Effect of Cationic Charge in Electrolyte-Amphoteric Ion-Exchange Membrane System

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In order to clarify the membrane phenomena in an amphoteric membrane, four different experiments were carried out in a simple electrolyte-amphoteric membrane system. The ion transport numbers obtained from the membrane potential and electrodialysis were approximately in agreement with each other. It was indicated that the transport numbers strongly depended on the ionic valence in electrolyte solution. The membrane permeability coefficient representing the dynamic behavior of ion within membrane was evaluated in terms of membrane potential, transport number, and membrane conductance. In addition, the ionic concentrations within membrane equilibrated with outer electrolyte solution were measured to obtain the mobilities within membrane. The membrane phenomena were discussed on basis of the present experimental results.

The studies on an amphoteric membrane with cation- and anion-exchange sites have not been reported so many in comparison with those as to an ion-exchange membrane with homogeneous exchange sites. One of the reasons from physicochemical standpoint would be the complexity of ionic behavior within the membrane. However, the attractive possibilities concerning the amphoteric character have been predicted in various fields.[1–5] We also have recognized the valuable properties and investigated the fundamental membrane phenomena generated in simple electrolyte solution-amphoteric membrane system in which the amphoteric membranes developed by Central Research Laboratory of Kanegafuchi Chemical Industry Co., Ltd. were used.[6–8] The membrane phenomena have been examined through only the measurements of membrane potentials and membrane conductances in one of the works.[6] However, the membrane phenomena in the amphoteric membrane containing two kinds of exchange sites are too complicated to obtain the better understanding. More informations such as the experiments due to different amphoteric membrane or the determination of the concentration within membrane should be therefore accumlated.

Thus, the studies on the membrane having the different base membrane but the similar ion exchange sites as that of previous paper have been started in this series. In the previous reports of this series,[9,10] the membrane potential controlled by the ionic charge in the electrolyte solution was observed and was explained qualitatively by the apparent transport number, which can be obtained from the relation between the membrane potential and the activity in outer electrolyte solution. In order to confirm the results further, the alternative transport number which is evaluated from the measurement of ions transfered under the supplied currents, i.e., the electrodialysis experiment should be examined. Thus, the electrodialysis experiments were carried out, and the transport numbers were obtained about three species of electrolytes involving the cations of different valences. In addition, the ionic mobilities were estimated owing to know the ionic concentration within membrane. The details about the behavior of ion within membrane will be discussed in this work.

Experimental

Materials. The amphoteric ion exchange membrane used in the present study is coded as a "Neosepta CSV" and was supplied by Tokuyama Soda Co., Ltd., which was characterized with sulfonic acid group for cation-exchange site and *N*-methylpyridinium group for anion-exchange site. The characteristics of membrane were shown elsewhere.[9,10]

Before measurements, the membranes were conditioned by immersing successively in 0.1 M[†] aqueous ammonia, 0.5 M HCl, and 1.0 M NaCl aqueous solution, and the process was repeated a few times. The membranes thus obtained were washed with twice distilled water until the washing solutions did not contain any ions. The electrolytes($NaCl$, $CaCl_2$, $LaCl_3$) were extra pure reagents and used without further purification. The aqueous electrolyte solutions indicated almost the same pH as that of distilled water equilibrated with carbon dioxides. For example, pH value of 10^{-2} mol dm^{-3} $LaCl_3$ solution was 5.46±0.05.

Apparatus. The cells for membrane potential, membrane conductance, and electrodialysis were made of glass, and consisted of two 20 cm^3 compartments. Two 1.57 cm^2 platinum black electrodes were equipped in the glass cells for membrane conductance. The membrane was placed between two compartments, and the available areas of membrane were 0.78 cm^2 for membrane potential and 3.14 cm^2 for membrane conductance and electrodialysis, respectively.

Measurements.

