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Multi-Ionic Potential and Membrane Permeability Matrix. II. Na^+-Ca^{2+} Bi-Ionic System with a Cation-Exchange Membrane and Effects of Cl^- on Cation Transport

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Transport characteristics of Na^+–Ca^{2+} bi-ionic system with a highly selective cation-exchange membrane were investigated on the basis of nonequilibrium thermodynamic theory. As a principal transport parameter, the membrane permeability matrix or membrane conductance matrix can be estimated from the membrane potential, conductance, and ion flux data. Significances of diffusional and electroconductive processes of ion transport across membrane were systematically discussed in terms of these matrix elements. Partial contributions of inter-cationic (Na^+–Na^+, Na^+–Ca^{2+}, and Ca^{2+}–Ca^{2+}) correlations to the membrane transport process of ions were examined by means of comparing the estimated values of corresponding matrix elements. It was suggested that Ca^{2+} ions, of which membrane concentrations are kept at high level independently of the Na^+/Ca^{2+} concentration ratio of external aqueous solutions, play a critical role in the membrane transport phenomena. Participations of Cl^- transport in the cation-exchange processes were also discussed on the basis of membrane conductance matrix theory.

Characterization of the ion-transport processes across membrane is a fundamental and important subject in wide varieties of artificial and biological systems, such as ion exchange membranes, lipid bilayers, and biological cellular membranes. Phenomenological analyses on the membrane-transport processes are performed generally utilizing linear formulations relating the thermodynamic driving forces with fluxes across membrane based on the nonequilibrium thermodynamics.[1,2] An appropriate set of the linear phenomenological equations formulating the coupling of driving forces and fluxes can be derived for various transport phenomena arising across membranes.[3]

In case of the ionic membrane transport processes, detailed descriptions of the electrochemical properties, by means of estimating the appropriate phenomenological coefficient as a membrane transport parameter of permselectivity index, are essential procedures to characterize the membrane systems. In this context, the membrane permeability matrix and the membrane conductance matrix were introduced as a principal membrane transport parameter in an earlier paper to describe membrane permselectivities to ions based on the electrochemical and ion flux measurements.[4] By utilizing these membrane permeability parameters in a matrix form, the membrane transport processes of ions can be characterized in terms of the correlations between permeating ions. Furthermore, fundamental aspects of the diffusional and electroconductive movements of ions within membrane phase can be discussed based on these transport parameters.[5,6]

The present investigations were designed to systematically analyze the ion permselectivities and electrochemical properties of $NaCl$-$CaCl_2$ aqueous systems with a cation-exchange membrane on the basis of nonequilibrium thermodynamics. Effects of Ca^{2+} as a bivalent cation on the ion transport across cation-exchange membrane and effects of Cl^- on the cation transport were examined and compared with the results obtained in the NaCl–CsCl systems reported in the preceding paper.[6] Detailed analyses on the correlations between ion fluxes across charged membranes would contribute toward an improvement of efficiencies in the membrane process operations. Recently, it was clarified that a part of K^+ flux across excitable cell membrane, Ca^{2+}-dependent K^+ flux, is strongly affected and triggered by the entry of Ca^{2+} into the cell.[7] Quantitative descriptions of the coupling between permeating ions are also important in biological systems, since the Ca^{2+}-dependent K^+ movement has become established and important physiological concept and Ca^{2+}, which plays a crucial role in many biological reactions, is considered to be a mediator for the ion transport across cellular membranes.

Experimental

Experimental systems consisted of a "CK-1, 1.0t" cation-exchange membrane (Asahi Chemical Industry, Co., Ltd.)[6] with aqueous solution phases I and II separated by the membrane, one of which contains NaCl and the other, $CaCl_2$. Transport numbers of the CK-1, 1.0t membrane to Na^+ and Ca^{2+} were estimated at 0.97—0.99 and 0.95—0.98 from the membrane potential measurements on concentration cell systems with electrolyte concentration ranges of 10^{-1}—10^{-3} mol dm^{-3}. In this study, electrochemical and ion flux measurements were carried out on the systems where concentrations of NaCl or $CaCl_2$ in phase I were varied from 10^{-1} to 10^{-3} mol dm^{-3} and those of the other electrolyte in phase II were kept constant at 10^{-1}, 10^{-2}, or 10^{-3} mol dm^{-3}. Electrolyte solutions were prepared from extra pure salts with conductivity water.

Experimental arrangements for the membrane potential and conductance measurements were the same as reported earlier.[6)] Cation fluxes were measured by the tracer flux method. ^{22}Na and ^{45}Ca in chloride form as a radioactive tracer were purchased from the Japan Radioisotope Association. Radioactive NaCl or $CaCl_2$ aqueous solution with an appropriate specific activity was set in the solution chamber on one side of the membrane, then, the time courses of increases in radioactivity of solution on the other side were detected by the γ-ray scintillation counter or liquid scintillation counter to estimate the steady cation fluxes across membrane. Cl^- fluxes were estimated from Na^+ and Ca^{2+} flux data under the experimental conditions where the total electric membrane currents were zero. Cl^- flux was also checked in some systems by measuring the tracer flux using ^{36}Cl as a tracer ion.

All the measurements were carried out at regulated room temperature, 25±1 °C.

