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Ion Transport Phenomena across the Parallel Composite Membrane

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The equations of ionic currents in the parallel composite membrane-NaCl system were derived from the phenomenological equations presented by Kedem and Katchalsky.

The elements of the conductance matrix for the composite membrane system, $g_{\alpha\beta}$, as well as those for the single membrane systems with cation-exchange or anion-exchange membranes, $\overline{g}^{\mathrm{c}}_{\alpha\beta}$ or $\overline{g}^{\mathrm{a}}_{\alpha\beta}$, respectively, were determined by the measurements of membrane potential, membrane conductance, and salt flux. It was found that $g^{\mathrm{c}}_{\alpha\beta}$ or $g^{\mathrm{a}}_{\alpha\beta}$ for the constituent elements of the composite membrane system was different from $\overline{g}^{\mathrm{c}}_{\alpha\beta}$ or $\overline{g}^{\mathrm{a}}_{\alpha\beta}$ for the single membrane systems, respectively. These differences may be attributed to the situation that $g^{\mathrm{c}}_{\alpha\beta}$ and $g^{\mathrm{a}}_{\alpha\beta}$ represent the intra- and intermembrane transport phenomena, while $\overline{g}^{\mathrm{c}}_{\alpha\beta}$ and $\overline{g}^{\mathrm{a}}_{\alpha\beta}$ represent the former phenomena only. The composite membrane system is characterized by the large cross coefficient which is comparable in the magnitude to the straight coefficients, i.e., $g_{\mathrm{Na\cdot Cl}} \approx g_{\mathrm{Na\cdot Na}} \approx g_{\mathrm{Cl\cdot Cl}}$. Kedem and Katchalsky have predicted that the strong circulation of current is produced by the partial currents through the element membranes even when the total membrane current is absent. However, because of the large cross coefficient, the partial current through each element membrane due to the conjugate force is nearly canceled by that due to the nonconjugate force.

Since the interesting transport properties of mosaic membranes were first noticed by Sollner,[1] mosaic membranes have been investigated by many workers who are interested in the functions of biological membranes[2,3] or in the desalination of sea water.[4,5] The simplest type of mosaic membranes is a composite membrane composed of a pair of cation-exchange and anion-exchange membranes.

In spite of many experimental works, however, not so many theories for describing transport phenomena across composite membranes have been presented so far. One of the theories has been presented on the basis of nonequilibrium thermodynamics by Kedem and Katchalsky,[6,7] but it was no easy matter to use the theory for analyzing experimental data. They have only estimated the transport coefficients of composite membranes by using the parameters assumed from transport properties of synthetic membranes.

On the other hand, the theory closely related with experimental measurements has also been developed on the basis of nonequilibrium thermodynamics mainly by one of the authors and has been applied to various membrane systems.[8—11]

In the present study, beginning with the phenomenological equations presented by Kedem and Katchalsky, the relations for analyzing experimental data on the composite membrane systems were derived in the same way as described previously.[9] The electrochemical measurements on the composite membrane system as well as on the single membrane systems were carried out and the results were analyzed according to the derived relations. The transport properties of the composite membrane system were compared with those of the single membrane systems.

Theoretical

We shall consider the ion transport phenomena through a parallel composite membrane, by which a NaCl solution in the phase I is separated from another NaCl solution in the phase II. A composite membrane is composed of a parallel array of cation-exchange and anion-exchange membranes as the constituent elements.

According to Kedem and Katchalsky, the flux of ion α through a composite membrane, j_α, is expressed as the area fraction-weighted sum of the partial fluxes through each element membrane,

$$j_\alpha = \sum_r \gamma^r j^r_\alpha \quad (\alpha; \mathrm{Na}^+, \mathrm{Cl}^-) \quad (r; \mathrm{c}, \mathrm{a}) \tag{1}$$

where γ^r is the area fraction of the r-th element, j^r_α, the flux of ion α through the r-th element, and c and a refer to cation-exchange and anion-exchange element membranes, respectively.

They have described ion fluxes through each element membrane by the following phenomenological equations,[7]

$$j^r_\alpha = -\sum_\beta l^r_{\alpha\beta} \Delta\tilde{\mu}_\beta, \tag{2}$$

where $l^r_{\alpha\beta}$ is a phenomenological coefficient and satisfies the reciprocal relation of Onsager,

$$l^r_{\alpha\beta} = l^r_{\beta\alpha}, \quad (\alpha \neq \beta) \tag{3}$$

and $\Delta\tilde{\mu}_\beta$ is the difference in the electrochemical potential of ion β.

The water flux is neglected in Eqs. 1 and 2, because it has already been confirmed that the solvent effect on the elements of conductance matrix is negligibly small in spite of high water permeability.[11]

Using Eqs. 1 and 2, the total flux of ion α can be written as

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$$j_\alpha = -\sum_\beta l_{\alpha\beta}\Delta\tilde{\mu}_\beta, \tag{4}$$

where

$$l_{\alpha\beta} = \sum_r \gamma^r l^r_{\alpha\beta}. \tag{5}$$

From Eqs. 3 and 5, $l_{\alpha\beta}$ also satisfies the reciprocal relation of Onsager.

$$l_{\alpha\beta} = l_{\beta\alpha}. \quad (\alpha \neq \beta) \tag{6}$$

According to the definition of electrochemical potential, $\Delta\tilde{\mu}_\beta$ can be written as

$$\Delta\tilde{\mu}_\beta = \tilde{\mu}^{\mathrm{II}}_\beta - \tilde{\mu}^{\mathrm{I}}_\beta = Z_\beta F(V - V_\beta), \tag{7}$$

where

$$V = \phi^{\mathrm{II}} - \phi^{\mathrm{I}}, \tag{8}$$

$$V_\beta = (RT/Z_\beta F)\ \ln a^{\mathrm{I}}_\beta / a^{\mathrm{II}}_\beta, \tag{9}$$

where Z_β is the valency of ion β, F; Faraday constant, ϕ; the electric potential, V; the transmembrane potential, V_β; the equilibrium membrane potential of ion β, R; gas constant, a_β; the activity of ion β.

