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Study of Ion Transport across Amphoteric Ion-Exchange Membrane.[1)] V. Nonequilibrium Thermodynamic Analyses of Ion Selectivity

Kozue Kaibara,* Hiroyoshi Inoue, Shigeru Tsuruyama, and Hideo Kimizuka
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812

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Ion-transport processes across an amphoteric ion-exchange membrane were investigated by means of estimating the membrane permeability matrix, a set of modified linear phenomenological coefficients, from the electrochemical and the ion flux data. Systematic comparisons of phenomenological analyses on an amphoteric ion-exchange membrane system with those on an ordinary cation-exchange membrane system were carried out to investigate the correlations of singly- and binary-charged membrane structures to characteristic transport properties. The modes of ion permselectivity of an amphoteric ion-exchange membrane in the metal chloride concentration-cell systems are characterized by the potentiometric selective response due to the ion-sieve effect, the low membrane conductance, and the large ion flux, while those of an ordinary cation-exchange membrane are characterized by the totally charge-dependent potential response, the high conductance, and the extremely small ion flux. The cross elements of the membrane permeability matrix, which represent the partial contributions of cation-anion interactions to the membrane permselectivity, are positive for an amphoteric membrane and negative for a cation-exchange membrane. The positive cross matrix elements act deceleratively on the membrane permeability, whereas the negative elements do acceleratively. It was pointed out based on the nonequilibrium thermodynamic theory that the preferable and efficient permeation mechanism is the simple diffusion process in an amphoteric ion-exchange membrane, whereas the electroconductive process in a cation-exchange membrane.

The linear phenomenological analysis is a powerful tool to characterize membrane transport processes on the basis of the nonequilibrium thermodynamics (see e.g., Refs. 2, 3). A variety of nonequilibrium thermodynamic theories on the membrane transport processes have been developed to investigate meterial transport phennomena arising across membranes. These membrane theories are useful to describe quantitatively the selective transport performance in some particular membrane samples by evaluating the linear phenomenological coefficients from the available experimental data. However, there seem to be some uncertain factors, even now, in the generalized correlations of phenomenological coefficients with membrane properties such as permeability, selectivity, polymeric and charged structures, and phase behavior of membrane substances. Therefore, it is still worth to examine differences in the linear phenomenological coefficients between the membrane systems showing distinguishable transport characteristics with each other.

As shown in earlier reports of this series, an amphoteric ion-exchange membrane, in which almost equal amounts of positively and negatively charged sites are homogeneously and regularly dispersed at high densities, shows unique transport characteristics different from those of a uniform ion-exchange membrane. By introducing equal amounts of positively and negatively charged sites into the membrane phase, the permselectivities to cations or anions are deteriorated inevitably; however, potentiometric permselectivities were demonstrated even for ions of the same charge as the most interesting transport properties of the homogeneous type amphoteric ion-exchange membrane, unlike the usual uniform ion-exchange membrane.[1,4)] It has been pointed out that a useful amphoteric ion-exchange membrane should have the membrane structure in which both the cation- and anion-exchange regions are as small as possible[5)] and also that the transport phenomena specific to an amphoteric ion-exchange membrane are observed when the ratio of cationic to anionic exchange capacity ranges from 0.8 to 1.[6)] Recently developed amphoteric ion-exchange membranes, in which cationic and anionic exchange sites are distributed homogeneously over the functionalized polymer network in microscopic dimensions with high density, are proved to be applicable to the processes separating organic compounds of low molecular weight from inorganic electrolyte mixtures.[7,8)]

In the present investigations, ion transport characteristics of an amphoteric ion-exchange membrane are examined by means of estimating the membrane permeability matrix as a principal membrane permselectivity parameter. The transport process analyses utilizing the membrane permeability matrix, of which element is recognized as a modified linear phenomenological coefficient describing a partial contribution of correlation between permeating ions on the membrane selectivity to respective ions, provide a quantitative description of ion transport process on the basis of nonequilibrium thermodynamics.[9—11)] The estimated membrane permeability matrix of an amphoteric ion-exchange membrane was compared with that of an ordinary cation-exchange membrane, since the present discussion also aims at inspecting how the charged membrane structure reflects on qualitative and quantitative aspects of the phenomenological coefficients.

Experimental

An amphoteric membrane used in the present experiments is 1.0-PA-29 amphoteric ion-exchange membrane (Kanegafuchi Chemical Industry Co., Ltd.) and CK-1, 1.0t cation-exchange membrane (Asahi Chemical Industry Co., Ltd.) was used as a reference membrane sample of ordinary highly selective cation-exchange membrane. Fundamental physicochemical properties and an outline of preparation procedures of these membranes were described in earlier papers.[1,4,7,10] Both the ion-exchange membranes have the same cation-exchange site, usual sulfonic acid type, and comparable ion-exchange capacities, ca. 1.7—2.0 eq·(kg wet-membrane)$^{-1}$. Accordingly, systematic and generalized discussions are available to investigate substantial differences in the ion transport characteristics of a binary-charged amphoteric ion-exchange membrane as compared with those of an ordinary singly-charged cation-exchange membrane.

Electrochemical properties, such as transmembrane potential and conductance, and inter-compartmental ion fluxes were measured for the concentration-cell systems to evaluate the membrane transport parameters based on the nonequilibrium thermodynamic theory. Experimental systems consisted of solution phase I, in which electrolyte concentration was varied from 10^{-1} to 10^{-3} mol dm^{-3}, and phase II with a fixed concentration of 10^{-2} mol dm^{-3} separated by a membrane phase. Electrolyte used in the present measurements included metal chlorides such as CsCl, KCl, NaCl, LiCi, $CaCl_2$, and $SrCl_2$. Electrolyte solutions were prepared from extra-pure salts with conductivity water. Measurements were carried out with a setup, essentially the same as reported in an earlier paper.[10] A high-input-impedance digital voltmeter (TR6877D, Takeda Riken Co.) and impedance measuring equipments (YHP4255A and YHP4440B, Yokogawa-Hewlett-Packard Co.; KC-530, Kokuyo Electric Co.) were employed to measure the electrochemical properties of the concentration-cell systems with the ion-exchange membrane by the ordinary methods. Inter-compartmental ion flux was estimated by means of tracing the time changes in solution conductivities of the solution phases I and II. All the measurements were carried out at regulated temperature, 25.0±0.1 °C, using a water-jacket glass-made measurement cell throughout the present experiments.

