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Study of Ion Transport across Amphoteric Ion Exchange Membrane. I. Electroconductive Membrane Permeability

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Basic ion transport characteristics of a homogeneous amphoteric ion exchange membrane (Kanegafuchi Chem. Ind. 1.0-PA-29) were studied by measuring the membrane potentials and conductances. Concentration cell systems of NaCl, KCl, $CaCl_2$, and $SrCl_2$ with a concentration range of 10^{-1}—10^{-3} mol dm^{-3} were studied and the electroconductive membrane permeabilities were estimated from the electrochemical data. Generally, Cl^- is slightly more permeable than cations under the present experimental conditions, except the result that K^+ is more permeable at low concentrations. Unlike the usual uniform cation exchange membrane of which transport characteristics to ions strongly depend upon the number of ionic charges, a "1.0-PA-29" amphoteric membrane exhibits different transport properties for the NaCl and KCl systems. In the NaCl system, the membrane was constantly anionic selective, while in the KCl system, biphasic ion selectivities were observed depending upon the external KCl concentration. Fundamental electrochemical properties of the membrane systems were discussed by examining the dependencies of membrane permeability on external electrolyte concentrations and on differences in ionic species. The present result suggests that the ionic size is one of the critical factors determining the transport characteristics across amphoteric ion exchange membrane.

Amphoteric membranes are specified upon a fact that both cationic and anionic sites are attached as ion exchange groups to polymeric substances which build up membrane phase. Since the early work on mosaic membranes by Sollner,[1] many studies on the amphoteric membranes were carried out with the charge-mosaic membrane systems.[2–4] In these investigations, unusual properties of the mosaic system, which cannot be observed in uniform ion exchange membranes, such as the piezodialysis and circulating electric current were found out. On the other hand, the layered type membrane systems in which the cation and anion exchange membranes form a contiguous layers were also studied.[5–7] Especially, the interesting current-voltage characteristics of the layered membrane have been extensively investigated.

These two types of amphoteric membranes or composite membranes have been investigated with several interests. From the theoretical point of views, Kedem and Katchalsky treated generally the transport phenomena observed in these systems on the basis of nonequilibrium thermodynamics in their series of papers.[8–10] Weinstein *et al.* also developed the theoretical model for the charge-mosaic membrane based on nonequilibrium thermodynamics[11] and the experimental verification of their model was carried out.[12] Practical applications of these membranes have been also extensively discussed. Large salt fluxes resulted from the structure of charge-mosaic membrane were paid an attention to utilize for the water conditioning processes. The layered membrane was also considered to be a generalized model involving the surface adsorption phenomena; therefore, the layered model was employed to solve the fouling phenomena which are serious problems in the electrodialysis processes. Many investigators have also taken a great interest in the biological membrane as an amphoteric ion exchange membrane and made an attempt to explain the mechanisms of bioelectrical phenomena in relation to the amphoteric properties of cell membranes.

Experimental studies on amphoteric ion exchange membranes were hitherto performed with the system where the cationic and anionic sites are macroscopically separated each other (see *e.g.*, Refs. 7 and 12). The physicochemical properties of amphoteric membranes should be examined on the system where the cationic and anionic sites are dispersed homogeneously within membrane phase.[13] However, investigations for the basic characteristics of the homogeneous type amphoteric membrane have not been systematically carried out yet. In the present and following papers of this communication series, the basic transport properties of amphoteric ion exchange membranes will be discussed from the theoretical and experimental points of views using the homogeneous type membrane recently developed by a Kanegafuchi Chemical Industry Co., Ltd.[14]