Using Eq. 7, Eq. 4 can be rewritten as

$$j_\alpha = -\sum_\beta Z_\beta F l_{\alpha\beta}(V - V_\beta). \tag{10}$$

Equation 10 multiplied by $Z_\alpha F$ gives the equation for ionic current,

$$i_\alpha = Z_\alpha F j_\alpha = -\sum_\beta g_{\alpha\beta}(V - V_\beta), \tag{11}$$

where the element of the conductance matrix, $g_{\alpha\beta}$, is given as

$$g_{\alpha\beta} = Z_\alpha Z_\beta F^2 l_{\alpha\beta}, \tag{12}$$

and the reciprocal relation of Onsager also holds for $g_{\alpha\beta}$ from Eq. 6.

Using Eq. 5, the overall coefficient can be related to the partial coefficients as follows,

$$g_{\alpha\beta} = \sum_r \gamma^r g^r_{\alpha\beta}, \tag{13}$$

where

$$g^r_{\alpha\beta} = Z_\alpha Z_\beta F^2 l^r_{\alpha\beta}. \tag{14}$$

Equation 11 is the same in the form as the equation of ionic current derived for the single membrane system and the same holds for the other relations derived from Eq. 11.

The relations required for analyzing the experimental data are summarized below.[9] For the present system, Eq. 11 is expressed in the explicit form as follows,

$$\begin{aligned} i_{\mathrm{Na}} &= -g_{\mathrm{Na\cdot Na}}(V - V_{\mathrm{Na}}) - g_{\mathrm{Na\cdot Cl}}(V - V_{\mathrm{Cl}}), \\ i_{\mathrm{Cl}} &= -g_{\mathrm{Cl\cdot Na}}(V - V_{\mathrm{Na}}) - g_{\mathrm{Cl\cdot Cl}}(V - V_{\mathrm{Cl}}). \end{aligned} \tag{15}$$

The membrane current, I, is given by the sum of the ionic currents.

$$\begin{aligned} I = i_{\mathrm{Na}} + i_{\mathrm{Cl}} &= -g_{\mathrm{Na}}(V - V_{\mathrm{Na}}) - g_{\mathrm{Cl}}(V - V_{\mathrm{Cl}}) \\ &= -G_{\mathrm{m}}(V - V_0), \end{aligned} \tag{16}$$

where

$$g_{\mathrm{Na}} = g_{\mathrm{Na\cdot Na}} + g_{\mathrm{Na\cdot Cl}}, \quad g_{\mathrm{Cl}} = g_{\mathrm{Cl\cdot Na}} + g_{\mathrm{Cl\cdot Cl}}, \tag{17}$$

$$G_{\mathrm{m}} = g_{\mathrm{Na}} + g_{\mathrm{Cl}}, \tag{18}$$

$$V_0 = (g_{\mathrm{Na}}V_{\mathrm{Na}} + g_{\mathrm{Cl}}V_{\mathrm{Cl}})/G_{\mathrm{m}} = t_{\mathrm{Na}}V_{\mathrm{Na}} + t_{\mathrm{Cl}}V_{\mathrm{Cl}} \tag{19}$$

$$t_{\mathrm{Na}} = g_{\mathrm{Na}}/G_{\mathrm{m}}, \quad t_{\mathrm{Cl}} = g_{\mathrm{Cl}}/G_{\mathrm{m}} \tag{20}$$

where g_α is the ionic conductance, G_{m}; the membrane conductance, V_0; the membrane potential at zero membrane current, t_α; the transport number of ion α.

Using Eqs. 13, 17, and 18, the relations between overall and partial coefficients are given as follows,

$$G_{\mathrm{m}} = \gamma^{\mathrm{c}} G^{\mathrm{c}}_{\mathrm{m}} + \gamma^{\mathrm{a}} G^{\mathrm{a}}_{\mathrm{m}}, \tag{21}$$

$$g_\alpha = \gamma^{\mathrm{c}} g^{\mathrm{c}}_\alpha + \gamma^{\mathrm{a}} g^{\mathrm{a}}_\alpha, \tag{22}$$

where

$$G^r_{\mathrm{m}} = g^r_\alpha + g^r_\beta, \quad g^r_\alpha = g^r_{\alpha\alpha} + g^r_{\alpha\beta}. \tag{23}$$

Using the conditions for zero membrane current, i.e., $V = V_0$ and $i^{\circ}_\alpha + i^{\circ}_\beta = 0$, and eliminating $(V_0 - V_\beta)$ in Eq. 11, we have the expression for the ionic current at zero membrane current, i°_α.

$$i^{\circ}_\alpha = -g^{\circ}_\alpha(V_0 - V_\alpha), \tag{24}$$

where the ionic conductance at zero membrane current, g°_α, is given as

$$g^{\circ}_\alpha = (g_{\alpha\alpha}g_{\beta\beta} - g^2_{\alpha\beta})/g_\beta. \tag{25}$$

Equation 25 divided by g_α gives the following relation,

$$g^{\circ}_\alpha / g_\alpha = 1 - g_{\alpha\beta}(1/g_\alpha + 1/g_\beta), \tag{26}$$

and $g^{\circ}_\alpha/g_\alpha$ is equal to g°_β/g_β because of $g_{\alpha\beta} = g_{\beta\alpha}$.

