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# Multi-ionic Potential and Membrane Permeability Matrix. I. NaCl–CsCl Bi-ionic System with a Cation Exchange Membrane

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This paper is concerned with analysis of membrane transport processes on the basis of nonequilibrium thermodynamics. Inter-ionic correlations between permeating ions are quantitatively estimated by applying the membrane permeability matrix theory to the system in which the NaCl and CsCl solution phases are divided by a highly selective cation exchange membrane. The membrane permeability matrix of the system may be expressed by four ionic correlation terms concerning with $Na^+$ and $Cs^+$. The electroconductive and diffusional membrane permeabilities are expressed as a function of the matrix elements having the dimension of permeating speed of ions. The conductive and diffusional permeabilities as well as the matrix elements are estimated from membrane potential, conductance, and ionic flux data. The external electrolyte concentration dependence of these permeability parameters is discussed. The conductive and diffusional permeabilities considerably differ from each other and their ratio changes with the external electrolyte concentration, whereas the permeability ratio of $Na^+$ to $Cs^+$ is constant. Electroconductive and diffusional characteristics of membrane transport processes are consistently analyzed in terms of the membrane permeability matrix theory.

The membrane permeability matrix theory was presented as an application of the nonequilibrium thermodynamics to the analysis of transport phenomena of ions across membrane.[1)] The fundamental idea of the theory is an estimation of permeability coefficients to offer a consistent explanation for membrane properties such as membrane potential, conductance, and ionic flux. In this context, the membrane permeability matrix was introduced as a fundamental parameter characterizing membrane properties. Each matrix element possesses the dimension of permeating speed of ions across membrane and represents a partial correlation between movements of migrating ions. The membrane permeability matrix can be regarded as a modified set of coefficients in the linear phenomenological equations describing membrane transport processes.

The commonly used membrane permeability theories formulated on the basis of the Nernst-Planck equation provide only one permeability coefficient for an ion (see, for example, Refs. 2—5), but any consistent explanation for membrane phenomena cannot be presented by these theories, since membrane permeabilities estimated from diffusional and electroconductive data are remarkably different as described later. In the preceding paper,[6)] an experimental verification of the permeability matrix theory was presented by using a cation exchange membrane-aqueous calcium chloride solution system and it was pointed out that the theory is advantageous for a better understanding of ionic memberane transport.

In the present paper, a bi-ionic system in which NaCl and CsCl aqueous solutions are divided by a cation exchange membrane is studied by measurement of membrane potential, membrane conductance, and ionic flux. The membrane permeability matrix is estimated from observed data and discussed in relation to membrane transport processes.

## Experimental

A "CK-1, 1.0 t" cation exchange membrane (Asahi Chemical Industry Co., Ltd.) was employed throughout the experiment with aqueous NaCl and CsCl solutions prepared from conductivity water and extra pure salts. The "CK-1, 1.0 t" membrane is composed of a styrene–divinylbenzene copolymer with ion exchange group of sulfonic acid type and its basic physicochemical properties are as follows: exchange capacity, 2.8 mequiv. (g dry-resin)$^{-1}$; water content, 38%; thickness, 1.09 mm. This membrane exhibits an ideal permselectivity to monovalent cations in single electrolyte systems (concentration cells), since apparent transport numbers to $Na^+$ and $Cs^+$ estimated from potential data are almost unity. The tracers used in the flux measurements, $^{22}Na$ and $^{137}Cs$ in chloride form, were obtained from the Japan Radioisotope Association.

Membrane potentials and conductances were measured by the ordinary method and ionic fluxes were estimated by measuring $^{22}Na$ and $^{137}Cs$ radioactivities transferred across membrane from one side of the solution chamber to the

