, \\ G_{12}^0 &= G_{21}^0 = g_{12} - G_m t_1 t_2, \\ G_{22}^0 &= g_{22} - G_m t_2^2. \end{aligned} \tag{12}$$

If the measurements of i_1^0 and i_2^0 are performed under the condition, either (V_3-V_1) or (V_3-V_2) is zero, Eq. 11 reduces to

$$\begin{aligned} i_1^0 &= -G_{12}^0(V_3-V_2), \\ i_2^0 &= -G_{22}^0(V_3-V_2), \end{aligned} \tag{13}$$

or

$$\begin{aligned} i_1^0 &= -G_{11}^0(V_3-V_1), \\ i_2^0 &= -G_{21}^0(V_3-V_1), \end{aligned} \tag{14}$$

respectively, Equations 13 and 14 serve to determine G_{11}^0, G_{12}^0, and G_{22}^0.

Combining Eq. 12 with Eqs. 3, 4 and 9, we obtain

$$\begin{aligned} g_{11} &= G_{11}^0 + G_m t_1^2, \quad g_{13} = G_m t_1(1-t_1-t_2) - G_{11}^0 - G_{12}^0, \\ g_{12} &= G_{12}^0 + G_m t_1 t_2, \quad g_{23} = G_m t_2(1-t_1-t_2) - G_{12}^0 - G_{22}^0, \\ g_{22} &= G_{22}^0 + G_m t_2^2, \quad g_{33} = G_m(1-t_1-t_2)^2 + G_{11}^0 + G_{22}^0 + 2G_{12}^0. \end{aligned} \tag{15}$$

Eq. 15 indicates that all the elements of conductance matrix can be determined when G_{11}^0, G_{12}^0, G_{22}^0, G_m, t_1, and t_2 are experimentally measured.

Experimental

In this study, Na, Ca, and Cl ions were chosen as three ions and six independent experiments were performed in order to determine the six independent conductance elements for the system consisting of membrane and mixed electrolyte solutions having the same concentrations of electrolytes in phases I and II.

Materials. An amphoteric ion-exchange membrane used in this work was supplied by Tokuyama Soda Co. Ltd.,[6,7] and the characteristics of the membrane and the conditioning before use were already described elsewhere.[8–10]

Procedure of Experiments. As outlined in theoretical section, six independent experiments such as the membrane conductance, G_m transport numbers, t_1 and t_2 and the ion fluxes, i_1^0 vs. V_3-V_1 and i_1^0 vs. V_3-V_2 under the condition of $V_3-V_1=0$ and i_2^0 vs. V_3-V_1 under the condition of $V_3-V_2=0$ were measured, respectively. Of these, the procedure of the experiments for G_m, t_1, and t_2 were the same as those described in the preceding papers.[8–10] As to ion fluxes, the concentration change of Na and Ca in mixed electrolyte solutions in chambers I and II across the membrane were measured against a lapse of time by an atomic absorption spectroscopy (Hitachi Co. Ltd., Model 180-50). All the experiments were carried out at 25 °C, and the electrolyte solutions in both chambers were sufficiently stirred by magnetic stirrer throughout the experiment.

Preparation of Mixed Electrolyte Solutions. On the preparation of mixed electrolyte solution, two kinds of electrolytes were suitably mixed so as to eliminate either of two driving forces in Eq. 11. That is, as NaCl and $CaCl_2$ are used in the present system and the subscripts 1, 2, and 3 correspond to Na, Ca, and Cl ion, respectively, the driving forces, V_3-V_1 and V_3-V_2 are written as

$$V_{Cl} - V_{Na} = \frac{RT}{F} \ln \frac{a_{Cl}^{II} a_{Na}^{II}}{a_{Cl}^{I} a_{Na}^{I}}, \tag{16}$$

$$V_{Cl} - V_{Ca} = \frac{RT}{F} \ln \frac{a_{Cl}^{II} (a_{Ca}^{II})^{1/2}}{a_{Cl}^{I} (a_{Ca}^{I})^{1/2}}, \tag{17}$$

where a denotes activity and the superscripts I and II refer to phases I and II, respectively. The prepared electrolyte solutions were summarized in Table 1(a), in which the concentrations of mixed electrolytes in phase II was kept constant while those in phase I were changed so as to make the values of Eq. 16 always zero. Table 1 (b) also shows the prepared electrolyte solutions in which the values of Eq. 17 are zero. For the membrane conductance and transport

Table 1. Concentration of Prepared Electrolyte Solutions

(a)

	NaCl / mol dm^{-3}	$CaCl_2$ / mol dm^{-3}
II	2.00×10^{-2}	1.50×10^{-2}
I-1	3.00×10^{-2}	0.05×10^{-2}
I-2	2.50×10^{-2}	0.60×10^{-2}
I-3	1.70×10^{-2}	2.20×10^{-2}
I-4	1.50×10^{-2}	3.00×10^{-2}