Membrane Potential: The membrane potential was measured according to the conventional method.[9,10] The results were obtained with the system in which the concentration of the electrolyte solution was kept constant in compartment(I) at 5.0×10^{-3} mol dm^{-3}, and was changed in compartment(II) from 1.0×10^{-3} to 1.0×10^{-1} mol dm^{-3}.

Electrodialysis: For the electrodialysis experiments, 10^{-2} mol dm^{-3} solutions of $NaCl$, $CaCl_2$, and $LaCl_3$ were used. In the electrodialysis experiment, a pair of silver–silver chloride electrodes with 2 cm^2 in area was inserted into aqueous electrolyte solutions at both sides of membrane. The currents of 0.1, 0.2, and 0.4 mA were supplied from phase(II) to phase(I) through Current Supply Equipment (Yokogawa

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[†] 1 M=1 mol dm^{-3}.

Electric Works DC Voltage Current Standard Type 2853). After a passage of time, a constant volume (1 ml) was pipetted from both compartments and the concentration changes of ion from the initial electrolyte solutions were determined by the atomic absorption spectroscopy (Hitachi Co., Ltd., Model 180-50). In the case of La ion, the colorimeric method with arsenazo III reagent was employed because the sensitivity of atomic absorption was not effective.

Membrane Conductance: The membrane resistance was measured with Universal Bridge (Yokogawa-Hewlett-Packard Co., Model 4265B) through two platinum black electrodes in the sample solutions. After 10^{-2} mol dm^{-3} solutions of the respective electrolytes were poured into both compartments, the electrical resistances of the system with and without membrane were measured. The membrane resistance, R_m was obtained by subtracting the solution resistance without membrane from the total resistance. The membrane conductance, G_m was calculated by dividing $1/R_m$ with the available membrane area, 3.14 cm^2.

Ionic Concentration within Membrane: After the membrane (5X5 cm^2) was equilibrated with 10^{-2} mol dm^{-3} electrolyte solution for 72 h, the membrane was dipped into the distilled water for 72 h in order to remove the electrolyte due to donnan adsorption. Then, the ionic concentrations within membrane due to ion exchange with sites were eluted by 1.0 M HNO_3. The concentrations were determined by the same method as in electrodialysis experiment. The concentration of Cl ion was determined by Mohr's method. The total concentration of the electrolytes was taken as the concentration within membrane.

Throughout this study, the twice experiments for a single system were at least performed and the average value was taken as a reliable value. The solution phases were sufficiently stirred by the magnetic stirrers and the temperature of phases were kept at 25 °C.

Results and Discussion

Figure 1 shows the relations between the potentials and the mean activities of ions in the outer solutions for NaCl, $CaCl_2$, and $LaCl_3$. The mean activities were taken from the values in literature.[11] From dependence of the membrane potentials on activities in 1—1 valent electrolyte, NaCl, it was suggested that the membrane functions as a cation-exchange membrane regardless of having the anion-exchange site. On the other hand, in the case of 2—1 valent electrolyte, $CaCl_2$, the relation between the membrane potential and logarithmic mean activity of $CaCl_2$ deviated slightly from the linearity and the slope of potential per decade concentration decreased with suggesting the strong interaction of divalent cation with the cation-exchange site. Furthermore, in the system of $LaCl_3$ having tervalent cation, the inversion of the slope took place as seen in Fig. 1. In order to discuss the results quantitatively, it is convenient to use transport numbers which can be calculated from the membrane potential vs. mean activity relationships in Fig. 1.