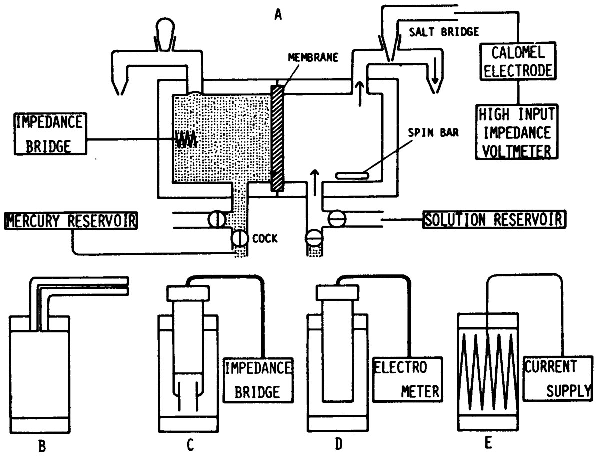

Fig. 1. Schematic representation of experimental assemblies. A shows the basic arrangement for the electrochemical measurements: potential measurements are performed by perfusing the chambers with electrolyte solutions (right-side diagram); conductance measurements are performed by means of filling the chamber with mercury as a conductivity electrode (left-side diagram). Accessary attachements B, C, and D (ion sensitive electrode) are employed to measure the volume flow, conductivity of solution, and ionic activity of solution, respectively. Attachement E is used when electric currents are applied externally.

other.[6-8] The schematic representation of experimental assemblies is given in Fig. 1. A high input impedance integrating voltmeter (Takeda Riken TR6856) and an impedance bridge circuit (Yokogawa-Hewlett-Packard 4255A and 4440B) were used to measure electrochemical properties. The detections of $\gamma$-activities of $^{22}$Na and $^{137}$Cs were performed by a $\gamma$-ray scintillation counter (Aloka Nd-151D). All experiments were carried out at a regulated room temperature, 20.0±1.0 °C.

## Results and Discussion

Experimental data are summarized in Figs. 2 and 3; measurements were carried out on the systems in which the NaCl or CsCl concentration of phase II was kept constant at $10^{-1}$, $10^{-2}$, or $10^{-3}$ mol dm$^{-3}$, while the CsCl or NaCl concentration of phase I was varied from $10^{-1}$ to $10^{-3}$ mol dm$^{-3}$. As illustrated in Fig. 2A, the membrane potential changed by about 58 mV for the tenfold alteration in electrolyte activity of phase I, whether NaCl or CsCl concentration was varied. Fig. 2A also shows that the system composed of NaCl and CsCl solutions of the same concentration generates a membrane potential of 8.7 mV where the NaCl side is positive. Membrane conductance *vs.* external salt concentration curves are given in Fig. 2B. Ionic fluxes estimated by means of the radiotracer method are plotted against the geometrical mean of NaCl and CsCl activities of external solutions in Fig. 3. These experimental results indicate that the Cl$^-$ flux is negligibly small as compared with cationic fluxes. Thus, the ionic fluxes in the present system can be expressed by only those of Na$^+$ and Cs$^+$ as a reasonable approximation. The membrane permeability matrix for the present system can be estimated from the above electrochemical and ionic flux data on the basis of the previous theory.[1]

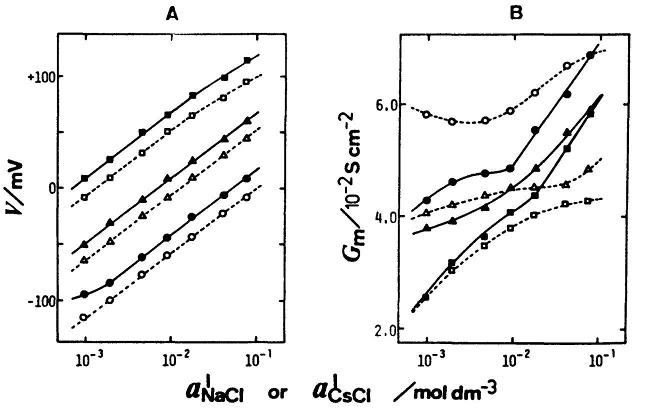

Fig. 2. Electrochemical data. Membrane potentials (A) and membrane conductances (B).
CsCl(I)–NaCl(II) systems, NaCl(II): ●; $10^{-1}$ mol dm$^{-3}$, ▲; $10^{-2}$ mol dm$^{-3}$, ■; $10^{-3}$ mol dm$^{-3}$. NaCl(I)–CsCl(II) systems, CsCl(II): ○; $10^{-1}$ mol dm$^{-3}$, △; $10^{-2}$ mol dm$^{-3}$, □; $10^{-3}$ mol dm$^{-3}$.