Experimental

Materials. The MC-3470 and MA-3475 membranes developed by Ionac Chem. Co. were used as cation-exchange and anion-exchange membranes, respectively. The 2-cyanoacrylate adhesive for dental use, Dental Cyanon, purchased from Koatsu Gas Ind. Co. was used for sticking the membranes on the glass cell.

Procedure. The glass cell used for the present experiments is schematically shown in Fig. 1. The glass cell is consisted of two half cells, connected with ground-glass joint. One of the half cells has two holes of the semicircular type, over which the membrane was stuck with the adhesive. Special care was taken to prevent the membrane from absorbing the adhesive. First the adhesive was applied around the hole of the glass cell and was allowed to stand for till it became gelatinous. The wetted membrane was pressed between two sheets of filter paper and was stuck on the edge of the hole, then it was left over night. The day after, the adhesive was again applied on the edge of the membrane, keeping the active area of the membrance wetted. The active areas of cation-exchange and anion- exchange membranes were 4.9 and 5.8 cm^2, respectively.

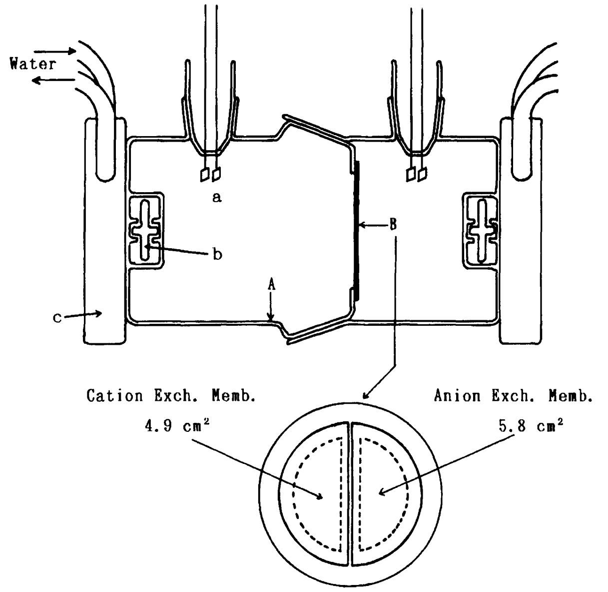

Fig. 1. Schematic diagram of the experimental cell assembly. A; Glass cell. B; Parallel composite membrane. a; The Pt–Pt electrode which was replaced by the Ag–AgCl electrode for the measurement of membrane potential. b; Magnetic spin bar. c; Magnetic stirrer driven by water stream.

For the experiments in the single membrane systems, one of the holes of the cell was blocked by sticking an acrylic plate on it with the adhesive.

The whole assembly was thermostated at 25±0.02°C. The solution in each compartment was stirred with the magnetic stirrer driven by a water stream.

The membrane potential was measured by means of two Ag–AgCl electrodes connected to the Orion digital pH meter Model 701.

The salt flux was followed by measuring the electric conductance of the solution by means of a pair of Pt–Pt electrodes connected to the Yanagimoto conductivity outfit Model MY-7.

The membrane conductance was separately measured with the procedure similar to that described elsewhere.[12)]

The concentration of NaCl in the phase I was varied from 10^{-1} to 10^{-3} mol dm^{-3}, while that in the phase II was kept constant at 10^{-2} mol dm^{-3}.

Results and Discussion

The membrane potential for the composite membrane system, V_0, as well as those for the single membrane systems with cation-exchange and anion-exchange membranes, $\overline{V}_0^{c}$ and $\overline{V}_0^{a}$, respectively, are plotted against the mean activity of NaCl in the phase I, as shown in Fig. 2. The physical properties in the single membrane systems, e.g., $\overline{V}_0^{c}$, are distinguished from those in the composite membrane system by an overbar.

The membrane conductances, G_m, $\overline{G}_m^{c}$, and $\overline{G}_m^{a}$ are shown in Fig. 3. The observed G_m can be approximately represented by substituting $\overline{G}_m^{c}$ and $\overline{G}_m^{a}$ for G_m^{c} and G_m^{a} in Eq. 21, respectively, suggesting $G_m^{c} \approx \overline{G}_m^{c}$ and $G_m^{a} \approx \overline{G}_m^{a}$.

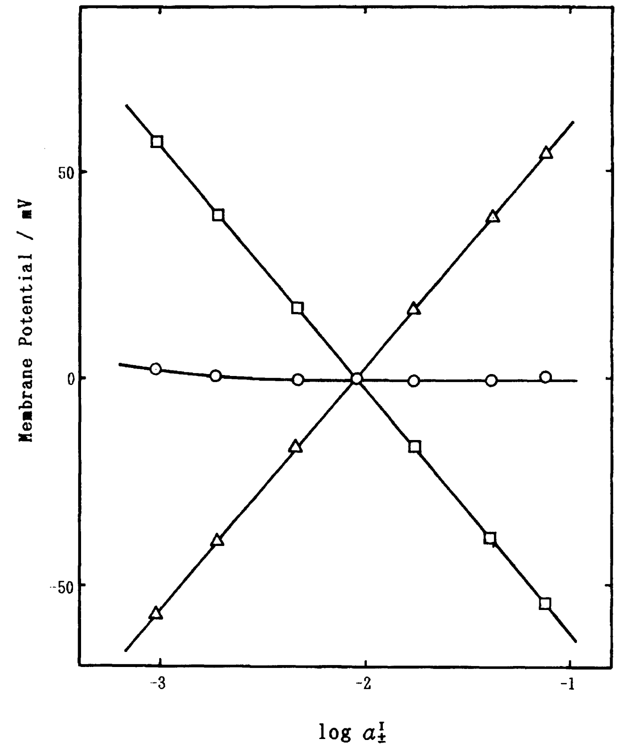

Fig. 2. Plots of membrane potential vs. logarithmic mean activity of NaCl in phase I. ○; Composite membrane, △; Cation-exchange membrane, □; Anion-exchange membrane.