Experimental

The amphoteric ion exchange membrane used in the present experiments is coded as a "1.0-PA-29," which was developed by a Central Research Laboratory of Kanegafuchi Chemical Industry Co., Ltd. and kindly supplied for our experiments. This membrane was developed for the membrane treatment to separate organic substances having a low molecular weight from inorganic salt mixture. A brief sketch of the membrane preparation is as follows.[14] Support membranes were prepared on a glass surface from a dope containing poly(vinyl chloride) (degree of polymerization: 1000) of 11 wt% dissolved in a tetrahydrofuran/*N*,*N*-dimethylformamide (1/1.6 in weight) mixture. On this support membrane, partially chloromethylated polystyrene of 0.5 wt% dissolved in a chloroform/ethanol (1/2 in weight) mixture were applied as a functioning membrane base; chloromethyl groups in polymer were partially treated with trimethylamine. After this step, crosslinking and sulfonation processes were performed by sulfuric acid. Concentration of sulfuric acid and reaction time were controlled to realize the minimum salt rejection rate, which is known to be minimized under the conditions where anionic to cationic exchange capacity ratio approaches to unity.[13,14] All the membrane preparation processes described above were carried out by means of the dip coating techniques. Primary permeation test of the membrane showed that the rejection rates, [(feed concentration — permeate concentration)/feed concentration] × 100%, under the operating pressure of 20 kg cm^{-2} were about 30% for 0.2% NaCl solution and over 93% for 2% sucrose solution, respectively. The ion exchange capacity estimated by ordinary titration method and by elementary analysis was 1 mequiv. (g-wet membrane)$^{-1}$ and the cationic/anionic exchange capacity ratio was ranged 1.0±0.2. The thickness of membrane was 0.1 mm when the membrane was immersed in electrolyte solutions used in the present study. The closest distance between cationic and anionic exchange sites can be roughly estimated to be *ca.* 0.75 nm when the total ion exchange capacity is 2 mequiv. and the degree of swelling is 0.5. Then Eguchi *et al.* suggested that the mosaic membrane model[11] is unsuitable for the analysis of transport characteristics in the present membrane.[14]

In the present preliminary experiments, the electrochemical properties were studied on the concentration cell systems using NaCl, KCl, $CaCl_2$, and $SrCl_2$ as electrolytes. Experimental setup was the same as that reported elsewhere.[15,16] The amphoteric membrane was placed in the measurement cell to separate solution phases I and II, and the electrolyte concentration of phase I was varied from 10^{-1} to 10^{-3} mol dm^{-3}, while that of phase II was kept constant at 10^{-2} mol dm^{-3}. In this study, the membrane potentials and conductances were measured by a Takeda Riken TR 6856 high input impedance voltmeter and a Yokogawa-Hewlett-Packard 4255A (connected with 4440B) impedance bridge circuit, respectively. All experiments were carried out at the regulated room temperature (25±1 °C).

Results and Discussion

Before the measurements were carried out, the sample membrane was checked on locally uniform properties of electrochemical data in the NaCl system and both sides of the membrane showed the identical electrochemical properties. The volume flow was also checked in the NaCl system; under the present experimental conditions, effects of solvent flow cause about 5% changes in transport parameters at most, which were within experimental errors.[17] More complete treatment involving the effects of solvent flow will be presented elsewhere based on nonequilibrium thermodynamics.

Membrane potential data as a function of the mean electrolyte activity of phase I are summarized in Fig. 1. In general, a 1.0-PA-29 amphoteric ion exchange membrane was more permselective to chloride ions than to metal cations under the present experimental conditions and this tendency became evident with increasing electrolyte concentration of phase I. Apparent transport numbers of Na^+ are nearly constant at 0.4, but those of Ca^{2+} and Sr^{2+} decrease from 0.45 to 0.29 and from 0.42 to 0.29, respectively, when the electrolyte concentrations of phase I are varied from 10^{-3} to 10^{-1} mol dm^{-3}. On the other hand, the KCl system exhibits biphasic ion selectivity behavior above and below the concentration of 10^{-2} mol dm^{-3} as illustrated in Fig. 1; apparent transport numbers of K^+ ranged from 0.42 to 0.46 and from 0.51 to 0.54 at lower and higher concentration ranges, respectively. In case of the usual cationic or anionic ion exchange membrane, the selectivity to ions is monophasic and the number of ionic charge is a dominant factor determining the ionic permselectivity, so the membrane potential responses to univalent cations are almost the same irrespective of ionic species. On the basis of present results, there seems to be a possibility to discriminate Na^+ from K^+ by means of the amphoteric type ion exchange membrane.