Results and Discussion

Membrane Transport Phenomena. Figure 1 summarizes the results obtained in the present experiments. Transmembrane potential data in Fig. 1-A indicate that the 1.0-PA-29 amphoteric ion-exchange membrane reveals potentiometric selectivities even to permeant metal cations of the same charge. It has been pointed out that these potentiometric selectivities are due to an "ion-sieve effect" to hydrated permeant ion demonstrated for all ions regardless of the electrolyte species and of positive or negative charges.[1,4] The ion-sieve effect responsible for shifting out the hydrated cations and anions permeating across the 1.0-PA-29 amphoteric ion-exchange membrane was suggested to be dependent upon the three-dimensional-array ion-exchange groups with an alternately charged regular arrangement.

Providing that equal numbers of the cation- and anion-exchange sites are introduced into the membrane phase and that both the ion-exchange sites

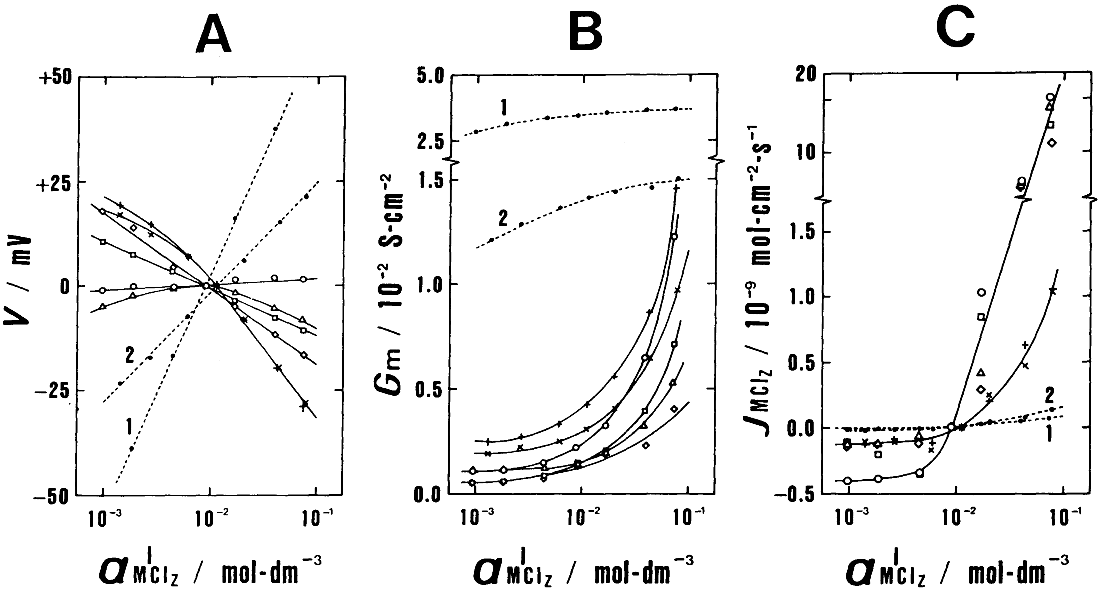

Fig. 1. Transmembrane potential (A), membrane conductance (B), and inter-compartmental ion flux (C) as a function of the mean electrolyte activity of phase I for a variety of aqueous metal chloride concentration-cell systems with an amphoteric ion-exchane membrane, 1.0-PA-29. ○: CsCl; △: KCl; □: NaCl; ◇: LiCl; ×: $CaCl_2$; +: SrCl. The broken lines 1 and 2 refer to the data for NaCl and $CaCl_2$ systems with a cation-exchange membrane, CK-1, 1.0t.

interact equivalently with oppositely charged permeant ions, the zero transmembrane potential should be observed for a 1-1 electrolyte system as an ideal amphoteric ion-exchange membrane potential, since the membrane permeabilities to cation and anion are identical with each other. In the present case, the CsCl system, in which transport numbers to Cs^+ and Cl^- are estimated at 0.51 and 0.49, respectively, from the membrane potential data, realizes apparently these situations as can be seen in Fig. 1-A. The Cs^+/Cl^- hydrated radius ratio is 0.99. The 1.0-PA-29 membrane also demonstrated almost ideal potential responses for an amphoteric ion-exchange membrane in the $NaClO_3$ concentration-cell systems, in which transport numbers to Na^+ and ClO_3^- are 0.51 and 0.49, and the Na^+/ClO_3^- hydrated radius ratio is 1.05.[1] In case of KCl systems composed of cation and anion with comparable hydrated radii, the 1.0-PA-29 membrane exhibited a biphasic ion selectivity in which cations are more permeable than anions at lower electrolyte concentrations, but at higher concentrations, the ion permselectivity is reversed. Transport numbers to cations are decreased with an increasing radius of hydrated cation as: K^+ (transport number, 0.43—0.54), Na^+ (0.40), and Li^+ (0.35). In the 1.0-PA-29 membrane, the ionic selectivity balance leans slightly toward an anion-selective side (see also Refs. 1 and 4).