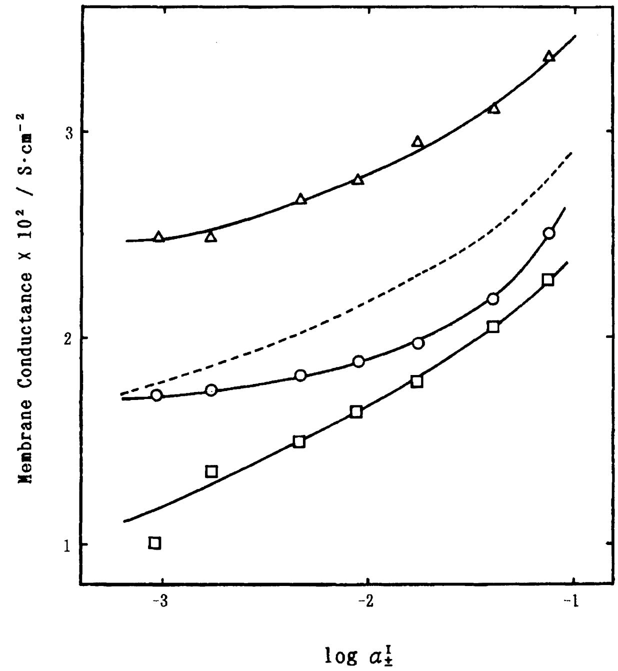

Fig. 3. Plots of membrane conductance vs. logarithmic mean activity of NaCl in phase I. ○; Composite membrane, △; Cation-exchange membrane, □; Anion-exchange membrane. Broken line; $\gamma^{c}\overline{G}_m^{c}+\gamma^{a}\overline{G}_m^{a}$.

The salt fluxes, J_s, $\overline{J}^c_s$, and $\overline{J}^a_s$, are shown in Fig. 4. Although J_s is larger than $\overline{J}^c_s$ or $\overline{J}^a_s$ by a factor of about ten, it seems to be not so large as expected from the transport properties of permselective membranes in the single membrane systems.

We will roughly estimate the salt flux expected from the transport properties of the permselective membranes. Assuming that $\overline{g}^r_{\alpha\beta}$ can be substituted for $g^r_{\alpha\beta}$, we have from Eqs. 11 and 13 at zero membrane current

$$\begin{aligned} i^{\circ}_{\alpha} &= -\sum_{\beta}\sum_{r}\gamma^r g^r_{\alpha\beta}(V_0 - V_\beta) \\ &= -\sum_{\beta}\sum_{r}\gamma^r \overline{g}^r_{\alpha\beta}(V_0 - V_\beta). \end{aligned} \tag{27}$$

For the ion exchange membrane, r, permselective to ion α, the relations, $\overline{g}^r_{\alpha\alpha} \gg \overline{g}^r_{\alpha\beta} \gg \overline{g}^r_{\beta\beta}$ and $\overline{G}^r_m \approx \overline{g}^r_\alpha \approx \overline{g}^r_{\alpha\alpha}$, have been observed[9] and this is also true for the present single membrane systems, as will be described later. Then, Eq. 27 reduces to

$$\begin{aligned} i^{\circ}_{\mathrm{Na}} &\approx -\gamma^c\overline{g}^c_{\mathrm{Na\cdot Na}}(V_0 - V_{\mathrm{Na}}) \approx -\gamma^c\overline{G}^c_m(V_0 - V_{\mathrm{Na}}), \\ i^{\circ}_{\mathrm{Cl}} &\approx -\gamma^a\overline{g}^a_{\mathrm{Cl\cdot Cl}}(V_0 - V_{\mathrm{Cl}}) \approx -\gamma^a\overline{G}^a_m(V_0 - V_{\mathrm{Cl}}). \end{aligned} \tag{28}$$

The properties in Eq. 28 observed at $a^{\mathrm{I}}_{\pm} = 4.08 \times 10^{-2}$ mol dm^{-3} were as follows,

$\gamma^c = 0.46$, $\overline{G}^c_m = 3.1 \times 10^{-2}$ S cm^{-2}, $V_0 - V_{\mathrm{Na}} = -0.041$ V,
$\gamma^a = 0.54$, $\overline{G}^a_m = 2.1 \times 10^{-2}$ S cm^{-2}, $V_0 - V_{\mathrm{Cl}} = 0.037$ V.