Results and Discussion

General Formulations. A set of the phenomenological equations characterizes well the ion transport processes by formulating the relationships of ion fluxes across membrane with coupled thermodynamic forces, gradients of electrochemical potentials of ions. For the present system studied, the linear phenomenological equations can be written as:[4,6)]

$$\begin{bmatrix} J_{\mathrm{Na}} \\ J_{\mathrm{Ca}} \\ J_{\mathrm{Cl}} \end{bmatrix} = -\begin{bmatrix} P_{\mathrm{Na\cdot Na}} & P_{\mathrm{Na\cdot Ca}} & P_{\mathrm{Na\cdot Cl}} \\ P_{\mathrm{Ca\cdot Na}} & P_{\mathrm{Ca\cdot Ca}} & P_{\mathrm{Ca\cdot Cl}} \\ P_{\mathrm{Cl\cdot Na}} & P_{\mathrm{Cl\cdot Ca}} & P_{\mathrm{Cl\cdot Cl}} \end{bmatrix} \times \begin{bmatrix} a_{\mathrm{Na}}^{\mathrm{II}} \exp(FV/2RT) - a_{\mathrm{Na}}^{\mathrm{I}} \exp(-FV/2RT) \\ a_{\mathrm{Ca}}^{\mathrm{II}} \exp(FV/RT) - a_{\mathrm{Ca}}^{\mathrm{I}} \exp(-FV/RT) \\ a_{\mathrm{Cl}}^{\mathrm{II}} \exp(-FV/2RT) - a_{\mathrm{Cl}}^{\mathrm{I}} \exp(FV/2RT) \end{bmatrix} \tag{1}$$

or

$$\begin{bmatrix} i_{\mathrm{Na}} \\ i_{\mathrm{Ca}} \\ i_{\mathrm{Cl}} \end{bmatrix} = -\begin{bmatrix} g_{\mathrm{Na\cdot Na}} & g_{\mathrm{Na\cdot Ca}} & g_{\mathrm{Na\cdot Cl}} \\ g_{\mathrm{Ca\cdot Na}} & g_{\mathrm{Ca\cdot Ca}} & g_{\mathrm{Ca\cdot Cl}} \\ g_{\mathrm{Cl\cdot Na}} & g_{\mathrm{Cl\cdot Ca}} & g_{\mathrm{Cl\cdot Cl}} \end{bmatrix} \begin{bmatrix} V - V_{\mathrm{Na}} \\ V - V_{\mathrm{Ca}} \\ V - V_{\mathrm{Cl}} \end{bmatrix} \tag{2}$$

In these formulations, solvent fluxes are neglected, since the effects of solvent transport across membrane on the interactions of permeant ions are fairly small in the highly charged membrane system.[8)] Here, J is the ion flux across membrane, a is the activity, V is the membrane potential, and i is the ionic membrane current; the subscripts Na, Ca, and Cl identify permeant ions; the superscripts I and II refer to the solution phases I and II separated by the membrane; F, R, and T are the Faraday constant, gas constant, and absolute temperature, respectively. V_{Na}, V_{Ca}, and V_{Cl} are the equilibrium membrane potentials to Na^+, Ca^{2+}, and Cl^- calculated by the Nernst equations for the respective ions. The 3×3 matrices in Eqs. 1 and 2 are the membrane permeability matrix and membrane conductance matrix, respectively. Elements of these matrices correspond to modified phenomenological coefficients indicating the participations of interactions between permeant ions specified by the subscript indices to the membrane transport processes. Only the membrane conductance elements satisfy the reciprocal relations, since, in Eq. 1, the permeability matrix element is recognized as a phenomenological coefficient relating the ion flux with electrochemical activity difference between solution phases I and II as a substituted conjugated thermodynamic force.[4,6)] The conductance matrix element is defined as a coefficient describing the ohmic relation between ionic membrane current with effective membrane potential difference.

The membrane permeability parameters, which indicate the permselectivities to ions by means of referring the permeating speed of ions across membrane, are expressed as a function of the permeability matrix elements:[4)]

$$\begin{aligned} P_{\mathrm{Na}} &= P_{\mathrm{Na\cdot Na}} + 2P_{\mathrm{Ca\cdot Na}} - P_{\mathrm{Cl\cdot Na}} \\ P_{\mathrm{Ca}} &= \tfrac{1}{2}P_{\mathrm{Na\cdot Ca}} + P_{\mathrm{Ca\cdot Ca}} - \tfrac{1}{2}P_{\mathrm{Cl\cdot Ca}} \\ P_{\mathrm{Cl}} &= -P_{\mathrm{Na\cdot Cl}} - 2P_{\mathrm{Ca\cdot Cl}} + P_{\mathrm{Cl\cdot Cl}} \end{aligned} \tag{3}$$

where P_{Na}, P_{Ca}, and P_{Cl} are the electroconductive permeabilities to Na^+, Ca^{2+}, and Cl^-, respectively. Similarly, the membrane conductance, G_{m}, and ionic membrane conductances, g_{Na}, g_{Ca}, and g_{Cl}, are expressed as a function of the conductance matrix elements:

$$\begin{aligned} G_{\mathrm{m}} &= g_{\mathrm{Na}} + g_{\mathrm{Ca}} + g_{\mathrm{Cl}} \\ &= (g_{\mathrm{Na\cdot Na}} + g_{\mathrm{Ca\cdot Na}} + g_{\mathrm{Cl\cdot Na}}) \\ &\quad + (g_{\mathrm{Na\cdot Ca}} + g_{\mathrm{Ca\cdot Ca}} + g_{\mathrm{Cl\cdot Ca}}) \\ &\quad + (g_{\mathrm{Na\cdot Cl}} + g_{\mathrm{Ca\cdot Cl}} + g_{\mathrm{Cl\cdot Cl}}) \end{aligned} \tag{4}$$