Similar situations, such as the cation transport number sequence depending upon the hydrated ionic radius, the slight unbalance of ionic permselectivity shifted to anion selective side, and the resultant potentiometric selective response to 1-1 metal chloride systems, were observed also in the different samples of an amphoteric ion-exchange membrane fabricated by the block copolymerization method.[12] In this amphoteric ion-exchange membrane composed of a pentablock copolymer having sulfonic acid type and quaternary ammonium type ion-exchange sites, it was reported that the permeabilities to cation and anion are balanced well in the KCl concentration-cell systems with an external electrolyte concentration ratio of 2 and that the transport numbers to cation decrease as: $K^+>Na^+>Li^+$.

The practical cation to anion permselectivity balance of an amphoteric ion-exchange membrane seems to be controlled by a variety of factors, such as the specific interactions of cation and anion with oppositely charged ion-exchange sites, detailed balance in numbers of cation- and anion-exchange sites, properties of functionalized network polymer, etc. Furthermore, it is one of the most interesting characteristics of an amphoteric ion-exchange membrane that the permselectivities to cations and anions shift either side depending upon the external electrolyte species and their concentrations.

In case that the permeating cation is bivalent, the 1.0-PA-29 amphoteric ion-exchange membrane showed more anion selective transport properties than the case of univalent cation as shown in Fig. 1-A. Transport numbers to Ca^{2+} and Sr^{2+} ranged from 0.27 to 0.45. Attractive interactions of permeating ions with the oppositely charged exchange sites, as well as repulsive interactions with equally charged sites, within the binary-charged amphoteric ion-exchange membrane phase are expected to be improved as an increase in the charge of permeating ions. Accordingly, the modes of ionic permselectivity of an amphoteric ion-exchange membrane are affected inevitably and definitely by ionic charges of permeants, as a common property of ion transport process across charged membranes. The present results suggest that the repulsive interactions of bivalent metal cations with fixed sites of the same charge exceed the attractive interactions with oppositely charged fixed sites (see also Ref. 1).

Membrane conductance and inter-compartmental ion flux data of the concentration-cell systems for a series of metal chlorides are given in Figs. 1-B and 1-C. The membrane conductances were larger in the bivalent cationic systems, while the inter-compartmental cationic flux was larger in the univalent cationic systems. External electrolyte concentration dependences of these data, increasing with an increasing external concentration, were observed also in the singly-charged ion-exchange membrane. Interesting and substantial differences in these transport properties, as well as in the membrane potential responses mentioned above, between the binary-charged amphoteric ion-exchange membrane, 1.0-PA-29, and the singly-charged cation-exchange membrane, CK-1, 1.0t, are discussed in a latter part of this section.

Membrane Permeability Matrix. A variety of the membrane transport theories based on the nonequilibrium thermodynamics provide an appropriate set of the linear phenomenological coefficients describing the transport phenomena across membranes. The membrane permeability matrix theory is shown to be useful to analyze quantitatively the permselective ion transport across a charged membrane.[9—11,13] According to these theoretical formulations, the membrane permeability matrix, which is introduced to describe partial contributions of correlations between the permeating ions on the membrane permselectivity to ions, can be expressed for the concentration-cell systems containing Z-valent metal cation M and chloride ion as:

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

where J is the ionic flux, V is the transmembrane potential, a is the ionic activity, F is the Faraday constant, R is the gas constant, and T is the absolute temperature; the superscripts I and II indicate the two solution phases separated by the membrane phase, respectively; the subscripts M and Cl refer to metal cation and chloride ion, respectively. The 2×2 matrix in Eq. 1 is the membrane permeability matrix. Each element represents a partial contribution on the permselective transport process due to the correlations between permeating ion species indicated by the subscript index. The cross coefficients of membrane permeability matrix, $P_{\mathrm{M \cdot Cl}}$ and $P_{\mathrm{Cl \cdot M}}$, are related with each other as:[9]

$$\frac{P_{\mathrm{M \cdot Cl}}}{P_{\mathrm{Cl \cdot M}}} = \frac{(a_{\mathrm{M}}^{\mathrm{I}} a_{\mathrm{M}}^{\mathrm{II}})^{1/2}}{(a_{\mathrm{Cl}}^{\mathrm{I}} a_{\mathrm{Cl}}^{\mathrm{II}})^{1/2}} \times$$

$$\frac{\sinh[ZF(V - V_{\mathrm{M}})/2RT]/[ZF(V - V_{\mathrm{M}})/2RT]}{\sinh[-F(V - V_{\mathrm{Cl}})/2RT]/[-\mathrm{F}(V - V_{\mathrm{Cl}})/2RT]} \tag{2}$$

The electroconductive membrane permeabilities to metal cation M and to Cl^-, P_{M} and P_{Cl}, are defined as a function of the elements of the 2×2 membrane permeability matrix and estimated from the transmembrane potential and conductance data as:

$$P_{\mathrm{M}} = P_{\mathrm{M \cdot M}} - (1/Z)P_{\mathrm{Cl \cdot M}}$$

$$= \frac{t_{\mathrm{M}} G_{\mathrm{m}} RT}{Z^2 F^2 (a_{\mathrm{M}}^{\mathrm{I}} a_{\mathrm{M}}^{\mathrm{II}})^{1/2}} \frac{[ZF(V - V_{\mathrm{M}})/2RT]}{\sinh[ZF(V - V_{\mathrm{M}})/2RT]} \tag{3}$$

$$P_{\mathrm{Cl}} = P_{\mathrm{Cl \cdot Cl}} - ZP_{\mathrm{M \cdot Cl}}$$

$$= \frac{t_{\mathrm{Cl}} G_{\mathrm{m}} RT}{F^2 (a_{\mathrm{Cl}}^{\mathrm{I}} a_{\mathrm{Cl}}^{\mathrm{II}})^{1/2}} \frac{[-F(V - V_{\mathrm{Cl}})/2RT]}{\sinh[-F(V - V_{\mathrm{Cl}})/2RT]} \tag{4}$$

where t is the transport number, G_{m} is the membrane conductance; V_{M} and V_{Cl} is the Nernstian equilibrium membrane potentials to metal cation M and Cl^-, respectively.