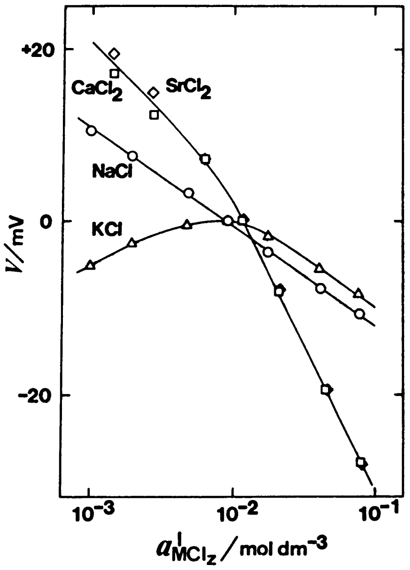

Fig. 1. Membrane potential data as a function of mean electrolyte activity of phase I.
○: NaCl, △: KCl, □: $CaCl_2$, ◇: $SrCl_2$.

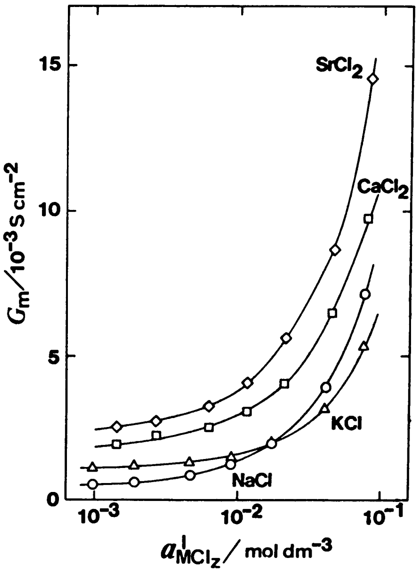

Fig. 2. Membrane conductance data as a function of mean electrolyte activity of phase I.
Symbols are the same as in Fig. 1.

The membrane conductance data are given in Fig. 2. Conductances continuously increase with increasing electrolyte concentrations of phase I in all the systems. It should be noted that the membrane conductances of 2-1 electrolyte systems are twice as high as those of 1-1 electrolyte systems.

According to the previous theory,[18] the present systems are described by the following modified phenomenological equation:

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

where J is the ionic flux, a is the activity, Z is the charge of metal cation M, and V is the transmembrane potential; F, R, and T indicate the usual physical meanings; the subscripts M and Cl refer to metal cations, $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Ca^{2+}}$, and $\mathrm{Sr^{2+}}$, and to anion, $\mathrm{Cl^-}$; the superscripts I and II indicate the solution phases separated by the membrane phase, respectively. $P_{\mathrm{M \cdot M}}$, $P_{\mathrm{M \cdot Cl}}$, $P_{\mathrm{Cl \cdot M}}$, and $P_{\mathrm{Cl \cdot Cl}}$ are the membrane permeability matrix elements representing the partial contributions to the membrane transport processes due to the inter-ionic correlations indicated by the subscripts. In the present study, the electroconductive membrane permeabilities, defined by the following equations as a function of the permeability matrix elements, were estimated from the electrochemical measurements:

$$P_{\mathrm{M}} = P_{\mathrm{M \cdot M}} - P_{\mathrm{Cl \cdot M}}/Z, \quad P_{\mathrm{Cl}} = -ZP_{\mathrm{M \cdot Cl}} + P_{\mathrm{Cl \cdot Cl}}, \tag{2}$$

where P_{M} and P_{Cl} are the electroconductive permeabilities to metal cation and chloride ion, respectively. Electrochemical properties of the membrane system are described by use of the electroconductive membrane permeability:

$$\begin{aligned} I &= -ZFP_{\mathrm{M}}[a_{\mathrm{M}}^{\mathrm{II}} \exp(ZFV/2RT) - a_{\mathrm{M}}^{\mathrm{I}} \exp(-ZFV/2RT)] \\ &\quad + FP_{\mathrm{Cl}}[a_{\mathrm{Cl}}^{\mathrm{II}} \exp(-FV/2RT) - a_{\mathrm{Cl}}^{\mathrm{I}} \exp(FV/2RT)] \\ &= -t_{\mathrm{M}}G_{\mathrm{m}}(V - V_{\mathrm{M}}) - t_{\mathrm{Cl}}G_{\mathrm{m}}(V - V_{\mathrm{Cl}}) \qquad (3) \\ &= -G_{\mathrm{m}}(V - V_0) \end{aligned}$$

$$V_0 = t_{\mathrm{M}}V_{\mathrm{M}} + t_{\mathrm{Cl}}V_{\mathrm{Cl}}, \tag{4}$$

where I is the electric current across membrane, G_{m} is the membrane conductance, t is the transport number, and V_0 is the membrane potential in absence of membrane current; V_{M} and V_{Cl} are the Nernst equilibrium potentials for metal cation and chloride ion, respectively. Therefore, the electroconductive membrane permeabilities, P_{M} and P_{Cl}, are calculated by the next equations with the membrane potential and conductance data:

$$\begin{aligned} P_{\mathrm{M}} &= \frac{t_{\mathrm{M}}G_{\mathrm{m}}RT}{Z^2F^2(a_{\mathrm{M}}^{\mathrm{I}}a_{\mathrm{M}}^{\mathrm{II}})^{1/2}} \frac{ZF(V - V_{\mathrm{M}})/2RT}{\sinh[ZF(V - V_{\mathrm{M}})/2RT]} \\ P_{\mathrm{Cl}} &= \frac{t_{\mathrm{Cl}}G_{\mathrm{m}}RT}{F^2(a_{\mathrm{Cl}}^{\mathrm{I}}a_{\mathrm{Cl}}^{\mathrm{II}})^{1/2}} \frac{-F(V - V_{\mathrm{Cl}})/2RT}{\sinh[-F(V - V_{\mathrm{Cl}})/2RT]}. \end{aligned} \tag{5}$$

The electroconductive permeability having a dimension of cm $\mathrm{s^{-1}}$ represents an electrically migrating speed of ions across the membrane phase and indicates a measure of the membrane permselectivity to ions.

Calculated results of these conductive permeabilities to metal cations and chloride ions are given in Figs. 3 and 4. In Fig. 5, the metal cation to chloride ion permeability ratios are plotted as a function of electrolyte activity in phase I. As expected from the membrane potential data, the conductive membrane permeabilities to chloride ions, P_{Cl}, exceeded those of cations, P_{M}. In the present study, the order of conductive membrane permeabilities to ions are as follows: $P_{\mathrm{Cl}}(\mathrm{Ca^{2+}},\mathrm{Sr^{2+}}) > P_{\mathrm{Cl}}(\mathrm{Na^+},\mathrm{K^+}) \geq P_{\mathrm{K}} > P_{\mathrm{Na}} > P_{\mathrm{Ca}}, P_{\mathrm{Sr}}$. These results may not be caused by unbalanced distribution of cationic and anionic exchange groups, since the membrane preparation processes are controlled to minimize the salt rejection rate and, accordingly, the capacity ratio is close to unity (see experimental section and Refs. 13 and 14). Furthermore, P_{Cl} also exceeded P_{M} even in 2-1 electrolyte systems in which cations seem to interact more strongly with fixed charges. Physical meanings of the electroconductive membrane permeabilities, P_{M} and P_{Cl}, are expressed as:[16,18,19]