(b)

	NaCl / mol dm^{-3}	$CaCl_2$ / mol dm^{-3}
II	2.00×10^{-2}	1.50×10^{-2}
I-5	3.50×10^{-2}	1.10×10^{-2}
I-6	2.50×10^{-2}	1.40×10^{-2}
I-7	1.00×10^{-2}	1.75×10^{-2}
I-8	0.50×10^{-2}	2.00×10^{-2}

number measurements, the mixed electrolyte solutions of identical composition and concentration were placed in chambers I and II across membrane. The single ion activities in Table 1 were calculated according to Debye-Hückel equation for activity coefficient.[11]

Results and Discussion

The concentration changes of ions in phases I and II in the absence of applied current were examined as a function of time for all the systems in Tables 1(a) and (b), which have the concentration difference of ions between phases I and II. Figure 1 shows a typical example about the system made of first two columns in Table 1(a) in which moles of Ca ions transported across membrane were plotted against times. It can be recognized that Ca ion concentration in phase I increase and that of phase II decrease with a lapse of time, and the concentration changes are linear against time within experimental error. This fact suggests that the transport of Ca ion is in a steady state. The mean absolute values of concentration changes in phases I and II were plotted against time in Figs. 2(a), 2(b), and 2(c). Figures 2(a) and 2(b) indicate Δn_{Na} vs. time plot and Δn_{Ca} vs. time plot under the condition, $V_{Cl}-V_{Na}=0$. The ion flux, J_i^0 was evaluated from the slopes in Fig . 2 as follows,

$$J_i^0=\frac{\Delta n_i}{tS}, \tag{18}$$

where t and S denote time interval in second and the membrane area in cm^2, respectively. Taking account of the electricity on the ion fluxes, one can obtain the

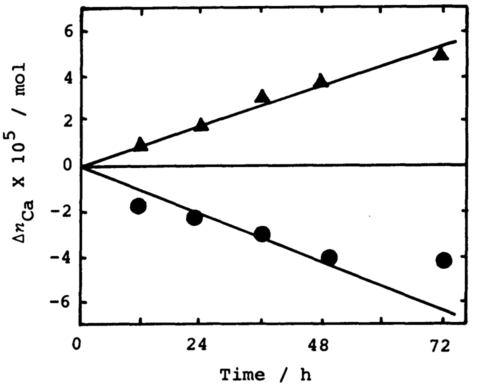

Fig. 1. A typical example of Ca concentration change across membrane against time.
System: NaCl, 3.00X10^{-2} mol dm^{-3}, CaCl$_2$, 0.05X10^{-2} mol dm^{-3} in phase I, ▲; NaCl, 2.00X10^{-2} mol dm^{-3}, CaCl$_2$, 1.50X10^{-2} mol dm^{-3} in phase II, ●.

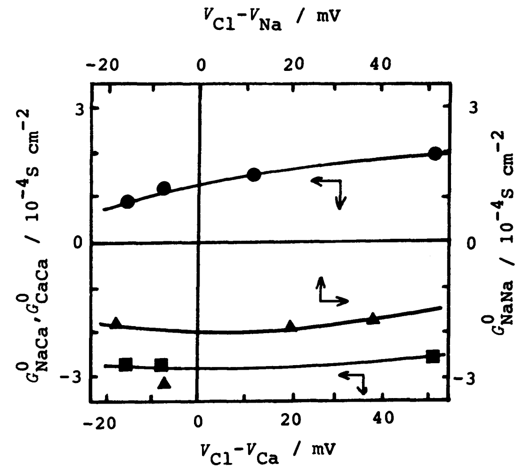

Fig. 3. Relation of G^0_{NaNa}, G^0_{NaCa}, and G^0_{CaCa} vs. $V_{Cl}-V_{Na}$ or $V_{Cl}-V_{Ca}$. ▲: G^0_{NaNa}, ●: G^0_{NaCa}, ■: G^0_{CaCa}.