Therefore, the ohmic relations for the total membrane electric current, I, are expressed as:

$$\begin{aligned} I &= -F\{P_{\mathrm{Na}}[a_{\mathrm{Na}}^{\mathrm{II}} \exp(FV/2RT) - a_{\mathrm{Na}}^{\mathrm{I}} \exp(-FV/2RT)] \\ &\qquad + 2P_{\mathrm{Ca}}[a_{\mathrm{Ca}}^{\mathrm{II}} \exp(FV/RT) - a_{\mathrm{Ca}}^{\mathrm{I}} \exp(-FV/RT) \\ &\qquad - P_{\mathrm{Cl}}[a_{\mathrm{Cl}}^{\mathrm{II}} \exp(-FV/2RT) - a_{\mathrm{Cl}}^{\mathrm{I}} \exp(FV/2RT)]\} \\ &= -g_{\mathrm{Na}}(V - V_{\mathrm{Na}}) - g_{\mathrm{Ca}}(V - V_{\mathrm{Ca}}) - g_{\mathrm{Cl}}(V - V_{\mathrm{Cl}}) \\ &= -G_{\mathrm{m}}(V - V_0) \end{aligned} \tag{5}$$

where V_0 is the membrane potential in the absence of membrane electric current and the following relation is satisfied:

$$\begin{aligned} &2P_{\mathrm{Ca}}a_{\mathrm{Ca}}^{\mathrm{II}} \exp(2FV_0/RT) + (P_{\mathrm{Na}}a_{\mathrm{Na}}^{\mathrm{II}} + P_{\mathrm{Cl}}a_{\mathrm{Cl}}^{\mathrm{I}})\exp(3FV_0/2RT) \\ &\quad - (P_{\mathrm{Na}}a_{\mathrm{Na}}^{\mathrm{I}} + P_{\mathrm{Cl}}a_{\mathrm{Cl}}^{\mathrm{II}})\exp(FV_0/2RT) - 2P_{\mathrm{Ca}}a_{\mathrm{Ca}}^{\mathrm{I}} = 0 \end{aligned} \tag{6}$$

Electrochemical and Flux Data. Figure 1 summarizes the membrane potential, membrane conductance, and cationic flux data. The NaCl-$CaCl_2$ biionic systems with a highly selective cation-exchange membrane studied here can be classified into two large groups: the systems in which Cl^- fluxes are negligible order and the membrane processes are characterized only by Na^+ and Ca^{2+} transports, and the systems in

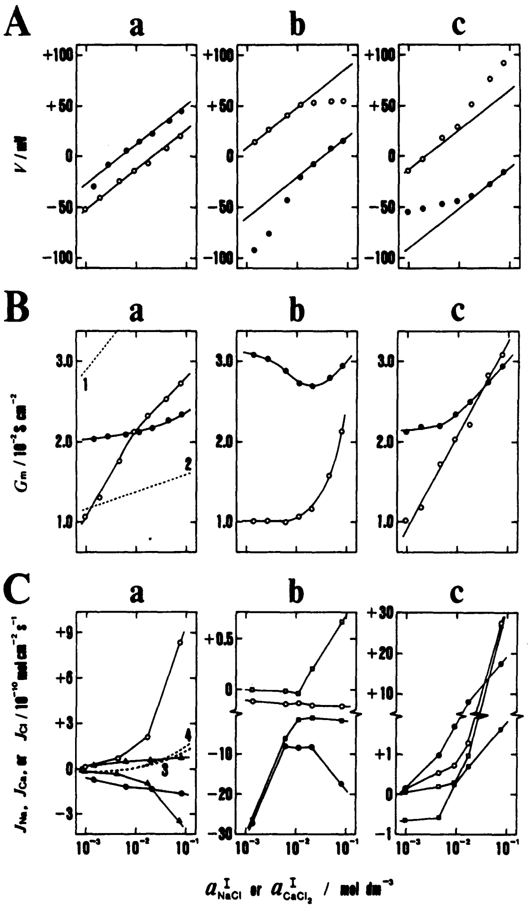

Fig. 1. Membrane potential (A), membrane conductance (B), and ionic flux (C) data as a function of mean electrolyte activity of phase I. Closed and open symbols refer to: a, $CaCl_2$(I)-10^{-2} mol dm^{-3} NaCl(II) and NaCl(I)-10^{-2} mol dm^{-3} $CaCl_2$(II); b, $CaCl_2$(I)-10^{-1} mol dm^{-3}NaCl(II) and $CaCl_2$(I)-10^{-3} mol dm^{-3} NaCl(II); c, NaCl(I)-10^{-1} mol dm^{-3} $CaCl_2$(II) and NaCl(I)-10^{-3} mol dm^{-3} $CaCl_2$(II). In A, the solid lines refer to the ideal Na^+-Ca^{2+} bi-ionic potential responses estimated by Eq. 7 with a constant P_{Na}/P_{Ca} assumption. In C, ●, ○: J_{Na}; ▲, △: J_{Ca}; ■, □: J_{Cl}. The broken lines 1 and 3 refer to membrane conductance data and J_{Na} data in NaCl(I)-10^{-2} mol dm^{-3} NaCl(II) system; the broken lines 2 and 4 refer to membrane conductance data and J_{Ca} data in $CaCl_2$(I)-10^{-2} mol dm^{-3} $CaCl_2$ (II) systems.

which Cl^- fluxes comparable to cationic fluxes are observed and, accordingly, the cation transport is affected considerably by Cl^- transport.