In a special case where total electric current across membrane is zero, Eq. 1 can be reduced to the next modified phenomenological equation:

$$\begin{bmatrix} J_{\mathrm{M}} \\ J_{\mathrm{Cl}} \end{bmatrix}_{I=0} = -\begin{bmatrix} P_{\mathrm{M}}^{0} & 0 \\ 0 & P_{\mathrm{Cl}}^{0} \end{bmatrix} \times$$

$$\begin{bmatrix} a_{\mathrm{M}}^{\mathrm{II}} \exp(ZFV_0/2RT) - a_{\mathrm{M}}^{\mathrm{I}} \exp(-ZFV_0/2RT) \\ a_{\mathrm{Cl}}^{\mathrm{II}} \exp(-FV_0/2RT) - a_{\mathrm{Cl}}^{\mathrm{I}} \exp(FV_0/2RT) \end{bmatrix} \tag{5}$$

where V_0 is the transmembrane potential in absence of membrane electric current. The diffusional membrane permeabilities to M^{Z+} and to Cl^-, P_{M}^{0} and P_{Cl}^{0}, which can be estimated directly from the transmembrane potential and inter-compartmental ion flux data, are expressed as a function of the membrane permeability matrix elements:

$$P_{\mathrm{M}}^{0} = (P_{\mathrm{M \cdot M}} P_{\mathrm{Cl \cdot Cl}} - P_{\mathrm{M \cdot Cl}} P_{\mathrm{Cl \cdot M}})/P_{\mathrm{Cl}} \tag{6}$$

$$P_{\mathrm{Cl}}^{0} = (P_{\mathrm{M \cdot M}} P_{\mathrm{Cl \cdot Cl}} - P_{\mathrm{M \cdot Cl}} P_{\mathrm{Cl \cdot M}})/P_{\mathrm{M}} \tag{7}$$

The electroconductive and diffusional membrane permeabilities are related with each other as:

$$P_{\mathrm{M}}^{0}/P_{\mathrm{M}} = P_{\mathrm{Cl}}^{0}/P_{\mathrm{Cl}} = 1 + (\mathrm{P}_{\mathrm{Cl \cdot M}}/ZP_{\mathrm{M}}) + (ZP_{\mathrm{M \cdot Cl}}/P_{\mathrm{Cl}}) \tag{8}$$

The electroconductive membrane permeability defined by Eqs. 3 and 4 should be discriminated on the basis of nonequilibrium thermodynamics from the diffusional membrane permeability defined by Eqs. 6 and 7.[9–11,13] The electroconductive permeability as a function of the ionic mobility across membrane phase represents the electrical conductive process of membrane transport, whereas the diffusional permeability as a function of the diffusion coefficient across membrane phase represents the ionic diffusion process. As discussed in latter part of this section, relative magnitudes of these two permeabilities prescribe characteristics of the modes of ion migration across

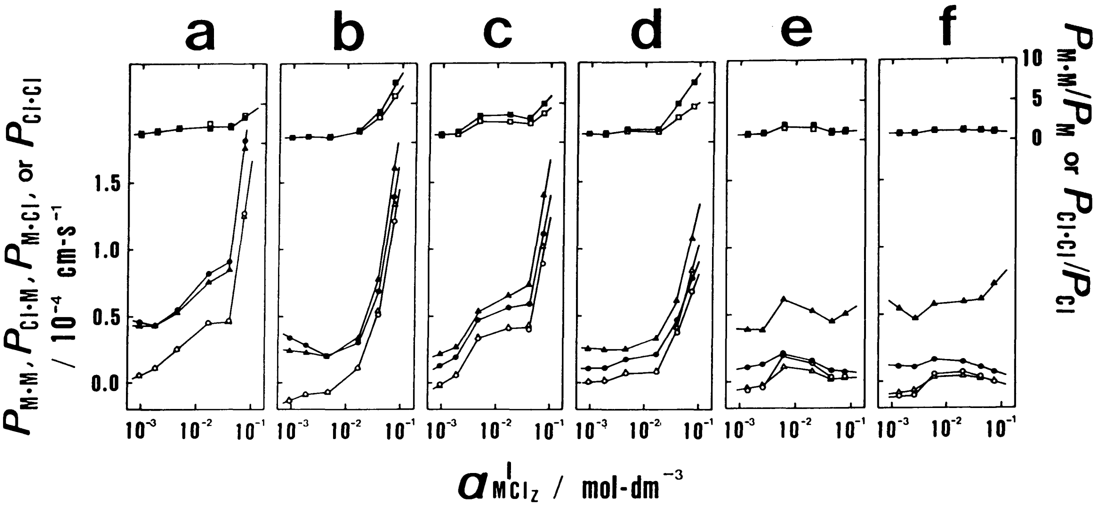

Fig. 2. Membrane permeability matrix elements and, $P_{\mathrm{M \cdot M}}/P_{\mathrm{M}}$ and $P_{\mathrm{Cl \cdot Cl}}/P_{\mathrm{Cl}}$ ratios as a function of the mean electrolyte activity of phase I for the 1.0-PA-29 amphoteric ion-exchange membrane systems. ●: $P_{\mathrm{M \cdot M}}$; ○: $P_{\mathrm{Cl \cdot M}}$; △: $P_{\mathrm{M \cdot Cl}}$; ▲: $P_{\mathrm{Cl \cdot Cl}}$; ■: $P_{\mathrm{M \cdot M}}/P_{\mathrm{M}}$; □: $P_{\mathrm{Cl \cdot Cl}}/P_{\mathrm{Cl}}$. a: CsCl; b: KCl; c: NaCl; d: LiCl; e: $\mathrm{CaCl_2}$; f: $\mathrm{SrCl_2}$.

membrane and also provide a practical index indicating the efficient way of the membrane utilization.