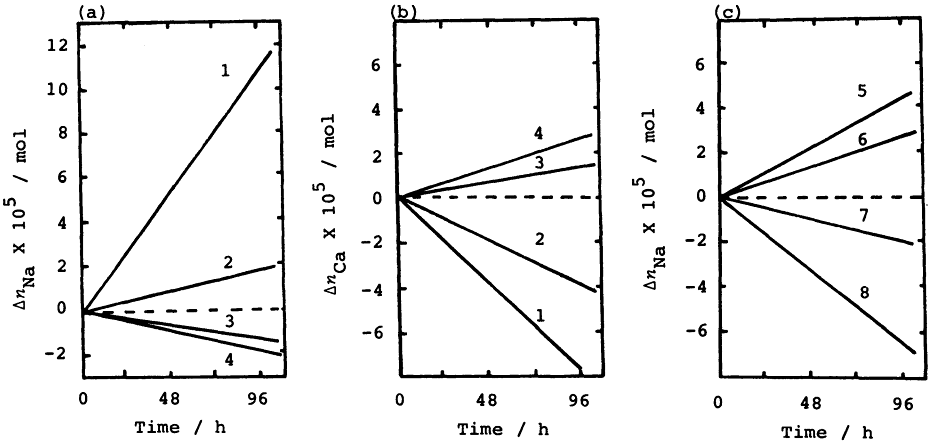

Fig. 2.(a). Na concentration change, Δn_{Na} against time under the condition that $V_{Cl}-V_{Na}=0$. The numbers in figure are those of phase I in Table 1(a).

(b). Δn_{Ca} against time under the condition that $V_{Cl}-V_{Na}=0$. The numbers are the same as in (a).

(c). Δn_{Na} against time under the condition that $V_{Cl}-V_{Ca}=0$. The numbers correspond to those of phase I in Table 1(b).

Table 2. Values of Membrane Conductance and Transport Numbers Together with Values of Conductance Elements

G_m (1.27×10^{-3})	g_{NaNa} (2.45×10^{-4})	g_{CaCa} (5.84×10^{-4})
t_{Na} (0.22)	g_{NaCa} (0.09×10^{-4})	g_{CaCl} (0.29×10^{-4})
t_{Ca} (0.49)	g_{NaCl} (0.25×10^{-4})	g_{ClCl} (3.14×10^{-4})

All the units are S cm^{-2} except the transport number, t.

ion current density, $i_i^0=z_iFJ_i^0$ in the absence of the supplied currents. The obtained i_1^0's were divided by $V_{Cl}-V_{Na}$ or $V_{Cl}-V_{Ca}$ and plotted against $V_{Cl}-V_{Na}$ or $V_{Cl}-V_{Ca}$ in Fig. 3. According to Eq. 12, the quantities in Fig. 3 contain important informations concerning the elements in conductance matrix given by Eqs. 1 or 5. As mentioned in experimental section, the membrane conductance and transport numbers were obtained under the experimental conditions that ionic concentration difference between the mixed electrolyte solutions in phases I and II are all zero. This corresponds to the case in which $V_{Cl}-V_{Na}$ or $V_{Cl}-V_{Ca}$ in Fig. 3 is extrapolated to zero. The values of G_{NaNa}^0, G_{NaCa}^0 and G_{CaCa}^0, at $V_{Cl}-V_{Na}=V_{Cl}-V_{Ca}=0$ were estimated from Fig. 3 by interpolation.

On the other hand, the electrodialysis[8] and the membrane resistance were measured to obtain the transport numbers, t_{Na} and t_{Ca} and the membrane conductance, G_m for the membrane-electrolyte solution system in which the electrolyte solutions in phases I and II are identical. The results are shown in Table 2 together with the values of conductance elements estimated according to Eq. 15.

It can be seen in Table 2 that $g_{CaCa}>g_{ClCl}>g_{NaNa}>g_{CaCl}>g_{NaCl}>g_{CaNa}$. It is impressive that the tendency is partly in accord with $g_{CaCa}\simeq g_{ClCl}>-g_{CaCl}$ in the other amphoteric membrane system[3] in contrast to the result in the cation-exchange membrane, $g_{CaCa}>g_{CaCl}>g_{ClCl}$ in the previous paper.[12] As to the first three elements, the order in the present work also corresponds to that of the transport numbers in Table 2 ($t_{Cl}=1-t_{Na}-t_{Ca}=0.29$). This means that the g factors partly reflect the ionic composition within membrane. As seen in comparison with t in a single electrolyte system that $t_{Na}=0.90$ and $t_{Cl}=0.10$ in NaCl system and $t_{Ca}=0.62$ and $t_{Cl}=0.38$ in $CaCl_2$ system, respectively, the situation in mixed electrolyte system is largely different from the single electrolyte system, however. The reason for the inversion of g_{NaNa} and g_{ClCl} in mixed system is not clear in the present, but a possible explanation is that Cl ion within membrane may be relatively concentrated. That is, for the sake of high selectivity of Ca ion over Na ion to the sites in the case of mixed solutions,[8] Na ion may be excluded from the membrane. On the contrary, Cl ion may sufficiently be retained around the anion-exchange sites. The smaller value of g_{NaNa} compared with g_{ClCl} may be attributed to the different behaviors in mixed electrolyte.

The remained three elements, which express the interactions between the different ionic species, can not be ignored. The small but finite values mean that the respective ion fluxes are subject to the coupled forces and the coupling plays an important role in ion-transport phenomena.

Thus, it may be concluded that the transport phenomena can not be predicted by a simple combination of the single electrolyte systems, but the interaction among ions should be taken into account.

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