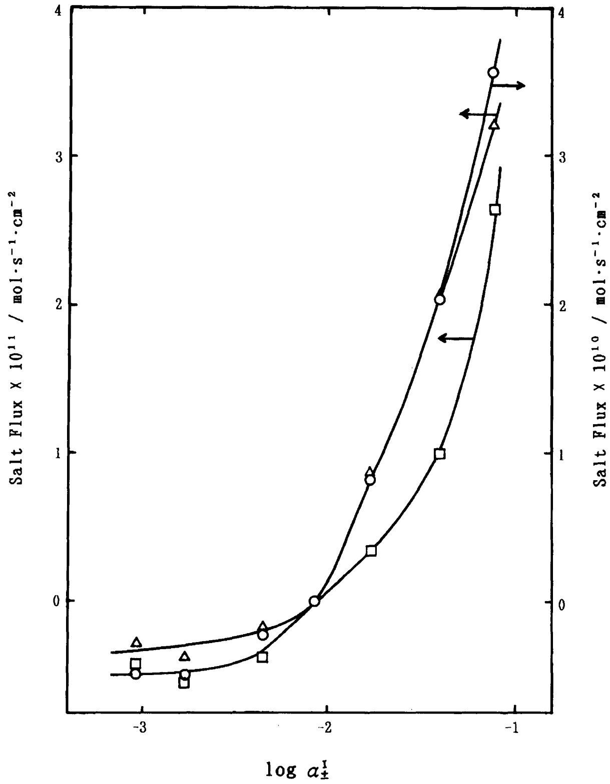

Fig. 4. Plots of salt flux vs. logarithmic mean activity of NaCl in phase I. ○; Composite membrane, △; Cation-exchange membrane, □; Anion-Exchange membrane.

Substituting these values in Eq. 28, we have $J_{\mathrm{Na}} = i^{\circ}_{\mathrm{Na}}/F \approx 6.0 \times 10^{-9}$ and $J_{\mathrm{Cl}} = -i^{\circ}_{\mathrm{Cl}}/F \approx 4.4 \times 10^{-9}$ mol s^{-1} cm^{-2}.

Since the above discussion is based on the assumption that $\overline{g}^r_{\alpha\beta}$ can be substituted for $g^r_{\alpha\beta}$, the ionic fluxes satisfying the requirement for salt flux, i.e., $J_s = J_{\mathrm{Na}} = J_{\mathrm{Cl}}$, can not be obtained. However, the estimated ionic fluxes are larger than the salt flux observed in the composite membrane system, 2.0×10^{-10} mol s^{-1} cm^{-2} at $a^{\mathrm{I}}_{\pm} = 4.08 \times 10^{-2}$ mol dm^{-3}, by a factor of several tens. The reason for this discrepancy will be discussed later.

The transport numbers of Na$^+$ ion, t_{Na}, $\overline{t}^c_{\mathrm{Na}}$ and $\overline{t}^a_{\mathrm{Na}}$, estimated from the potential data according to Eq. 19 are summarized in Table 1. The ionic conductances, g_α, $\overline{g}^c_\alpha$, and $\overline{g}^a_\alpha$, were estimated from the membrane conductances and the transport numbers according to Eq. 20 and are shown in Fig. 5. The ionic conductances at zero membrane current, g°_α, $\overline{g}^{\circ c}_\alpha$ and $\overline{g}^{\circ a}_\alpha$, were estimeted from the potential and salt flux data according to Eq. 24 and are also shown in Fig. 5. We see in this figure that $g_{\mathrm{Na}} \approx g_{\mathrm{Cl}}$, $g^{\circ}_{\mathrm{Na}} \approx g^{\circ}_{\mathrm{Cl}}$, $g_{\mathrm{Na}} \gg g^{\circ}_{\mathrm{Na}}$, and $g_{\mathrm{Cl}} \gg g^{\circ}_{\mathrm{Cl}}$ for the composite membrane system, while $\overline{g}^c_{\mathrm{Na}} \gg \overline{g}^{\circ c}_{\mathrm{Na}} \gg \overline{g}^c_{\mathrm{Cl}} \gg \overline{g}^{\circ c}_{\mathrm{Cl}}$ and $\overline{g}^a_{\mathrm{Cl}} \gg \overline{g}^{\circ a}_{\mathrm{Cl}} \gg \overline{g}^a_{\mathrm{Na}} \gg \overline{g}^{\circ a}_{\mathrm{Na}}$ for the single membrane systems with cation-exchange and anion-exchange membranes, respectively.

The observed g_α can be approximately represented by substituting $\overline{g}^c_\alpha$ and $\overline{g}^a_\alpha$ for g^c_α and g^a_α in Eq. 22, respectively, as seen in Fig. 5, suggesting $g^c_\alpha \approx \overline{g}^c_\alpha$ and $g^a_\alpha \approx \overline{g}^a_\alpha$.

According to Eq. 26, the values of $g_{\alpha\beta}$ were estimated from g_α, g°_α, and g_β, then they were substituted in Eq. 17 to obtain $g_{\alpha\alpha}$ and $g_{\beta\beta}$. The corresponding values of $\overline{g}^c_{\alpha\beta}$ and $\overline{g}^a_{\alpha\beta}$ were similarly estimated and are shown in Fig. 6 together with those of $g_{\alpha\beta}$.

The characteristic feature of the composite membrane system appears in the elements of the conductance matrix, as seen in Fig. 6, where the cross coefficient is as large as the straight coefficients, i.e., $g_{\mathrm{Na\cdot Cl}} \approx g_{\mathrm{Na\cdot Na}} \approx g_{\mathrm{Cl\cdot Cl}}$. According to Eq. 17, g_α is, therefore, consisted of $g_{\alpha\alpha}$ and $g_{\alpha\beta}$ of nearly the same magnitude, while $\overline{g}^c_{\mathrm{Na}}$ or $\overline{g}^a_{\mathrm{Cl}}$ are exclusively represented by $\overline{g}^c_{\mathrm{Na\cdot Na}}$ or $\overline{g}^a_{\mathrm{Cl\cdot Cl}}$, respectively.