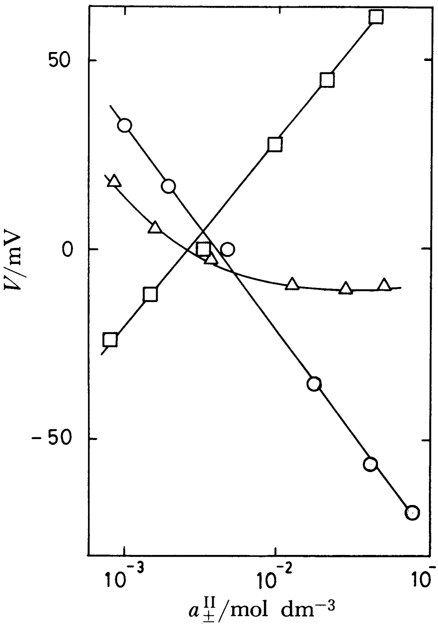

Fig. 1. Membrane potentials as a function of mean activities of electrolytes uni- to tervalent cations in phase (II). ○: NaCl, △: $CaCl_2$, □: $LaCl_3$.

Generally, the relationship between the membrane potential, V, and the mean activity of electrolyte, $a_\pm$, for amphoteric membrane was given as follows,

$$V = \left(\frac{t_M}{Z_M} + \frac{t_{Cl}}{Z_{Cl}}\right)\frac{RT}{F}\ln\frac{a_\pm(I)}{a_\pm(II)}, \tag{1}$$

where t_M and t_{Cl} indicate the transport numbers of cation and anion; Z_M and Z_{Cl}, the valences of M and Cl ions; respectively. Transport numbers were calculated from the slope in Fig. 1 by means of Eq. 1 and were summarized in Table 1. In the case of $CaCl_2$, the transport number was calculated from the tangent slope at 10^{-2} mol dm^{-3} $CaCl_2$ concentration.

As shown in Table 1, it is obvious that the transport numbers, t_M or t_{Cl}, correspond to the slopes in membrane potential vs. the activity of electrolyte solution relationships. In the case of $LaCl_3$, t_{La} was remarkably reduced to 0.13. The value means that Cl ion can be relatively transported more than La ion, and it may be supposed that La ion is trapped around the cation-exchange sites owing to the strong electrostatic attraction.

In order to confirm the results obtained above further, the transport number by electrodialysis method was estimated. A typical example for NaCl system (10^{-2} mol dm^{-3}, 0.2 mA) was shown in Fig. 2. Sodium ion in phase(I) increased and that in phase(II) decreased with a passage of time under the supplied

Table 1. Transport Numbers, t_M and t_{Cl} Evaluated from Membrane Potential and Electrodialysis

Salt	Membrane potential		Electrodialysis	
	t_M	t_{Cl}	t_M	t_{Cl}
NaCl	0.95	0.05	0.94	0.06
$CaCl_2$	0.82	0.18	0.83	0.17
$LaCl_3$	0.13	0.87	0.12	0.88

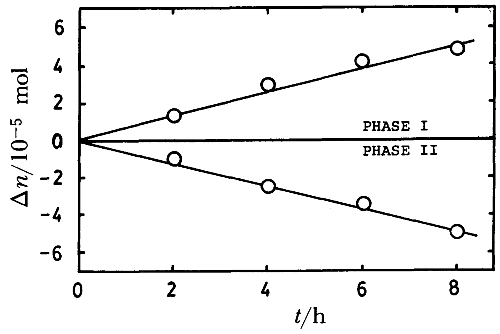

Fig. 2. The increase and decrease of Na ions in phase (I) and phase (II) against the passage of time for NaCl system (1.0×10^{-2} mol dm^{-3}, 0.2 mA).

current of 0.2 mA. The concentration change from the initial Na ion concentration, Δn_{Na}, showed the straight line against time in both phases and the absolute values of the slope were approximately the same. The similar results were also obtained at the other systems. The absolute values of the concentration change in both phases were averaged, and the ion fluxes were evaluated with Eq. 2 from the slopes of the linear portion,

$$J_M = \frac{\Delta n}{sA}, \tag{2}$$

where Δn, s, and A denote moles of transfered ion, time in sec during the supplied currents and membrane area in cm^2, respectively. The relation between flux and current for each cation was shown in Fig. 3. The cationic current due to cation transfered, i_M, can be evaluated by the Eq. 3 taking account of the quantity of electricity on the flux,

$$i_M = Z_M F J_M A. \tag{3}$$

The transport number, t_M, can be obtained from the relationship between i_M and I according to the following relation,

$$t_M = \frac{i_M}{I}, \tag{4}$$

where I is the total supplied current. The transport numbers, t_M, due to the electrodialysis were shown together with t_{Cl} which were calculated by a relation, $t_M + t_{Cl} = 1$, in Table 1. As seen in Table 1, the values of t_M decrease with increase of the cationic valences in accordance with t_M obtained by the membrane potential measurement.