The membrane permselectivity parameters, such as the permeability matrix elements, $P_{M \cdot M}$, $P_{Cl \cdot M}$, $P_{M \cdot Cl}$, and $P_{Cl \cdot Cl}$, electroconductive permeabilities, P_M and P_{Cl}, and diffusional permeabilities, P^0_M and P^0_{Cl}, can be estimated from the membrane potential, the membrane conductance, and the inter-compartmental ion flux data based on these thermodynamic relationships, Eqs. 2—8. These parameters indicate the membrane permselectivities to respective ions by referring the apparent permeation speed across membrane. The membrane potential can be expressed as a function of the membrane permeability ratio or relative membrane permebility, $P_{Cl}/P_M(=P^0_{Cl}/P^0_M)$.[1,11,13] The membrane conductance and the ionic membrane conductance, product of the transport number and membrane conductance, are proportional directly to the electroconductive membrane permeability as indicated in Eqs. 3 and 4, while the diffusional membrane permeability is proportional to the ionic flux under the conditions of $ZJ_M=J_{Cl}$.

Figure 2 summarizes the values of membrane permeability matrix elements for a series of metal chlorides. In case of the univalent metal chloride systems, all the four membrane permeability matrix elements increased with increasing external concentrations, while in the bivalent metal systems, the matrix elements remained at almost constant levels. A sequence in the matrix element was $P_{Cl \cdot Cl} \geqq P_{M \cdot M} > P_{Cl \cdot M}$, $P_{M \cdot Cl}$; however, differences in the matrix element values between the terms based on a correlation of equally charged ions and those of oppositely charged ions are quite small. As indicated by Eqs. 3 and 4, the positive $P_{Cl \cdot M}$ and $P_{M \cdot Cl}$ contribute deceleravively to the respective permeabilities to metal cation and chloride ion. The positive values of these cross elements, in addition, result in the situations where the diffusional permeabilities exceed the electroconductive permeabilities as illustrated in Fig. 3. As expected from the results of transmembrane potential measurements, the 1.0-PA-29 amphoteric ion-exchange membrane is, in general, more permeable to chloride ions than to respective metal cations. Detailed discussion on the characteristic ion transport process across an amphoteric ion-exchange membrane is carried out in the following part of this section based on these membrane permeability parameters.

Comparisons with an Ordinary Singly-Charged Cation-Exchange Membrane. Systematic comparisons of the transport parameters for the 1.0-PA-29 membrane systems with those for the CK-1, 1.0t membrane are useful to investigate further the ionic transport processes across an amphoteric ion-exchange membrane. It is also interesting to clarify substantial differences in the ionic transport processes between singly- and binary-charged ion-exchange membranes.

In Fig. 1, the transmembrane potential, conductance, and ion flux data for the NaCl and $CaCl_2$ concentration-cell systems with the CK-1, 1.0t cation exchange membrane are presented as typical examples of 1-1 and 2-1 electrolyte systems. As discussed already, the 1.0-PA-29 amphoteric ion-exchange membrane reveals potentiometric selectivities even to ions of the same charge due to the ion-sieve effect based on the binary-charged membrane structure, in which the alternately charged sites seem to form the networks of three-dimensional-array ion-exchange groups responsible for shifting out the cations and anions. On the contrary to the potentiometric selective responses of the 1.0-PA-29 membrane, the CK-1, 1.0t membrane demonstrated a strictly charge-dependent potential response. An almost ideal

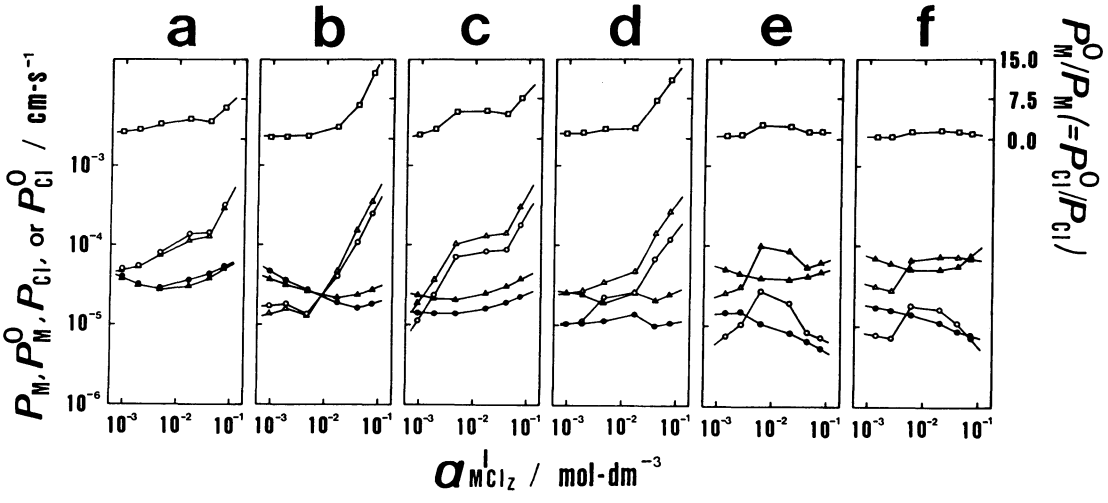

Fig. 3. Electroconductive and diffusional membrane permeabilities and diffusional/conductive permeability ratio as a function of the mean electrolyte activity of phase I for the 1.0-PA-29 amphoteric ion-exchange membrane systems. ●: P_M; ○: P^0_M; ▲: P_{Cl}; △: P^0_{Cl}; □: P^0_M/P_M $(=P^0_{Cl}/P_{Cl})$. a: CsCl; b: KCl; c: NaCl; d: LiCl; e: $CaCl_2$; f: $SrCl_2$.