Using Eqs. 18 and 20, Eq. 26 can be rewritten as

$$g_{\mathrm{Na\cdot Cl}} = t_{\mathrm{Cl}}(g_{\mathrm{Na}} - g^{\circ}_{\mathrm{Na}}) = t_{\mathrm{Na}}(g_{\mathrm{Cl}} - g^{\circ}_{\mathrm{Cl}}) = g_{\mathrm{Cl\cdot Na}}, \tag{29}$$

and we have from Eqs. 17 and 29

Table 1. Transport Numbers of Na$^+$ Ion

$a^{\mathrm{I}}_{\pm}$/ mol dm^{-3}	t_{Na}	$\overline{t}^c_{\mathrm{Na}}$	$\overline{t}^a_{\mathrm{Na}}$
7.66×10^{-2}	0.49	0.99_2	0.00_5
4.08×10^{-2}	0.48	0.99_2	0.00_3
1.74×10^{-2}	0.45	0.98_2	0.00_3
9.01×10^{-3}	—	—	—
4.64×10^{-3}	0.50	0.98_8	0.00_3
1.90×10^{-3}	0.48	0.99_5	0.00_3
9.65×10^{-4}	0.46	0.99_7	0.00_2

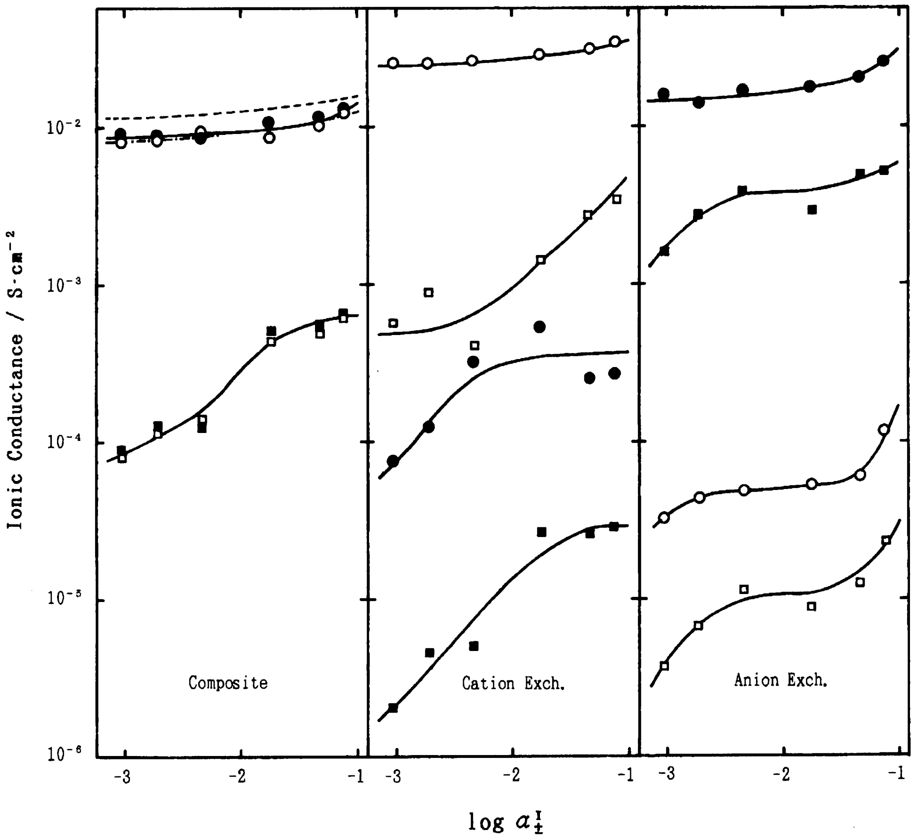

Fig. 5. Plots of ionic conductance and ionic conductance at zero membrane current vs. logarithmic mean activity of NaCl in phase I. ○; g_{Na}, $\bar{g}^{\mathrm{c}}_{\mathrm{Na}}$, and $\bar{g}^{\mathrm{a}}_{\mathrm{Na}}$, ●; g_{Cl}, $\bar{g}^{\mathrm{c}}_{\mathrm{Cl}}$, and $\bar{g}^{\mathrm{a}}_{\mathrm{Cl}}$, □; $g^{\mathrm{o}}_{\mathrm{Na}}$, $\bar{g}^{\mathrm{oc}}_{\mathrm{Na}}$, and $\bar{g}^{\mathrm{oa}}_{\mathrm{Na}}$, ■; $g^{\mathrm{o}}_{\mathrm{Cl}}$, $\bar{g}^{\mathrm{oc}}_{\mathrm{Cl}}$, and $\bar{g}^{\mathrm{oa}}_{\mathrm{Cl}}$. Broken line; $\gamma^{\mathrm{c}}\bar{g}^{\mathrm{c}}_{\mathrm{Na}}+\gamma^{\mathrm{a}}\bar{g}^{\mathrm{a}}_{\mathrm{Na}}$, Chain-dottet line; $\gamma^{\mathrm{c}}\bar{g}^{\mathrm{c}}_{\mathrm{Cl}}+\gamma^{\mathrm{a}}\bar{g}^{\mathrm{a}}_{\mathrm{Cl}}$.