As illustrated in Fig. 1-C-a, Cl^- fluxes are negligible order as compared with Na^+ and Ca^{2+} fluxes in the $CaCl_2$(I)-10^{-2} mol dm^{-3} NaCl(II) and NaCl(I)-10^{-2} mol dm^{-3} $CaCl_2$(II) systems. When the membrane processes in these systems are characterized only by the cation transport, the next equation can be derived from Eq. 6:

$$\begin{aligned} V_0 &= -(2RT/3F)\ln(P_{Na}a_{Na}^{II}/2P_{Ca}a_{Ca}^{I}) \quad \text{or} \\ &\quad -(2RT/3F)\ln(2P_{Ca}a_{Ca}^{II}/P_{Na}a_{Na}^{I}) \qquad (7) \\ &= V_{Na-Ca} \end{aligned}$$

The membrane potential expressed by Eq. 7 can be recognized as a cationic equilibrium potential for bi-ionic system being equivalent to the Nernst potential in concentration cell systems. In the present cases, observed membrane potentials correspond to the equilibrium potentials for Na^+ and Ca^{2+}, V_{Na-Ca}. Equation 7 deduces that the constant Na^+/Ca^{2+} permeability ratio is realized for the system in which the linear membrane potential responses of 39.44 mV/(logarithmic electrolyte activity of phase I) at 25 °C are observed.[9-11] Figure 1-A-a indicates that the 10^{-2}mol dm^{-3} NaCl(II) and 10^{-2}mol dm^{-3} $CaCl_2$ (II) systems realize these situations.

On the contrary, non-linear potential responses were observed in the systems where the NaCl or $CaCl_2$ concentrations in phase II were fixed at 10^{-1} or 10^{-3}mol dm^{-3} as can be seen in Figs. 1-A-b and A-c. The ideal slope of the Na^+-Ca^{2+} bi-ionic membrane potential plots mentioned above, 39.44 mV/logarithmic activity of phase I, shifted to increase as relative NaCl concentrations increased and to decrease as relative $CaCl_2$ concentrations increased. In these systems, definite amounts of Cl^- are transported simultaneously with two cations as shown in Figs. 1-C-b and C-c, and it is expected that the Na^+/Ca^{2+} permeability ratio is no longer constant with the external electrolyte concentration changes.

Membrane conductances of the present systems changed within the limits of the conductance values lower than those of NaCl concentration cell system and higher than those of $CaCl_2$ concentration cell system. Accordingly, it is suggested to occur a competitive sharing of available ion-exchange sites by Na^+ and Ca^{2+}.

In the following part of this section, membrane transport characteristics of the present systems are discussed firstly for the case in which only cations, Na^+ and Ca^{2+}, are permeable with a constant membrane permselectivity ratio, and secondly for the case in which the transport of Cl^- has significant effects on the membrane selectivity to these cations.

System with a Constant Na^+/Ca^{2+} Permeability Ratio. The membrane processes in the 10^{-2} mol dm^{-3} NaCl(II) or 10^{-2} mol dm^{-3} $CaCl_2$(II) systems are characterized by the cation transport alone and, consequently, by four membrane permeability matrix elements, $P_{Na\cdot Na}$, $P_{Ca\cdot Na}$, $P_{Na\cdot Ca}$, and $P_{Ca\cdot Ca}$. Including these matrix elements, all the membrane transport parameters can be evaluated from the available experimental data, the membrane potential, conductance, and ion flux, by the same manner as reported earlier based on the following relationships, Eqs. 8—11, with Eqs. 3, 5, and 7.[4,6] The membrane conductance is expressed as:

$$\begin{aligned} G_m &= (F^2/RT)[P_{Na}a^{I}_{Na}\exp(-FV_0/2RT) \\ &\qquad + 2P_{Ca}a^{I}_{Ca}\exp(-FV_0/RT)] \\ &= (F^2/RT)[P_{Na}a^{II}_{Na}\exp(FV_0/2RT) \\ &\qquad + 2P_{Ca}a^{II}_{Ca}\exp(FV_0/RT)] \end{aligned} \tag{8}$$

When the membrane electric current is absent, Na^+ and Ca^{2+} fluxes are characterized by diffusional membrane permeabilities, P^0_{Na} and P^0_{Ca}:

$$\begin{aligned} J_{Na} &= -P^0_{Na}[a^{II}_{Na}\exp(FV_0/2RT) - a^{I}_{Na}\exp(-FV_0/2RT)] \\ &= 2P^0_{Ca}[a^{II}_{Ca}\exp(FV_0/RT) - a^{I}_{Ca}\exp(-FV_0/RT)] \\ &= -2J_{Ca} \end{aligned} \tag{9}$$

The diffusional permeability to electroconductive permeability ratio is expressed as:

$$\begin{aligned} P^0_{Na}/P_{Na} &= P^0_{Ca}/P_{Ca} \\ &= 1-(2P_{Ca\cdot Na}/P_{Na}) - (P_{Na\cdot Ca}/2P_{Ca}) \end{aligned} \tag{10}$$

The cross coefficients of membrane permeability matrix, $P_{Na\cdot Ca}$ and $P_{Ca\cdot Na}$, are related each other as:

$$\begin{aligned} \frac{P_{Na\cdot Ca}}{P_{Ca\cdot Na}} &= \frac{(a^{I}_{Na}a^{II}_{Na})^{1/2}}{(a^{I}_{Ca}a^{II}_{Ca})^{1/2}} \\ &\quad \times \frac{\sinh[F(V_O-V_{Na})/2RT]/[F(V_O-V_{Na})/2RT]}{\sinh[F(V_O-V_{Ca})/RT]/[F(V_O-V_{Ca})/RT]} \end{aligned} \tag{11}$$

The diffusional membrane permeabilities to Na^+ and to Ca^{2+}, P^0_{Na} and P^0_{Ca}, are expressed as a function of the permeability matrix elements.

$$\begin{aligned} P^0_{Na} &= (P_{Na\cdot Na}P_{Ca\cdot Ca} - P_{Na\cdot Ca}P_{Ca\cdot Na})/P_{Ca} \\ P^0_{Ca} &= (P_{Na\cdot Na}P_{Ca\cdot Ca} - P_{Na\cdot Ca}P_{Ca\cdot Na})/P_{Na} \end{aligned} \tag{12}$$