Nernstian potential response was observed for the concentration-cell systems with the CK-1, 1.0t membrane containing univalent cations, even for the system containing bulky cations such as tetrabutylammonium cation. The transport number of the CK-1, 1.0t membrane to univalent cation estimated from the potential data for a variety of systems is ranged from 0.97 to 0.99 regardless of the electrolyte species in the concentration range studied, 10^{-1}—10^{-3} mol dm^{-3}. These situations are the same as in an ordinary highly permselective anion-exchange membrane system. An almost ideal Nernstian potential response was observed in simple inorganic univalent anion systems as well as in univalent long-hydrocarbon-chain surfactant anion systems.[14—16] The CK-1, 1.0t membrane developed for a desalination process is less permeable to bivalent cations than univalent cations. The membrane potential response showing the transport number of 0.90—0.98 to bivalent cations were observed in the concentration-cell systems containing CaCl$_2$, SrCl$_2$, or MgCl$_2$. In case of the LaCl$_3$ concentration-cell systems with the CK-1, 1.0t membrane, the transport number to La^{3+} was suppressed further to 0.72—0.83.

As seen in Figs. 1-B and 1-C, there is a great difference in the membrane conductance and inter-compartmental ion flux data between the 1.0-PA-29 and CK-1, 1.0t membrane systems. The membrane conductance changes in the 1.0-PA-29 membrane depending upon the external concentration are due to the fact that the membrane-solution distribution factors of ions (cation concentration within membrane phase [mol·(kg-wet membrane)$^{-1}$]/cation concentration in external solution [mol·dm^{-3}]) are almost unity in the concentration ranges studied.[17] Whereas high and relatively constant conductance values of the CK-1, 1.0t membrane are caused from the high and constant cation concentrations within membrane phase corresponding to the ion-exchange capacity. One of the objects to develop an amphoteric ion-exchange membrane was to get a large salt flux by means of the specific and unique transport mechanisms based on the binary-charged membrane structure.[5,18] On the other hand, only a fairly small ion flux can be observed across the singly-charged CK-1, 1.0t membrane as shown in Fig. 1-C, since the membrane systems are close to the equilibrium conditions as expected from the membrane potential data. Considering the thickness of these two membranes (1.0-PA-29: 0.1 mm; CK-1, 1.0t: 1.09 mm), the membrane conductance and inter-compartmental ion flux of the 1.0-PA-29 membrane are less than 1/10—1/100 and more than 10—100 times of those of the CK-1, 1.0t membrane, respectively.

Figures 4 and 5 summarizes the permselectivity parameters estimated for the NaCl and CaCl$_2$ concentration-cell systems with the CK-1, 1.0t cation-exchange membrane, corresponding to Figs. 2 and 3 for the 1.0-PA-29 amphoteric ion-exchange membrane system. Calculated results of other univalent metal chloride systems were comparable with those of the NaCl system in Figs. 4-a and 5-a, and the SrCl$_2$ system, with the CaCl$_2$ system in Figs. 4-b and 5-b. The sequences in the membrane permeability matrix elements were $P_{M \cdot M} \gg P_{Cl \cdot Cl} > P_{M \cdot Cl} > P_{Cl \cdot M}$ in the CK-1, 1.0t membrane system, since the exchange-sites-bound cations come up to 99% of the total cation concentrations within the

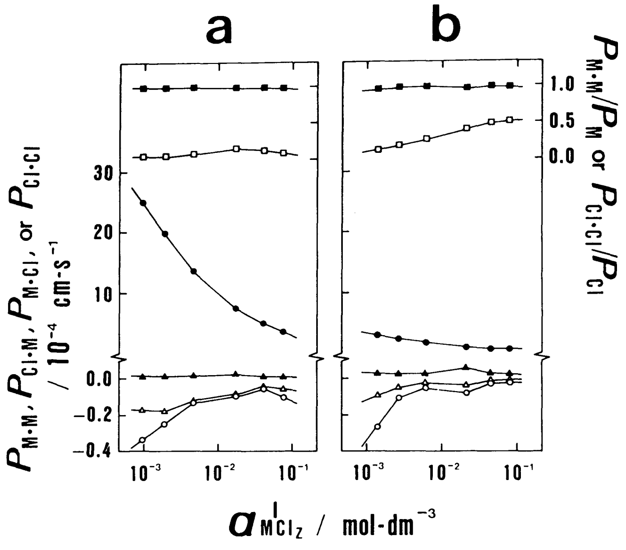

Fig. 4. Membrane permeability matrix elements and, $P_{M \cdot M}/P_M$ and $P_{Cl \cdot Cl}/P_{Cl}$ ratios as a function of the mean electrolyte activity of phase I for the CK-1, 1.0t cation-exchange membrane systems. Symbols are the same as those in Fig. 2. a: NaCl; b: CaCl$_2$.

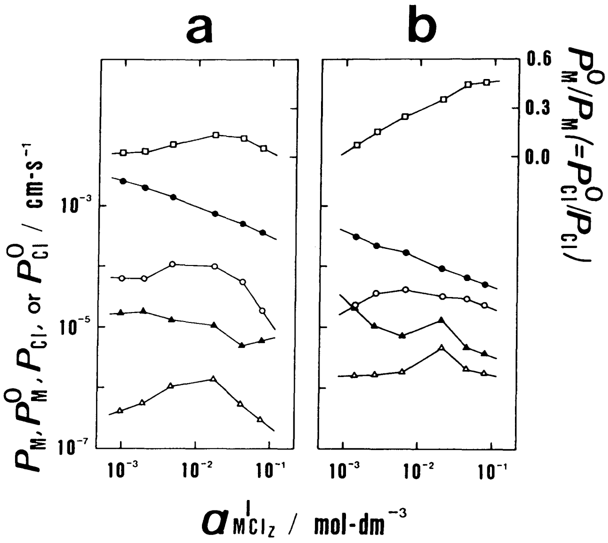

Fig. 5. Electroconductive and diffusional membrane permeabilities and diffusional/conductive permeability ratio as a function of the mean electrolyte activity of phase I for the CK-1, 1.0t cation-exchange membrane systems. Symbols are the same as those in Fig. 3. a: NaCl; b: CaCl$_2$.