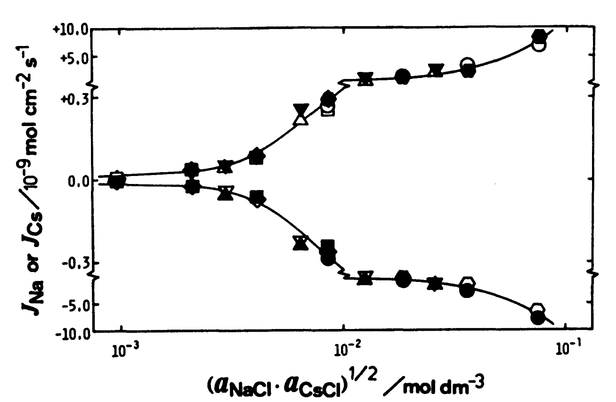

Fig. 3. Cationic flux data as a function of the geometrical mean of external NaCl and CsCl activities.
The closed and open symbols indicate $J_{Na}$ and $J_{Cs}$, respectively. CsCl(I)–NaCl(II) systems, NaCl(II): (●, ○); $10^{-1}$ mol dm$^{-3}$, (▲, △); $10^{-2}$ mol dm$^{-3}$, (■, □); $10^{-3}$ mol dm$^{-3}$. NaCl(I)–CsCl(II) systems, CsCl(II): (⬢, ⬡); $10^{-1}$ mol dm$^{-3}$, (▼, ▽); $10^{-2}$ mol dm$^{-3}$, (◆, ◇); $10^{-3}$ mol dm$^{-3}$.

The membrane transport process in the present system can be characterized by the following modified phenomenological equation:

$$\begin{bmatrix} J_{Na} \\ J_{Cs} \end{bmatrix} = -\begin{bmatrix} P_{Na.Na} & P_{Na.Cs} \\ P_{Cs.Na} & P_{Cs.Cs} \end{bmatrix} \times \begin{bmatrix} a^{II}_{Na}\exp(FV/2RT) - a^{I}_{Na}\exp(-FV/2RT) \\ a^{II}_{Cs}\exp(FV/2RT) - a^{I}_{Cs}\exp(-FV/2RT) \end{bmatrix}, \tag{1}$$

where $J$ is the ionic flux, $a$ is the activity, and $V$ is the membrane potential; $F$, $R$, and $T$ have the usual physical meanings; the subscripts Na and Cs refer to Na$^+$ and Cs$^+$; the superscripts I and II denote the solution phases I and II divided by the membrane, respectively. The 2×2 membrane permeability matrix in the right hand side of Eq. 1 is a principal parameter to describe membrane phenomena for the present system. Each matrix element represents the partial contribution to the ionic transport caused by the interionic correlation denoted by the subscript. The participation of volume flow in the mebrane transport process was neglected in the present study, since the assumption of zero volume flow was experimentally verified for the studied electrolyte concentration range with the CK-1, 1.0t membrane in a previous paper.[9] At low electrolyte concentrations less than $10^{-1}$ mol dm$^{-3}$, the estimated changes in phenomenological coefficients were so small as to be within the experimental error, whether the volume flow was taken into account or not. This may be due to the low water content and high fixed charge density of the CK-1, 1.0t cation exchange membrane.[6]

From Eq. 1, the total membrane current, $I$, is expressed as:

$$I = -F\{P_{Na}[a^{II}_{Na}\exp(FV/2\mathrm{RT}) - a^{I}_{Na}\exp(-FV/2RT)] + P_{Cs}[a^{II}_{Cs}\exp(FV/2RT) - a^{I}_{Cs}\exp(-FV/2RT)]\}, \tag{2}$$

where $P_{Na}$ and $P_{Cs}$ are the electroconductive membrane permeabilities to Na$^+$ and Cs$^+$ defined as a function of the permeability matrix elements, respectively:

$$P_{Na} = P_{Na.Na} + P_{Cs.Na},\ P_{Cs} = P_{Na.Cs} + P_{Cs.Cs}. \tag{3}$$

On the other hand, Eq. 1 is reduced to the next form when the membrane current is absent:

$$\begin{bmatrix} J_{\mathrm{Na}} \\ J_{\mathrm{Cs}} \end{bmatrix}_{I=0} = -\begin{bmatrix} P^{0}_{\mathrm{Na}} & 0 \\ 0 & P^{0}_{\mathrm{Cs}} \end{bmatrix} \times \begin{bmatrix} a^{\mathrm{II}}_{\mathrm{Na}} \exp(FV_0/2RT) - a^{\mathrm{I}}_{\mathrm{Na}} \exp(-FV_0/2RT) \\ a^{\mathrm{II}}_{\mathrm{Cs}} \exp(FV_0/2RT) - a^{\mathrm{I}}_{\mathrm{Cs}} \exp(-FV_0/2RT) \end{bmatrix}, \tag{4}$$