The diffusional permeabilities, P^0_{Na} and P^0_{Ca}, which should be discriminated from the electroconductive permeabilities, P_{Na} and P_{Ca}, satisfy the following phenomenological equation in the absence of membrane electric current:

$$\begin{aligned} \begin{bmatrix} J_{Na} \\ J_{Ca} \end{bmatrix}_{I=0} &= -\begin{bmatrix} P^0_{Na} & 0 \\ 0 & P^0_{Ca} \end{bmatrix} \\ &\quad \times \begin{bmatrix} a^{II}_{Na}\exp(FV_0/2RT) - a^{I}_{Na}\exp(-FV_0/2RT) \\ a^{II}_{Ca}\exp(FV_0/RT) - a^{I}_{Ca}\exp(-FV_0/RT) \end{bmatrix} \end{aligned} \tag{13}$$

The electroconductive permeability represents conductive process of ions across membrane, while the diffusional permeability represents diffusion process of ions, and accordingly, the former is related to the mobility of permeant ion and the latter, to the diffusion coefficient.[5,6]

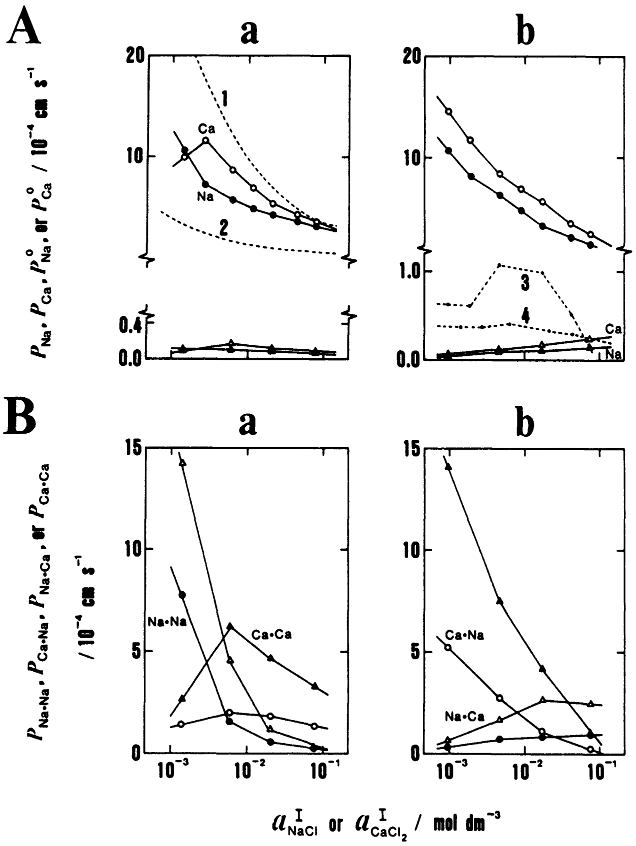

Fig. 2. Electroconductive and diffusional membrane permeabilities (A) and permeability matrix elements (B) as a function of mean electrolyte activity of phase I. a: $CaCl_2$(I)-10^{-2} mol dm^{-3} NaCl(II). b: NaCl(I)-10^{-2} mol dm^{-3} $CaCl_2$(II). In A, ●: P_{Na}; ○: P_{Ca}; ▲: P^0_{Na}; △: P^0_{Ca}. The broken lines 1 and 3 refer to P_{Na} and P^0_{Na} in NaCl(I)-10^{-2} mol dm^{-3} NaCl(II) system; the broken lines 2 and 4 refer to P_{Ca} and P^0_{Ca} in $CaCl_2$(II)-10^{-2} mol dm^{-3} $CaCl_2$(II) systems. In B, ●: $P_{Na\cdot Na}$; ○: $P_{Ca\cdot Na}$; △: $P_{Na\cdot Ca}$; ▲: $P_{Ca\cdot Ca}$.

Evaluated membrane transport parameters are summarized in Fig. 2. As illustrated in Figs. 2-A-a and A-b, the CK-1, 1.0t membrane is more permselective to Ca^{2+} than to Na^+ in these systems. Since the CK-1, 1.0t membrane is developed so as to be more permeable to univalent cations than to bivalent cations for the desalination process applications, the membrane permeability to Na^+ in concentration cell system is almost 10 times larger than that to Ca^{2+}. Furthermore, Figs. 2-B-a and B-b indicate that the calculated values of the membrane permeability matrix element conjugated with an electrochemical activity difference of Ca^{2+} between phases I and II are larger than those conjugated with an electrochemical activity difference of Na^+, namely, $P_{Ca\cdot Na}>P_{Na\cdot Na}$ and $P_{Ca\cdot Ca}>P_{Na\cdot Ca}$. These influential contributions of Ca^{2+} to the membrane transport processes seem to be due to the fact that membrane concentrations of Ca^{2+} relative to those of Na^+ are kept at high level within a wide range of external Na^+/Ca^{2+} concentration ratio. In the present 10^{-2} mol dm^{-3} NaCl(II) and 10^{-2} mol dm^{-3} $CaCl_2$(II) systems, measurements of the cation concentrations in the CK-1, 1.0t membrane phase indicated that 90—99% of cations in the membrane phase are site-bound and that more than 80% of cations are Ca^{2+} in the membrane (unpublished observations). In general both the membrane/solution partition of ions and the migration speed of ions across membrane are dominant factors to control the membrane permselectivity to ions. The Ca^{2+} controlled membrane processes in the present systems are due to the facts that the greater part of fixed cation-exchange sites are occupied by Ca^{2+} and the Donnan adsorption of electrolyte is suppressed at quite low level.