membrane and chloride ions are almost perfectly excluded from the membrane phase.(17) In case of the binary-charged 1.0-PA-29 membrane, almost equal amounts of cations and anions are distributed within the membrane phase, so the four permeability matrix elements contribute comparably to the permselective ion transport process as $P_{\mathrm{Cl\cdot Cl}} \geqq P_{\mathrm{M\cdot M}} > P_{\mathrm{Cl\cdot M}}, P_{\mathrm{M\cdot Cl}}$. The membrane permeability to metal cation is dependent upon the major contributions of the cation–cation correlation term, $P_{\mathrm{M}} \cong P_{\mathrm{M\cdot M}}$, as indicated in Fig. 4 and negative values of cross elements, $P_{\mathrm{Cl\cdot M}}$ and $P_{\mathrm{M\cdot Cl}}$, act acceleratively on the permeabilities to cation and anion as expected from Eqs. 3 and 4 in the singly-charged CK-1, 1.0t membrane system.

Drastic increases in the membrane/solution partition factor of cations in the CK-1, 1.0t membrane with decreasing external concentration cause an improvement of permselectivity with decreasing external concentrations. As discussed in an earlier part, the cross matrix elements are positive in the 1.0-PA-29 membrane, and accordingly, the permselective transport process across a binary-charged membrane depends upon the accelerative contributions based on the correlations between equally charged ions and upon the decelerative contributions based on the correlations between oppositely charged ions. Both of these positive and negative contributions in the 1.0-PA-29 membrane system containing univalent metal chlorides, as seen in Fig. 2, increased with increasing ion concentration of the membrane phase which are proportional to the external concentrations. Then, almost constant electroconductive permeabilities to cation and anion are revealed in the 1.0-PA-29 membrane system.

It has been a theoretically and experimentally established concept that the ionic permselectivity across charged membrane is a function of the permeation speed across membrane and of the membrane/solution partition factor of respective ions. The binary-charged membrane structure results in the totally different situations of ions in membrane phase from those in the singly-charged membrane phase as an origin of the unique ion transport characteristics of an amphoteric ion-exchange membrane.(17) Nonequilibrium thermodynamic analyses on the electrolyte transport process in free aqueous media pointed out that the correlation terms between cation and anion contribute negatively to the transport process similarly as in the binary-charged 1.0-PA-29 membrane.(19)

Equation 8 deduces that the signs of $P_{\mathrm{Cl\cdot M}}$ and $P_{\mathrm{M\cdot Cl}}$ prescribe a preferential transport mechanism across membranes, the electroconductive or diffusional processes. If these two cross elements are zero, namely none of the interactions between cation and anion exists, both the membrane permeabilities coincide with each other.(9,13) The diffusional/conductive membrane permeability ratio, $P^0_{\mathrm{M}}/P_{\mathrm{M}}(=P^0_{\mathrm{Cl}}/P_{\mathrm{Cl}})$, can be recognized as a practical index judging whether the electro-dialytic or mechano-dialytic application is efficient for some membrane samples. As shown in Fig. 3, these ratios were larger than unity and increased with an increasing external concentration in the univalent metal chloride system with the 1.0-PA-29 membrane, and in case of the bivalent metal chloride system, these ratios charged from 0.5 to 2.5 depending upon the external concentration. On the other hand in the CK-1, 1.0t membrane system as seen in Fig. 5, the diffusional/conductive membrane permeability ratios were smaller than unity, 0.025—0.17 for univalent metal chloride system and 0.07—0.5 for bivalent system. Whether the diffusional/conductive membrane permeability ratio is larger than or smaller than unity, the sign of the cross elements of membrane permeability matrix is dependent upon the balance of magnitudes of electrical membrane conductance and ionic flux.

Transmembrane potential can be expressed, in general, as a function of the membrane permeability ratio between permeating ions. According to the present membrane transport theory, the following equation for the membrane potential in absence of electric membrane current is obtained from Eqs. 1, 3, and 4:

$$\begin{aligned} &Za^{\mathrm{II}}_{\mathrm{M}}\exp[(Z+1)FV_0/2RT] + (P_{\mathrm{Cl}}/P_{\mathrm{M}})a^{\mathrm{I}}_{\mathrm{Cl}}\exp(FV_0/RT) \\ &\quad -Za^{\mathrm{I}}_{\mathrm{M}}\exp[-(Z-1)FV_0/2RT] - (P_{\mathrm{Cl}}/P_{\mathrm{M}})a^{\mathrm{II}}_{\mathrm{Cl}} = 0 \end{aligned} \tag{9}$$

Identical equation for $P^0_{\mathrm{Cl}}/P^0_{\mathrm{M}}$ can be also derived from Eq. 5. In case of the univalent metal chloride systems, Eq. 9 is reduced to the next equation, which is equivalent in form to the well known membrane potential equations for a symmetrical electrolyte such as the Goldman equation, Eisenman equation, etc.:(3)

$$\begin{aligned} V_0 &= -(RT/F)\ln[(a^{\mathrm{II}}_{\mathrm{M}} + (P_{\mathrm{Cl}}/P_{\mathrm{M}})a^{\mathrm{I}}_{\mathrm{Cl}})/(a^{\mathrm{I}}_{\mathrm{M}} + (P_{\mathrm{Cl}}/P_{\mathrm{M}})a^{\mathrm{II}}_{\mathrm{Cl}})] \\ &= -(RT/F)\ln[(a^{\mathrm{II}}_{\mathrm{M}} + (P^0_{\mathrm{Cl}}/P^0_{\mathrm{M}})a^{\mathrm{I}}_{\mathrm{Cl}})/(a^{\mathrm{I}}_{\mathrm{M}} + (P^0_{\mathrm{Cl}}/P^0_{\mathrm{M}})a^{\mathrm{II}}_{\mathrm{Cl}})]. \end{aligned} \tag{10}$$