where $V_0$ is the membrane potential at zero membrane current. $P^0_{\mathrm{Na}}$ and $P^0_{\mathrm{Cs}}$ are the diffusional membrane permeabilities which are defined as a function of the matrix elements and differ from the electroconductive permeabilities defined by Eq. 3:

$$P^0_{\mathrm{Na}} = |P|/P_{\mathrm{Cs}},\ P^0_{\mathrm{Cs}} = |P|/P_{\mathrm{Na}}\ ;\ |P| = \begin{vmatrix} P_{\mathrm{Na.Na}} & P_{\mathrm{Na.Cs}} \\ P_{\mathrm{Cs.Na}} & P_{\mathrm{Cs.Cs}} \end{vmatrix}. \tag{5}$$

As pointed out in the preceding paper,[1,6] the conductive and diffusional membrane permeabilities are transport parameters which represent electronductive and diffusional characteristics of membrane systems. From Eqs. 3 and 5, relationships between these permeabilities are obtained as:

$$P^0_{\mathrm{Na}}/P_{\mathrm{Na}} = P^0_{\mathrm{Cs}}/P_{\mathrm{Cs}} = 1-(P_{\mathrm{Cs.Na}}/P_{\mathrm{Na}}) - (P_{\mathrm{Na.Cs}}/P_{\mathrm{Cs}}). \tag{6}$$

The conductive permeability can be discriminated from the diffusional permeability only on the basis of nonequilibrium thermodynamical theory and it should be noted that both the permeabilities are identical when the ionic correlation between $Na^+$ and $Cs^+$ is absent. The diffusional membrane permeability can be estimated according to Eq. 4 by using the ionic flux and potential data. The conductive permeability can be calculated from the electrochemical data using the following relations:[4,7]

$$\begin{aligned} P_{\mathrm{Na}}a^{\mathrm{II}}_{\mathrm{Na}} + P_{\mathrm{Cs}}a^{\mathrm{II}}_{\mathrm{Cs}} &= (RT/F^2)G_{\mathrm{m}} \exp(-FV_0/2RT), \\ P_{\mathrm{Na}}a^{\mathrm{I}}_{\mathrm{Na}} + P_{\mathrm{Cs}}a^{\mathrm{I}}_{\mathrm{Cs}} &= (RT/F^2)G_{\mathrm{m}} \exp(FV_0/2RT), \end{aligned} \tag{7}$$

where $G_{\mathrm{m}}$ is the membrane conductance.

Four elements of the membrane permeability matrix, $P_{\mathrm{Na.Na}}$, $P_{\mathrm{Na.Cs}}$, $P_{\mathrm{Cs.Na}}$, and $P_{\mathrm{Cs.Cs}}$, characterizing the present system were estimated from Eqs. 3 and 6 with the following relation between the cross matrix elements:[1]

$$\frac{P_{\mathrm{Na.Cs}}}{P_{\mathrm{Cs.Na}}} = \frac{(a^{\mathrm{I}}_{\mathrm{Na}}a^{\mathrm{II}}_{\mathrm{Na}})^{1/2} \sinh[F(V-V_{\mathrm{Na}})/2RT]/[F(V-V_{\mathrm{Na}})/2RT]}{(a^{\mathrm{I}}_{\mathrm{Cs}}a^{\mathrm{II}}_{\mathrm{Cs}})^{1/2} \sinh[F(V-V_{\mathrm{Cs}})/2RT]/[F(V-V_{\mathrm{Cs}})/2RT]}, \tag{8}$$

where $V_{\mathrm{Na}}$ and $V_{\mathrm{Cs}}$ are the Nernst equilibrium membrane potentials for $Na^+$ and $Cs^+$, respectively, which are defined as:

$$\begin{aligned} V_{\mathrm{Na}} &= -(RT/F)\ln(a^{\mathrm{II}}_{\mathrm{Na}}/a^{\mathrm{I}}_{\mathrm{Na}}), \\ V_{\mathrm{Cs}} &= -(RT/F)\ln(a^{\mathrm{II}}_{\mathrm{Cs}}/a^{\mathrm{I}}_{\mathrm{Cs}}). \end{aligned} \tag{9}$$