$$\begin{aligned} g_{\mathrm{Na}\cdot\mathrm{Na}} &= g_{\mathrm{Na}} - g_{\mathrm{Na}\cdot\mathrm{Cl}} = t_{\mathrm{Na}}g_{\mathrm{Na}} + t_{\mathrm{Cl}}g^{\mathrm{o}}_{\mathrm{Na}}, \\ g_{\mathrm{Cl}\cdot\mathrm{Cl}} &= g_{\mathrm{Cl}} - g_{\mathrm{Na}\cdot\mathrm{Cl}} = t_{\mathrm{Cl}}g_{\mathrm{Cl}} + t_{\mathrm{Na}}g^{\mathrm{o}}_{\mathrm{Cl}}. \end{aligned} \tag{30}$$

Taking into account the results that $g_{\mathrm{Na}}\approx g_{\mathrm{Cl}}$, $g_{\mathrm{Na}}\gg g^{\mathrm{o}}_{\mathrm{Na}}$, $g_{\mathrm{Cl}}\gg g^{\mathrm{o}}_{\mathrm{Cl}}$, and $t_{\mathrm{Na}}\approx t_{\mathrm{Cl}}$, the observed relation, i.e. $g_{\mathrm{Na}\cdot\mathrm{Cl}}\approx g_{\mathrm{Na}\cdot\mathrm{Na}}\approx g_{\mathrm{Cl}\cdot\mathrm{Cl}}$, is understandable from Eqs. 29 and 30.

Since the cross coefficient for the single membrane system can also be expressed by the equation of the same form as Eq. 29, the cross coefficient of less permselective membranes is expected to be large and this is the case for amphoteric membranes.[10] In the case of amphoteric membranes, the absolute value of $g_{\mathrm{Na}\cdot\mathrm{Cl}}$ is nearly equal to $g_{\mathrm{Na}\cdot\mathrm{Na}}$ and $g_{\mathrm{Cl}\cdot\mathrm{Cl}}$, though $g_{\mathrm{Na}\cdot\mathrm{Cl}}<0$ because of $g_{\mathrm{Na}}\ll g^{\mathrm{o}}_{\mathrm{Na}}$ and $g_{\mathrm{Cl}}\ll g^{\mathrm{o}}_{\mathrm{Cl}}$.

It can be seen from Fig. 6 that $g_{\alpha\beta}=\gamma^{\mathrm{c}}g^{\mathrm{c}}_{\alpha\beta}+\gamma^{\mathrm{a}}g^{\mathrm{a}}_{\alpha\beta}\neq\gamma^{\mathrm{c}}\bar{g}^{\mathrm{c}}_{\alpha\beta}+\gamma^{\mathrm{a}}\bar{g}^{\mathrm{a}}_{\alpha\beta}$, especially, $g_{\mathrm{NaCl}}=\gamma^{\mathrm{c}}g^{\mathrm{c}}_{\mathrm{NaCl}}+\gamma^{\mathrm{a}}g^{\mathrm{a}}_{\mathrm{Na}\cdot\mathrm{Cl}}\gg\gamma^{\mathrm{c}}\bar{g}^{\mathrm{c}}_{\mathrm{Na}\cdot\mathrm{Cl}}+\gamma^{\mathrm{a}}\bar{g}^{\mathrm{a}}_{\mathrm{Na}\cdot\mathrm{Cl}}$. This implies that $g^{\mathrm{c}}_{\alpha\beta}$ and $g^{\mathrm{a}}_{\alpha\beta}$ for the constituent elements of the composite membrane system are different from $\bar{g}^{\mathrm{c}}_{\alpha\beta}$ and $\bar{g}^{\mathrm{a}}_{\alpha\beta}$ for the single membrane systems, respectively. Thus, the ion transport phenomena in the composite membrane system cannot be explained in terms of the properties of the single membrane systems.

Since it has already been confirmed that the solvent effect on the elements of the conductance matrix is negligibly small,[11] the differences between $g^{\mathrm{c}}_{\alpha\beta}$ and $\bar{g}^{\mathrm{c}}_{\alpha\beta}$ or between $g^{\mathrm{a}}_{\alpha\beta}$ and $\bar{g}^{\mathrm{a}}_{\alpha\beta}$ cannot be attributed to the ion-solvent interaction which is neglected in our theoretical treatment. These differences may be attributable to the situation that $g^{\mathrm{c}}_{\alpha\beta}$ and $g^{\mathrm{a}}_{\alpha\beta}$ represent the intra- and intermembrane transport phenomena, while $\bar{g}^{\mathrm{c}}_{\alpha\beta}$ and $\bar{g}^{\mathrm{a}}_{\alpha\beta}$ represent the former phenomena only. In other words, there is the possibility in the composite membrane system that the current through one of the elements can be produced not only by the force acting the same element but also by the force acting the different element.

Kedem and Katchalsky have predicted that the partial currents through each element membrane give rise to the strong circulation of current even when the total membrane current is absent.[7] From Eq. 15, the ionic currents at zero membrane current can be written as follows,

$$\begin{aligned} i^{\mathrm{o}}_{\mathrm{Na}} &= -g_{\mathrm{Na}\cdot\mathrm{Na}}(V_{\mathrm{O}} - V_{\mathrm{Na}}) - g_{\mathrm{Na}\cdot\mathrm{Cl}}(V_{\mathrm{O}} - V_{\mathrm{Cl}}), \\ i^{\mathrm{o}}_{\mathrm{Cl}} &= -g_{\mathrm{Cl}\cdot\mathrm{Na}}(V_{\mathrm{O}} - V_{\mathrm{Na}}) - g_{\mathrm{Cl}\cdot\mathrm{Cl}}(V_{\mathrm{O}} - V_{\mathrm{Cl}}). \end{aligned} \tag{31}$$