Figure 6 summarizes the chloride ion/metal cation membrane permeability ratios, $P_{\mathrm{Cl}}/P_{\mathrm{M}}$ $(=P^0_{\mathrm{Cl}}/P^0_{\mathrm{M}})$, estimated for the 1.0-PA-29 and CK-1, 1.0t membrane systems. As expected from the membrane potential data and Eqs. 9 and 10, the $P_{\mathrm{Cl}}/P_{\mathrm{M}}$ values varied with electrolyte species in the 1.0-PA-29 membrane system. As shown in Fig. 3, the electroconductive membrane permeabilities to univalent metal cations and chloride ion are decreased as $P_{\mathrm{Cs}} \geqq P_{\mathrm{K}} \geqq P_{\mathrm{Cl}} > P_{\mathrm{Na}} > P_{\mathrm{Li}}$ with increasing radius of the hydrated ion due to the ion-sieve effect (see also Ref. 1). It has been an established concept that the permeant ion size is one of the dominant factors to control the membrane permselectivity.(20) Indeed also in the CK-1, 1.0t membrane system, the permeability sequences to univalent metal cations were the same as those in the 1.0-PA-29 membrane. However the P_{Cl} values were also changed

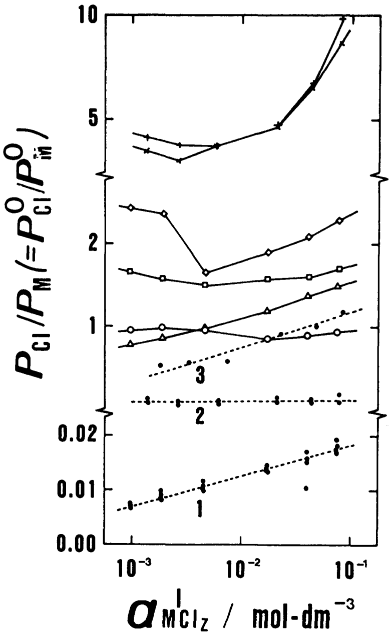

Fig. 6. Chloride ion/metal cation membrane permeability ratio, P_{Cl}/P_M, as a function of the mean electrolyte activity of phase I for the 1.0-PA-29 amphoteric ion-exchange membrane. Symbols are the same as those in Fig. 1. The broken lines 1, 2, and 3 refer to P_{Cl}/P_M values for univalent metal (Cs, K, Na, and Li) chloride, bivalent metal (Ca and Sr) chloride, and $LaCl_3$ concentration-cell systems with the CK-1, 1.0t cation-exchange membrane, respectively.

proportionally with the changes in P_M values as expected from Eq. 10, since the CK-1, 1.0t membrane shows an identical Nernstian response to all the univalent cation systems. Membrane permeability sequences for the Ck-1, 1.0t membrane are as: $P_{Cs}>P_K>P_{Na}>P_{Li}\gg P_{Cl(Cs)}>P_{Cl(K)}>P_{Cl(Na)}>P_{CL(Li)}$, where $P_{Cl(M)}$ indicates the chloride permeability in 1-1 electrolyte, MCl, system. Accordingly, the ion transport process across the binary-charged 1.0-PA-29 membrane is characterized as: the permeabilities both to cation and to anion depend upon the size of the hydrated ions and the permeability to a given ion has a definite value regardless of the electrolyte species. On the contrary, a highly selective cation transport across the CK-1, 1.0t membrane is characterized by the quite low anion/cation permeability ratio, in which the ion size effects on membrane permselectivity are shielded due to tight interactions between oppositely charged ion and fixed site, and accordingly, a potentiometric response to ions of the same charge cannot be observed.

In the ion transport processes across charged membranes, whether the singly- or binary-charged membranes, interactions between permeating ions and fixed ion-exchange sites control the permselectivity as a primary physicochemical factor. Therefore, in a nontreated singly-charged ion-exchange membrane, it has been well-known that the permeability and selectivity parameters to multivalent ions exceed those of univalent ions. In case of the singly-charged membrane developed for the concentration processes of sea water such as the CK-1, 1.0t cation-exchange membrane, the membrane surface was treated by polycationic substance to suppress the permeation of multivalent cations to prevent from $CaSO_4$ scale formation. Figure 6 shows a stepwise increase in P_{Cl}/P_M values with an increasing cation valency from 1 to 3. Once a large amount of multivalent cation has penetrated into the membrane phase; however, the multivalent cations are more permselective than univalent cations due to the tight interaction with oppositely charged exchange sites, as reported in the NaCl–$CaCl_2$, NaCl–$LaCl_3$, and $CaCl_2$–$LaCl_3$ biionic systems with the CK-1, 1.0t membrane.[11,21] As already discussed, the permeability to bivalent metal cation in the binary-charged 1.0-PA-29 membrane is decelerated due to the repulsive interactions with positively charged exchange site, while the permeability to Cl^- is accelerated almost as twice as those in the univalent metal chloride system (see also Ref. 1).

Present results suggest that a qualitative improvement of the membrane permselectivity to ions can be provided by means of introducing the carefully selected pairs of oppositely charged ion-exchange sites into the membrane phase with high densities. Further investigations on the detailed aspects of ion transport process across a binary-charged amphoteric ion-exchange membrane will be achieved by examining the ion conditions within membrane phase such as membrane/solution partition and diffusion process of permeating ions.[17] These studies contribute also to the developments of more useful and efficient membrane-related processes.

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