In the present study, Eq. 8 must be modified under the limited experimental conditions; the relation, $-V_{\mathrm{Na}} = V_{\mathrm{Cs}} = \infty$, would be satisfied in the CsCl(I)-NaCl(II) system where $a^{\mathrm{I}}_{\mathrm{Na}} = a^{\mathrm{II}}_{\mathrm{Cs}} = o$, and the relation, $V_{\mathrm{Na}} = -V_{\mathrm{Cs}} = \infty$, in the NaCl(I)-CsCl(II) system where $a^{\mathrm{II}}_{\mathrm{Na}} = a^{\mathrm{I}}_{\mathrm{Cs}} = o$. In these limiting cases, the following relations can be obtained from Eq. 8:

$$P_{\mathrm{Na.Cs}}/P_{\mathrm{Cs.Na}} = \begin{cases} a^{\mathrm{II}}_{\mathrm{Na}}/a^{\mathrm{I}}_{\mathrm{Cs}} & \text{for the CsCl(I)-NaCl(II) system} \\ a^{\mathrm{I}}_{\mathrm{Na}}/a^{\mathrm{II}}_{\mathrm{Cs}} & \text{for the NaCl(I)-CsCl(II) system.} \end{cases} \tag{10}$$

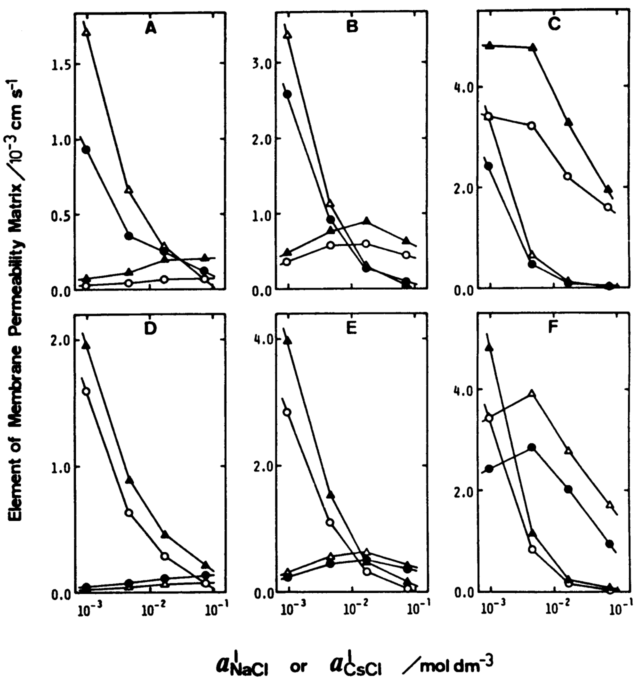

Fig. 4. Membrane permeability matrix elements as a function of mean electrolyte activity of phase I. CsCl(I)-NaCl(II) systems, NaCl(II): A; $10^{-1}$ mol dm$^{-3}$, B; $10^{-2}$ mol dm$^{-3}$, C; $10^{-3}$ mol dm$^{-3}$. NaCl(I)-CsCl(II) systems, CsCl(II): D; $10^{-1}$ mol dm$^{-3}$, E; $10^{-2}$ mol dm$^{-3}$, F; $10^{-3}$ mol dm$^{-3}$. ●; $P_{\mathrm{Na.Na}}$, ○; $P_{\mathrm{Ca.Na}}$, ▲; $P_{\mathrm{Cs.Cs}}$, △; $P_{\mathrm{Na.Cs}}$.

Calculated transport parameters are summarized in Figs. 4 and 5. The membrane permeability matrix elements estimated for the six studied systems are plotted, in Fig. 4, against the mean electrolyte activity of phase I. From this figure, effects of inter-ionic correlations on the membrane ionic transport processes can be quantitatively evaluated. In Fig. 5, the conduc-

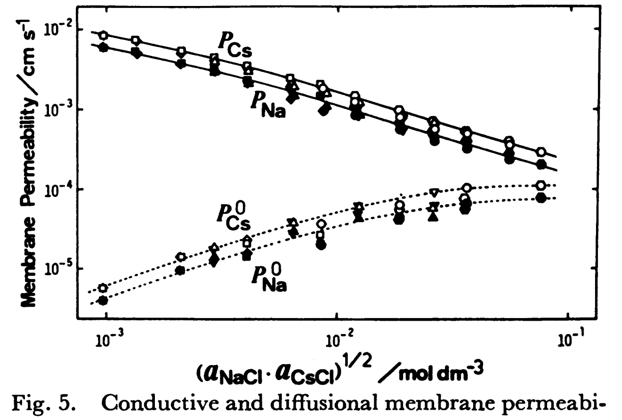

Fig. 5. Conductive and diffusional membrane permeabilities as a function of the geometrical mean of external NaCl and CsCl activities.