Figure 3 shows Na^+/Ca^{2+} membrane permeability ratios and diffusional/electroconductive membrane permeability ratios, as well as comparisons with these ratios evaluated in concentration cell systems. The P_{Na}/P_{Ca} values in the present bi-ionic systems changed drastically from those in the concentration cell systems so as to reverse the cationic permselectivity sequences. As expected from the linear membrane potential responses and Eq. 7, almost constant P_{Na}/P_{Ca} vslues were obtained. P^0_{Na}/P_{Na} $(=P^0_{Ca}/P_{Ca})$ values less than 0.1 indicate that electroconductive movements of cations progress much more efficiently than diffusion of cations. These situations were more remarkable in the bi-ionic systems than in the concentration cell systems. Furthermore as indicated by Eq. 10, deviations of the diffusional/conductive permeability ratio from unity denote the order of participations of the correlative or cooperative effects between different permeant ions, namely the Na^+-Ca^{2+} correlations in the present bi-ionic systems and Na^+-Cl^- or Ca^{2+}-Cl^- correlations in the respective concentration cell systems, to the membrane processes.[5]

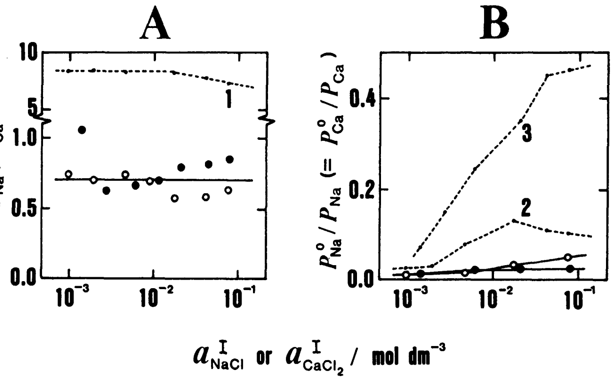

Fig. 3. Cationic membrane permeability ratio ($P_{Na}/P_{Ca}=P^0_{Na}/P^0_{Ca}$) (A) and diffusional/electroconductive permeability ratio ($P^0_{Na}/P_{Na}=P^0_{Ca}/P_{Ca}$) (B) as a function of mean electrolyte activity of phase I. Closed and open circles indicate $CaCl_2$(I)-10^{-2} mol dm^{-3} NaCl(II) and NaCl(I)-10^{-2} mol dm^{-3} $CaCl_2$(II) systems, respectively. The broken lines 1, 2, and 3 refer to P_{Na}/P_{Ca}, P^0_{Na}/P_{Na}, and P^0_{Ca}/P_{Ca} values estimated in NaCl(I)-10^{-2} mol dm^{-3}NaCl(II) and $CaCl_2$(I)-10^{-2} mol dm^{-3} $CaCl_2$(II) systems.

System with a Varying Na^+/Ca^{2+} Permeability Ratio and Effect of Cl^- Permeation. Estimations for the transport parameters relating Cl^- are required for the systems where NaCl or $CaCl_2$ concentrations of phase II are fixed constant at 10^{-1} or 10^{-3} mol dm^{-3}, since definite amounts of Cl^- are transported across the membrane as can be seen in Figs. 1-C-b and C-c. Within the limits of approximately 10-fold concentration difference between the external NaCl and $CaCl_2$ solutions, almost all the Cl^- fluxes were suppressed and only Na^+ and Ca^{2+} permeated across the membrane holding the relationship, $J_{Na}=-2J_{Ca}$. However, as the external NaCl concentrations increased, Na^+-Ca^{2+} bi-cationic transport processes shifted gradually to NaCl transport processes ($J_{Na}=J_{Cl}$) and, as the $CaCl_2$ concentrations increased, to $CaCl_2$ transport processes ($J_{Ca}=1/2J_{Cl}$). These experimental facts seem to indicate redistribution processes of Na^+ and Ca^{2+} within membrane, in which the one cation species tend to occupy entirely the negatively charged fixed sites and simultaneously to exclude the other cation species from the membrane phase depending upon the external cation concentrations.

Equation 5 can be modified to the following form in which the membrane electric current is expressed as the sum of two terms describing currents carried by cations, Na^+ and Ca^{2+}, and Cl^-:

$$\begin{aligned} I &= -2FP_{Na-Ca}a_{Na-Ca}\sinh[3F(V-V_{Na-Ca})/4RT] \\ &\qquad -2FP_{Cl}(a^{I}_{Cl}a^{II}_{Cl})^{1/2}\sinh[F(V-V_{Cl})/2RT] \\ &= -g_{Na-Ca}(V-V_{Na-Ca})-g_{Cl}(V-V_{Cl}) \end{aligned} \tag{14}$$

where P_{Na-Ca} is the membrane permeability to whole cations refer to P_{Cl} defined as:

$$P_{Na-Ca} = (2P_{Na}P_{Ca})^{1/2}\exp(\pm FV/4RT) \tag{15}$$

The signs in the exponential term in Eq. 15 refer to + for NaCl (I)-$CaCl_2$(II) system and to − for $CaCl_2$(I)-NaCl(II) system. a_{Na-Ca} $(=(a^{I}_{Na}a^{II}_{Ca})^{1/2}$ or $(a^{I}_{Ca}a^{II}_{Na})^{1/2})$ is the averaged concentration of external cations. g_{Na-Ca} is the cationic membrane conductance dependent upon Na^+ and Ca^{2+} refer to g_{Cl}:

$$\begin{aligned} g_{Na-Cl} &= \frac{3F^2}{2RT}P_{Na-Ca}a_{Na-Ca}\frac{\sinh[3F(V-V_{Na-Ca})/4RT]}{3F(V-V_{Na-Ca})/4RT} \\ g_{Cl} &= \frac{F^2}{2RT}P_{Cl}(a^{I}_{Cl}a^{II}_{Cl})^{1/2}\frac{\sinh[-F(V-V_{Cl})/2RT]}{-F(V-V_{Cl})/2RT} \end{aligned} \tag{16}$$