$$P_{\mathrm{M}} = \frac{RT\bar{U}_{\mathrm{M}}}{\delta} \frac{\bar{C}_{\mathrm{M}}}{(a_{\mathrm{M}}^{\mathrm{I}}a_{\mathrm{M}}^{\mathrm{II}})^{1/2}}, \quad P_{\mathrm{Cl}} = \frac{RT\bar{U}_{\mathrm{Cl}}}{\delta} \frac{\bar{C}_{\mathrm{Cl}}}{(a_{\mathrm{Cl}}^{\mathrm{I}}a_{\mathrm{M}}^{\mathrm{II}})^{1/2}}, \tag{6}$$

where $\bar{U}$ and $\bar{C}$ are the integral average values of ionic mobility and concentration within membrane of thickness of δ. Membrane potential is expressed as a function of the permeability ratio[18] and the biphasic response observed in the KCl system seems to be due to the concentration dependent change in $\bar{U}_{\mathrm{K}}$ and $\bar{U}_{\mathrm{Cl}}$, since it is reasonable to consider $\bar{C}_{\mathrm{K}}$ is nearly equal to $\bar{C}_{\mathrm{Cl}}$. The permeability ratios, namely the relative membrane permeabilities, seem to decrease with the

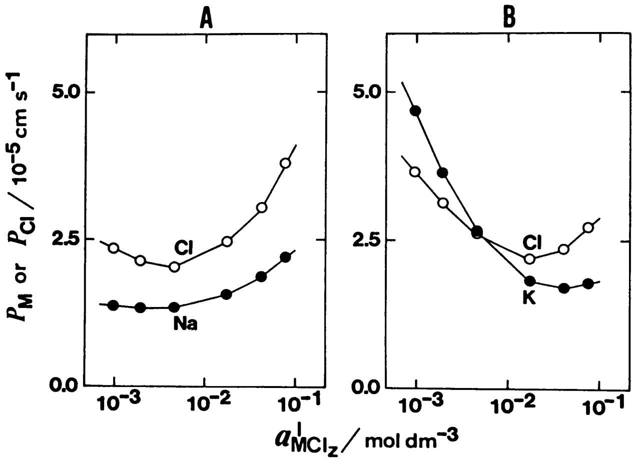

Fig. 3. Electroconductive membrane permeabilities for NaCl (A) and KCl (B) systems.
Closed and open circles indicate metal cation and chloride ion, respectively.

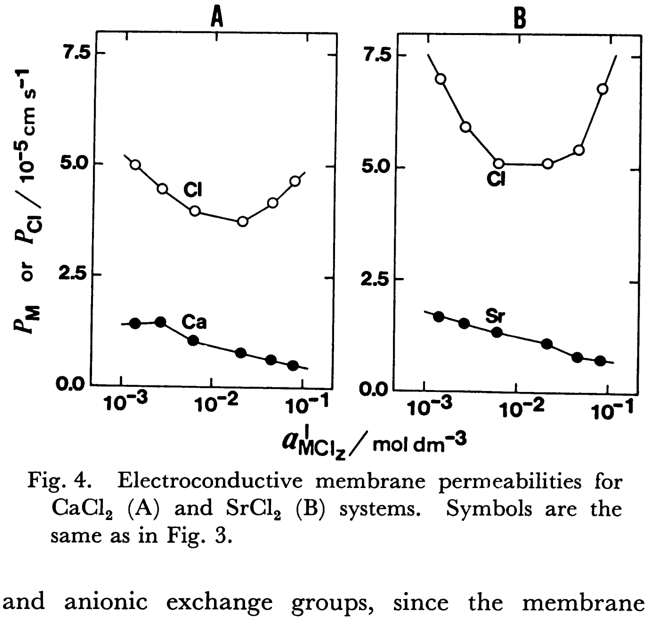

Fig. 4. Electroconductive membrane permeabilities for $\mathrm{CaCl_2}$ (A) and $\mathrm{SrCl_2}$ (B) systems. Symbols are the same as in Fig. 3.