Solid and broken lines refer to the conductive and diffusional permeabilities; the closed and open symboles indicate the permeabilities to $Na^+$ and $Cs^+$, respectively. CsCl(I)-NaCl(II) systems, NaCl(II): (●, ○); $10^{-1}$ mol dm$^{-3}$, (▲, △); $10^{-2}$ mol dm$^{-3}$, (■, □); $10^{-3}$ mol dm$^{-3}$. NaCl(I)-CsCl(II) systems, CsCl(II): (⬢, ⬡); $10^{-1}$ mol dm$^{-3}$, (▼, ▽); $10^{-2}$ mol dm$^{-3}$, (◆, ◇); $10^{-3}$ mol dm$^{-3}$.

tive and diffusional membrane permeabilities are plotted as a function of the geometrical mean of NaCl and CsCl activities of phases I and II. As can be seen in this figure, the two types of the permeabilities are considerably different from each other and exhibit an opposite dependence upon the external electrolyte activity. The disagreement between the electroconductive and diffusional characteristics in the membrane transport processes indicates the failure of the Nernst-Einstein equation which relates the diffusion coefficient to the mobility. The deviation from the Nernst-Einstein equation has hitherto been interpreted as a contribution of electroosmotic effects (see, for example, Refs. 10 and 11). However, this effect seems to be minor especially in a highly permselective membrane system such as the CK-1, 1.0t membrane as suggested in the preceding papers.[6,9] These results showed that only a quite small electroosmotic effect is operative for the membrane having both a low water content and a homogeneous highly-charged polymer structure. In addition, the discrepancy between the diffusional and conductive permeabilities was also observed for a liquid ion exchange membrane system where no charged pores exist and accordingly where the electroosmotic permeation mechanism of solvent is not conceivable.[12,13] Moreover, the transport processes can be affected by the inter-ionic correlations even in a simple aqueous electrolyte system.[14–18] Thus, it is quite reasonable that the interaction between permeating ions should be taken into consideration as an origin for the failure of th Nernst-Einstein equation. Only when the cross terms of the permeability matrix are zero, the conductive and diffusional membrane permeabilities to ions coincide with each other; namely, the conductive and diffusional characteristics of the membrane system are consistently explained based on the classical Nernst-Einstein relation.

In Fig. 6, ratios of the diffusional to conductive membrane permeabilities, $P^0_{\mathrm{Na}}/P_{\mathrm{Na}}$ and $P^0_{\mathrm{Cs}}/P_{\mathrm{Cs}}$, are plotted together with the permeability ratios, $P_{\mathrm{Na}}/P_{\mathrm{Cs}}(=P^0_{\mathrm{Na}}/P^0_{\mathrm{Cs}})$. In the present system, the membrane potentials are determined by Na$^+$ and Cs$^+$ excluding Cl$^-$, so the following equations may be termed as the cationic pseudo-equilibrium potential:

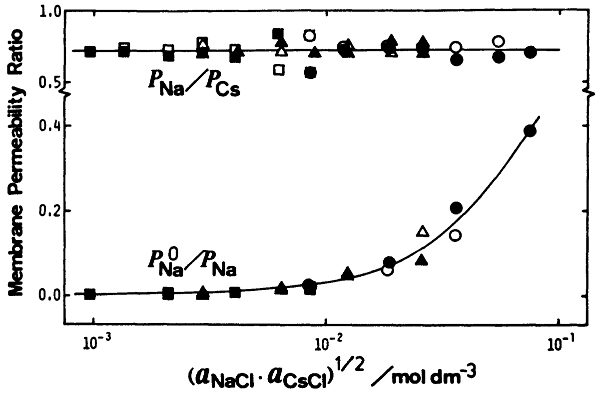

Fig. 6. Membrane permeability ratios as a function of the geometrical mean of external NaCl and CsCl activities.