The membrane conductance, G_m, and potential, V_0 for these systems are expressed as:

$$\begin{aligned} G_m &= g_{Na-Ca} + g_{Cl} \\ &= (F^2/RT)\exp(-FV_0/2RT) \\ &\quad \times[P_{Na}a^{I}_{Na}+2P_{Ca}a^{I}_{Ca}\exp(-FV_0/2RT)+P_{Cl}a^{II}_{Cl}] \\ &= (F^2/RT)\exp(FV_0/2RT) \\ &\quad \times[P_{Na}a^{II}_{Na}+2P_{Ca}a^{II}_{Ca}\exp(FV_0/2RT)+P_{Cl}a^{I}_{Cl}] \end{aligned} \tag{17}$$

$$
\begin{aligned}
V_0 &= (g_{\mathrm{Na-Ca}}/G_{\mathrm{m}})V_{\mathrm{Na-Ca}} + (g_{\mathrm{Cl}}/G_{\mathrm{m}})V_{\mathrm{Cl}} \\
&= t_{\mathrm{Na-Ca}}V_{\mathrm{Na-Ca}} + t_{\mathrm{Cl}}V_{\mathrm{Cl}} \qquad (18)
\end{aligned}
$$

where $t_{\mathrm{Na-Ca}}$ and t_{Cl} are the transport number to whole cations and to Cl^-, respectiely.

On the basis of assumptions where permeability ratios are constant within the limits of narrow concentration range of the external electrolyte solution, $P_{\mathrm{Na}}/P_{\mathrm{Ca}}$ values can be evaluated by utilizing Eq. 6 to a pair of membrane potential values. Then, at given electrolyte concentrations, $V_{\mathrm{Na-Ca}}$ values are determined by Eq. 7, and consequently, P_{Na}, P_{Ca}, and P_{Cl} values can be calculated using the above equations and electrochemical data. Figure 4 shows $t_{\mathrm{Na-Ca}}$ values with $P_{\mathrm{Na}}/P_{\mathrm{Ca}}$ and $P_{\mathrm{Cl}}/P_{\mathrm{Na}}$ ratios; the plotted membrane permeability ratios were calculated from the respective permeability values to Na^+, Ca^{2+}, and Cl^- estimated as described above. Furthermore, in this figure, the $P_{\mathrm{Na}}/P_{\mathrm{Ca}}$ values were compared with those calculated by Eq. 7 assuming that Cl^- permeations can be ignored, namely, that the relation, $V_0 = V_{\mathrm{Na-Ca}}$, is satisfied. For the case where relative NaCl concentrations are high (see Fig. 4-a: 10^{-1} mol dm^{-3} NaCl(II) system and Fig. 4-d: 10^{-3} mol dm^{-3} $\mathrm{CaCl_2}$(II) system), $P_{\mathrm{Na}}/P_{\mathrm{Ca}}$ values increase rapidly as relative Na^+ concentration increases, while $P_{\mathrm{Cl}}/P_{\mathrm{Na}}$ and t_{Cl} values are kept at almost constant and low levels. On the contrary, when relative $\mathrm{CaCl_2}$ concentrations are high (see Fig. 4-b: 10^{-3} mol dm^{-3} NaCl(II) system and Fig. 4-c: 10^{-1} mol dm^{-3} $\mathrm{CaCl_2}$(II) system), $t_{\mathrm{Na-Ca}}$ values decrease gradually as relative Ca^{2+} concentrations increase, while $P_{\mathrm{Na}}/P_{\mathrm{Ca}}$ values are kept at almost constant levels similarly to those in the system with a negligible Cl^- permeation discussed in earlier parts of this section. So it is suggested that the positive deviations from the linear relationships of ideal Na^+–Ca^{2+} bi-ionic potential responses are due to a rise in the Na^+ permeation and that the negative deviations are due to a rise in the Cl^- permeatins.

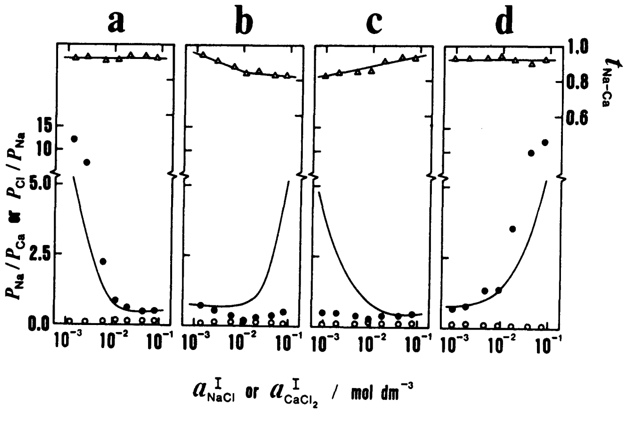

Fig. 4. Transport number to whole cations, $t_{\mathrm{Na-Ca}}$ (△), and permeability ratios, $P_{\mathrm{Na}}/P_{\mathrm{Ca}}$(●) and $P_{\mathrm{Cl}}/P_{\mathrm{Na}}$ (○), as a function of mean electrolyte activity of phase I. a: $\mathrm{CaCl_2}$(I)-10^{-1} mol dm^{-3} NaCl(II). b: $\mathrm{CaCl_2}$(I)-10^{-3} mol dm^{-3} NaCl(II). c: NaCl(I)-10^{-1} mol dm^{-3} $\mathrm{CaCl_2}$(II). d: NaCl(I)-10^{-3} mol dm^{-3} $\mathrm{CaCl_2}$(II). The solid lines refer to $P_{\mathrm{Na}}/P_{\mathrm{Ca}}$ values calculated by Eq. 7 from membrane potential data assuming $P_{\mathrm{Cl}}=0$.