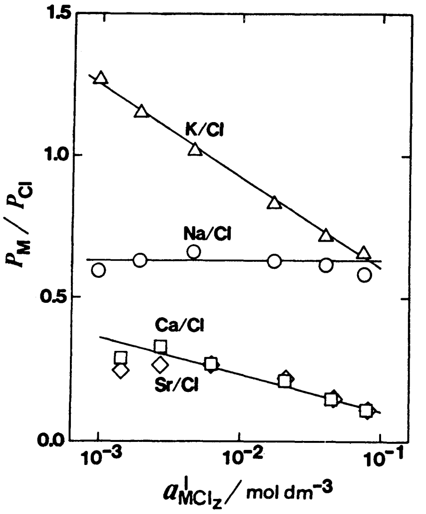

Fig. 5. Membrane permeability ratios as a function of mean electrolyte activity of phase I.
○: P_{Na}/P_{Cl}, △: P_K/P_{Cl}, □: P_{Ca}/P_{Cl}, ◇: P_{Sr}/P_{Cl}.

increasing cationic size. The ratios of hydrated ionic radii of metal cations to chloride ion are as follows: Na^+/Cl^-, 1.08; K^+/Cl^-, 1.00; Ca^{2+}/Cl^- and Sr^{2+}/Cl^-, 1.24. Thus it is suggested that the ionic size plays an important role to determine the ionic transport characteristics of amphoteric membrane.

Ion exchange membranes capable to separate ions of opposite charges have been practically used in various fields. It is also possible to exclude multivalent ion permeations by means of the membrane surface finishing with polyionic substances as in the case of ion exchange membranes selective to univalent ions used for the desalination processes. Further studies to improve the ionic selectivity of membranes and to aim at the perfect separation of two ions have been extensively continued. One possible way to realize the higher ionic selectivity is to introduce the exchange groups which can interact with specific ions, and the other is to apply the sieve effects to discriminate ionic sizes. The sieve effects are typically illustrated in the membrane systems having antibiotics and crown compounds as ionophores.[20,21] Even in case of the usual uniform ion exchange membrane, there exists indeed a difference in permeability to ions of the same charge determined by ionic mobility and concentration within membrane (see Eq. 6); however, the uniform ion exchange membrane is not so selective to generate the different membrane potential responses to each ionic species. It is the most noticeable difference between uniform and amphoteric ion exchange membranes with high charge densities that potential responses of the former are expressed by the Nernst relation characterized by the number of ionic charges, while those of latter are strongly affected by ionic size effects.

The transport mechanisms of amphoteric ion exchange membrane in which both cationic and anionic exchange groups are homogeneously dispersed within membrane phase seem to differ from those of mosaic membrane in which both the exchange groups form blocks of respective charges. Eguchi *et al.* suggested that salt permeation processes across the 1.0-PA-29 membrane are not controlled by coupling flow mechanisms which are remarkable features of the charge-mosaic membrane and they concluded that the analysis based on the mosaic model cannot be applicable to the present membrane.[14]

The present results indicate that the number of ionic charge is not a dominant factor to determine the ionic transport characteristics across the amphoteric ion exchange membrane. On the other hand, the membrane potentials, as a fundamental transport property, of usual polymeric ion exchange membrane with the same fixed charges, either the cationic or anionic exchange type, depend completely upon the number of ionic charge of permeant ions, and accordingly it is very difficult to endow a permselectivity to ions with the same charge. The 1.0-PA-29 amphoteric ion exchange membrane exhibits a possibility to discriminate Na^+ from K^+ as indicated in the membrane potential data and the permeability values. The origin of these permselectivities of amphoteric ion exchange membrane would be based on the discrimination of the hydrated radius of permeant ion. The effects of ionic size on transport characteristics, namely the sieve effect, across amphoteric ion exchange membrane are more clearly illustrated by the experimental results using symmetric tetraalkylammonium salts, which will be reported in the following communication. These transport characteristics of amphoteric membrane may be partly involved in the functions of biological membrane having a steep ionic selectivity, although the specific proteinic substances are known to control the complex and delicate ion transport mechanism.

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