As an example, the ionic currents given by each term of the above equations were calculated from the estimated values of $g_{\alpha\beta}$ at $a^{\mathrm{I}}_{\pm}=4.08\times10^{-2}$ mol dm^{-3} and are shown in Fig. 7. The Na^{+} current through the cation-exchange element driven by the conjugate force,

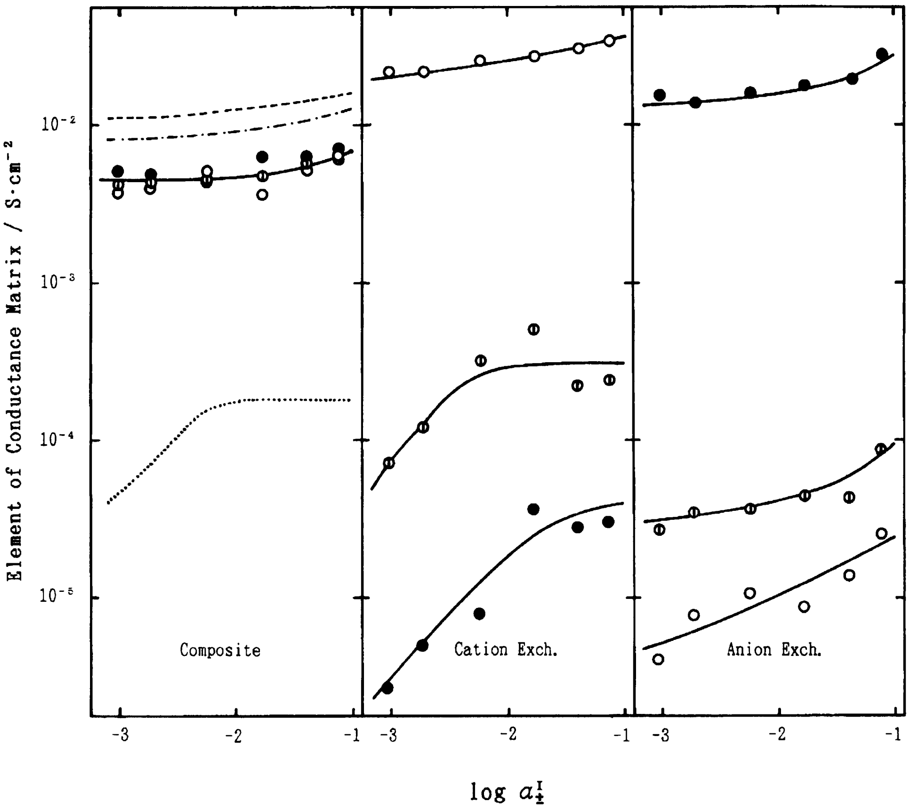

Fig. 6. Plots of element of conductance matrix vs. logarithmic mean activity of NaCl in phase I. ○; $g_{Na\cdot Na}$, $\overline{g}^c_{Na\cdot Na}$, and $\overline{g}^a_{Na\cdot Na}$, ⦶; $g_{Na\cdot Cl}$, $\overline{g}^c_{Na\cdot Cl}$, and $\overline{g}^a_{Na\cdot Cl}$, ●; $g_{Cl\cdot Cl}$, $\overline{g}^c_{Cl\cdot Cl}$, and $\overline{g}^a_{Cl\cdot Cl}$. Broken line; $\gamma^c\overline{g}^c_{Na\cdot Na}+\gamma^a\overline{g}^a_{Na\cdot Na}$, Dotted line; $\gamma^c\overline{g}^c_{Na\cdot Cl}+\gamma^a\overline{g}^a_{Na\cdot Cl}$ Chain-dotted line; $\gamma^c\overline{g}^c_{Cl\cdot Cl}+\gamma^a\overline{g}^a_{Cl\cdot Cl}$.

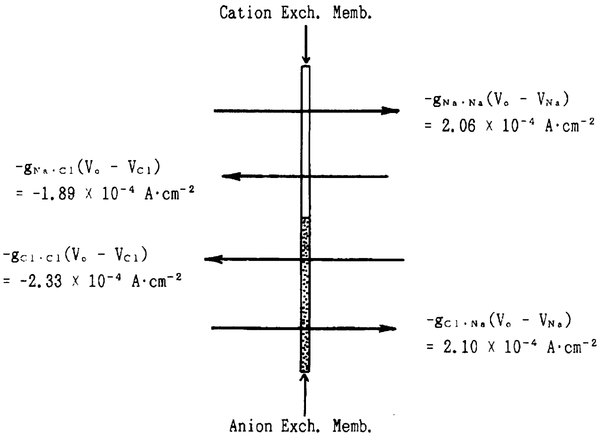

Fig. 7. Ionic currents at zero membrane current given by each term of Eq. 31 at $a^I_\pm=4.08\times10^{-2}$ mol dm^{-3}.

V_0-V_{Na}, is nearly canceled by that driven by the non-conjugate force, V_0-V_{Cl}, and hence the net partial current of Na^+ ion is of the order of 10^{-5} A cm^{-2}, corresponding to the salt flux of the order of 10^{-10} mol s^{-1} cm^{-2}. The same can be said of the net partial current of Cl^- ion through the anion-exchange element. For this reason, the circulation of current at zero membrane current is not so strong as expected from transport properties of permselective membranes in the single membrane systems.

The effect of the large cross coefficient should be considered in interpreting the ion transport phenomena through less permselective membranes such as biological, mosaic, or amphoteric membranes.

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