When three ionic species, Na^+, Ca^{2+}, and Cl^-, are involved in the transport processes, the membrane system is characterized by the 3×3 permeability matrix or conductance matrix as shown in Eqs. 1 and 2. Accordingly, detailed phenomenological analyses on membrane permselectivity are required to estimate nine elements of the permeability matrix or six elements of the conductance matrix from available experimental data. However, estimations of the complete sets of these phenomenological coefficients are required to carry out complicated measurements with extreme cares under various experimental conditions. In the present study, only the effects of Cl^- permeation on the entire cation transport are discussed according to the following simplified formulations based on the potential, conductance, and flux data:

$$
\begin{bmatrix} i_{\mathrm{Na-Ca}} \\ i_{\mathrm{Cl}} \end{bmatrix} = -\begin{bmatrix} g_{\mathrm{Na-Ca \cdot Na-Ca}} & g_{\mathrm{Na-Ca \cdot Cl}} \\ g_{\mathrm{Cl \cdot Na-Ca}} & g_{\mathrm{Cl \cdot Cl}} \end{bmatrix} \begin{bmatrix} V - V_{\mathrm{Na-Ca}} \\ V - V_{\mathrm{Cl}} \end{bmatrix} \qquad (19)
$$

where $i_{\mathrm{Na-Ca}}$ $(=i_{\mathrm{Na}}+i_{\mathrm{Ca}})$ is the cationic membrane current. By means of evaluating three matrix elements, such as $g_{\mathrm{Na-Ca \cdot Na-Ca}}$ depending only upon cations, $g_{\mathrm{Na-Ca \cdot Cl}}$ $(=g_{\mathrm{Cl \cdot Na-Ca}})$ describing the correlations between whole cation and Cl^-, and $g_{\mathrm{Cl \cdot Cl}}$, the effects of Cl^- permeations on the permselectivities to cations are characterized quantitatively on the basis of nonequilibrium thermodynamics. Results are given in Fig. 5. It can be seen in these figures that the changes in $g_{\mathrm{Na-Ca \cdot Na-Ca}}$ and $g_{\mathrm{Na-Ca \cdot Cl}}$ with external electrolyte concentration are relatively small, whereas $g_{\mathrm{Cl \cdot Cl}}$ increases rapidly as the concentration differences between NaCl and $\mathrm{CaCl_2}$ solutions separated by the

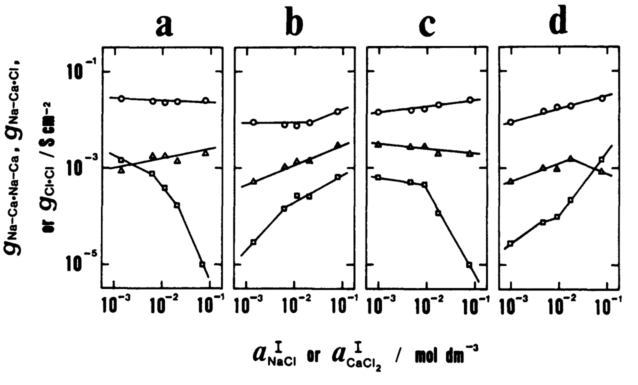

Fig. 5. Membrane conductance matrix elements, $g_{\mathrm{Na-Ca \cdot Na-Ca}}$(○), $g_{\mathrm{Na-Ca \cdot Cl}}$(=$g_{\mathrm{Cl \cdot Na-Ca}}$)(△), and $g_{\mathrm{Cl \cdot Cl}}$(□), as a function of mean electrolyte activity of phase I. a, b, c, and d denote the same systems as in Fig. 4.

membrane increase. By referring Fig. 5 with Figs. 1-A-b, A-c, and 4, it is seen that the conductance matrix element as a linear phenomenological coefficient in Eq. 19 can describe well the deviation from ideal Na^+–Ca^{2+} bi-ionic potential response and the mode of ionic permselectivity in the CK-1, 1.0t membrane sytem.

Na^+–Cs^+ and Na^+–Ca^{2+} Bi-Ionic Systems. As reported earlier for the NaCl–CsCl system,[6] Na^+ and Cs^+ contributed equally to the transport processes across highly selective cation-exchange membrane, CK-1, 1.0t. The extents of participations of Na^+ and Cs^+ to the membrane processes depended simply on the rates of external concentrations of respective cations, which should be parallel to the rates of membrane concentrations of cations. In case of the Na^+–Cs^+ bi-ionic systems, effects of Cl^- permeations were almost perfectly excluded within the limits of wide ranges of external electrolyte concentrations.

On the contrary in the present NaCl–CaCl$_2$ system, Ca^{2+} contributions to the membrane processes are dominant and the permselectivity to Ca^{2+} is improved to reverse the sequences to Na^+ compared with those in the respective concentration cell systems. These Ca^{2+} effects originate in the high membrane concentrations of Ca^{2+}. Cation-exchange membranes developed for the applications in desalination processes are usually performed the membrane surface treatments to prevent from penetrations of multivalent cations, especially Ca^{2+}, into the membrane phase. However, Ca^{2+}, once penetrating into the membrane due to the high external $CaCl_2$ concentrations, plays a dominant role in the membrane transport processes according to the high concentrations and tight interactions with negatively charged sites within the membrane phase. It was also suggested that increases in Cl^- permeations are closely related to the increase in external Ca^{2+} concentrations. The present studies served as a quantitative representations of these cooperative interactions between permeating ions and of Ca^{2+} effects on the basis of nonequilibrium thermodynamic theory.

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