Upper and lower traces indicate the values of $P_{\mathrm{Na}}/P_{\mathrm{Cs}}$ and $P^0_{\mathrm{Na}}/P_{\mathrm{Na}}$ $(=P^0_{\mathrm{Cs}}/P_{\mathrm{Cs}})$, respectively. CsCl(I)–NaCl(II) systems, NaCl(II): ●; $10^{-1}$ mol dm$^{-3}$, ▲; $10^{-2}$ mol dm$^{-3}$, ■; $10^{-3}$ mol dm$^{-3}$. NaCl(I)–CsCl(II) systems, CsCl(II): ○; $10^{-1}$ mol dm$^{-3}$, △; $10^{-2}$ mol dm$^{-3}$, □; $10^{-3}$ mol dm$^{-3}$.

$$V_{\mathrm{Na-Cs}} = \begin{cases} -(RT/F)\ln(P_{\mathrm{Na}}a^{\mathrm{II}}_{\mathrm{Na}}/P_{\mathrm{Cs}}a^{\mathrm{I}}_{\mathrm{Cs}}) \\ \text{for the CsCl(I)–NaCl(II) system} \\ -(RT/F)\ln(P_{\mathrm{Cs}}a^{\mathrm{II}}_{\mathrm{Cs}}/P_{\mathrm{Na}}a^{\mathrm{I}}_{\mathrm{Na}}) \\ \text{for the NaCl(I)–CsCl(II) system.} \end{cases} \tag{11}$$

This equation suggests that the membrane potential possesses the Nernstian slope against the logarithmic activity of phase I, in the case of a constant permeability ratio, $P_{\mathrm{Na}}/P_{\mathrm{Cs}}$. As illustrated in Figs. 2A and 6, the potential data show the characteristics described above and the average value of $P_{\mathrm{Na}}/P_{\mathrm{Cs}}$ is 0.72. This fact also verifies the approximation that the system is characterized by Na$^+$ and Cs$^+$ excluding the effect of Cl$^-$.

The significance of constant permeability ratio in the ionic membrane transport phenomena was studied from experimental and theoretical points of views.[5,7,19–21] According to the preceding paper, the following relations are satisfied:[4,6]

$$\begin{aligned} (P_{\mathrm{Na}})^{-1} &= \exp(-FV/2RT)\times \\ &\quad \int (RTU_{\mathrm{Na}})^{-1}\exp[(F\psi/RT)+\zeta_{\mathrm{Na}}]\mathrm{d}x \\ (P^0_{\mathrm{Na}})^{-1} &= \exp(-FV/2RT)\times \\ &\quad \int (D_{\mathrm{Na}})^{-1}\exp[(F\psi/RT)+\zeta_{\mathrm{Na}}]\mathrm{d}x, \end{aligned} \tag{12}$$

where $U_{\mathrm{Na}}$ and $D_{\mathrm{Na}}$ are the ionic mobility and diffusion coefficient of Na$^+$ within the membrane phase, $\psi$ is the electrical potential, and $\zeta_{\mathrm{Na}}$ is the partition factor of Na$^+$ between the membrane and solution phases. The integration is carried out with respect to the membrane phase. An identical relation is also satisfied for Cs$^+$. Since the ionic mobilities, diffusion coefficients, and partition factors of Na$^+$ and Cs$^+$ are considered to be constant, the next relation is obtained from Eq. 12:

$$\begin{aligned} P_{\mathrm{Na}}/P_{\mathrm{Cs}} &= (U_{\mathrm{Na}}/U_{\mathrm{Cs}})\exp(\zeta_{\mathrm{Na}}-\zeta_{\mathrm{Cs}}) \\ &= (U_{\mathrm{Na}}/U_{\mathrm{Cs}})K_{\mathrm{Na-Cs}} \\ &= (D_{\mathrm{Na}}/D_{\mathrm{Cs}})K_{\mathrm{Na-Cs}} \\ &= P^0_{\mathrm{Na}}/P^0_{\mathrm{Cs}}, \end{aligned} \tag{13}$$

where $K_{\mathrm{Na-Cs}}$ is the equilibrium constant for the exchange reaction between Na$^+$ and Cs$^+$ in the membrane system. This equation suggests that the ratio of diffusion coefficients as well as that of ionic mobilities takes a constant value, since the observed permeability ratios are constant. The diffusional to conductive membrane permeability ratios are indications of the interaction between Na$^+$ and Cs$^+$. The values of $P^0_{\mathrm{Na}}/P_{\mathrm{Na}}(=P^0_{\mathrm{Cs}}/P_{\mathrm{Cs}})$ increase with increasing electrolyte activity as shown in Fig. 6.

To examine the dependence of the inter-ionic correlation on the external electrolyte activity, $P_{\mathrm{Na.Na}}/P_{\mathrm{Na}}$ and $P_{\mathrm{Cs.Cs}}/P_{\mathrm{Cs}}$ are plotted against the external NaCl/CsCl activity ratio in Fig. 7. The Na$^+$ contributions to the conductive permeabilities, $P_{\mathrm{Na.Na}}/P_{\mathrm{Na}}$ and $P_{\mathrm{Na.Cs}}/P_{\mathrm{Cs}}$, increase as the relative activity of Na$^+$ to Cs$^+$ increases. For usual cation exchange membranes such as CK-1, 1.0t, the NaCl/CsCl concentration ratio in the membrane phase is approximately the same as that

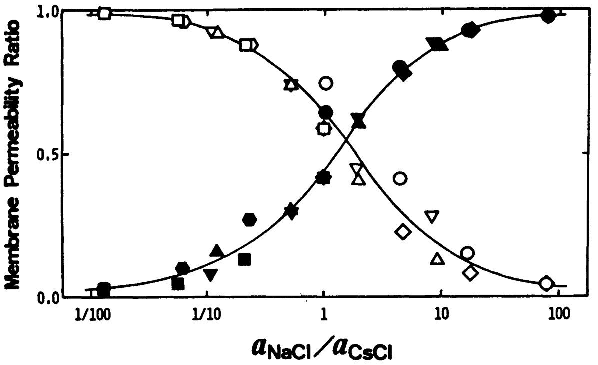

Fig. 7. $P_{Na.Na}/P_{Na}$ and $P_{Cs.Cs}/P_{Cs}$ *vs.* NaCl/CsCl activity ratio of external solutions I and II relations.
The closed and open symbols refer to the ratios for $Na^+$ and $Cs^+$. CsCl(I)–NaCl(II) systems, NaCl(II): (●, ○); $10^{-1}$ mol dm$^{-3}$, (▲, △); $10^{-2}$ mol dm$^{-3}$, (■, □); $10^{-3}$ mol dm$^{-3}$. NaCl(I)–CsCl(II) systems, CsCl(II): (●, ○); $10^{-1}$ mol dm$^{-3}$, (▼, ▽); $10^{-2}$ mol dm$^{-3}$, (◆, ◇); $10^{-3}$ mol dm$^{-3}$.

in the solution phase when the membrane is equilibrated with the electrolyte solution (unpublished data). The degree of participation of cations in the membrane transport processes would be parallel to their concentrations within the membrane phase. In the present system, the cross elements of the permeability matrix, $P_{Na.Cs}$ and $P_{Cs.Na}$, are positive quantities, so Eq. 6 leads to:

$$0 \leq 1 - (P_{Cs.Na}/P_{Na}) - (P_{Na.Cs}/P_{Cs}) \leq 1. \tag{14}$$

which is equivalent to the next relation:

$$1 \leq P_{Na.Na}/P_{Na} + P_{Cs.Cs}/P_{Cs} \leq 2. \tag{15}$$

As a limiting case, the equal signs in the right hand side of these inequalities are satisfied when the ionic interactions between $Na^+$ and $Cs^+$ are absent, *i.e.*, $P_{Na.Cs} = P_{Cs.Na} = 0$. In this case, the system is characterized by:

$$P_{Na} = P^0_{Na} = P_{Na.Na}P_{Cs} = P^0_{Cs} = P_{Cs.Cs}. \tag{16}$$

Such a situation is equivalent to that of an electrolyte solution at infinite dilution where no inter-ionic interactions exist. On the other hand, the equal signs in the left hand sides are realized in the case of the situation expressed as:

$$P_{Na.Na}/P_{Na} = P_{Na.Cs}/P_{Cs}, \quad P_{Cs.Na}/P_{Na} = P_{Cs.Cs}/P_{Cs}. \tag{17}$$

But, the situation of this limiting case where $P^0_{Na} = P^0_{Cs} = 0$ is physically meaningless, although $P^0_{Na}/P_{Na}$ is very small and close to zero for lower concentrations.

These results suggest that the transport of cations takes place through the inter-ionic exchange of $Na^+$ and $Cs^+$. The participation of the rate of inter-exchange of ions in the bi-ionic systems was discussed on the basis oft he Nernst-Planck approach.[22] However, it may be pointed out that only with the aid of the membrane permeability matrix the conductive and diffusional permeabilities can be related directly to the electrical mobility and diffusion coefficient, respectively, therefore, the movement of ions in the membrane system should be interpreted on the basis of nonequilibrium thermodynamics.

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