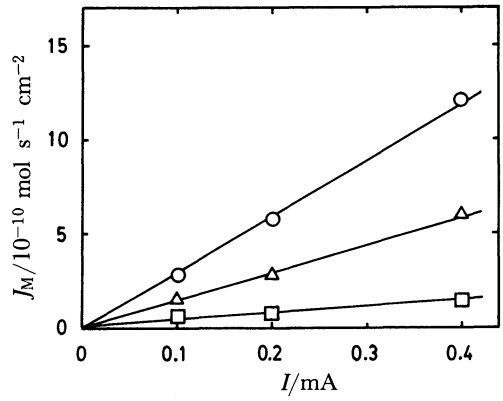

Fig. 3. The relationship between flux and current for each cation. ○: Na, △: Ca, □: La.

In order to discuss the dynamic behavior of ions within the membrane in more detail, it would be effective to introduce the membrane permeability coefficients presented in previous papers.[6,12] The permeability coefficient reflects the dynamic behavior of ion within membrane and is a function of the membrane potential, V, membrane conductance, G_m, and transport number, t, and is expressed as follows,

$$P_M = \frac{t_M G_m RT}{Z_M^2 F^2 (a_M^{I} \cdot a_M^{II})^{1/2}} \cdot \frac{Z_M F(V - V_M)/2RT}{\sinh(Z_M F(V - V_M)/2RT)}, \tag{5}$$

$$P_{Cl} = \frac{t_{Cl} G_m RT}{Z_{Cl}^2 F^2 (a_{Cl}^{I} \cdot a_{Cl}^{II})^{1/2}} \cdot \frac{Z_{Cl} F(V - V_{Cl})/2RT}{\sinh(Z_{Cl} F(V - V_{Cl})/2RT)}, \tag{6}$$

where V_M and V_{Cl} denote the equilibrium potentials of ions, M and Cl, respectively, and $(a^{I} \cdot a^{II})^{1/2}$, geometrical mean activity in phase(I) and phase(II). On the

Table 2. Membrane Resistances, R_m and Membrane Conductances, G_m

Salt[a]	R_m	G_m
	Ω	S cm^{-2}
NaCl	30	1.06×10^{-2}
$CaCl_2$	68	4.68×10^{-3}
$LaCl_3$	1050	3.03×10^{-4}

a) Concentration of salt solution: 1.0×10^{-2} mol dm^{-3}.

Table 3. Membrane Permeabilities, P_M and P_{Cl} Evaluated from Membrane Potential and Electrodialysis

Salt	Membrane potential			Electrodialysis		
	P_M	P_{Cl}	P_M/P_{Cl}	P_M	P_{Cl}	P_M/P_{Cl}
	cm s^{-1}	cm s^{-1}		cm s^{-1}	cm s^{-1}	
NaCl	4.14×10^{-4}	2.18×10^{-5}	18.99	2.97×10^{-4}	1.56×10^{-5}	19.04
$CaCl_2$	4.75×10^{-5}	4.17×10^{-5}	1.14	7.06×10^{-5}	2.90×10^{-5}	2.43
$LaCl_3$	2.27×10^{-7}	1.64×10^{-5}	0.017	5.77×10^{-7}	1.27×10^{-5}	0.045

other hand, G_m was measured in the same system as that of electrodialysis experiment. In calculation of P_M and P_{Cl}, the membrane potentials generated between 5×10^{-3} mol dm^{-3} in phase(I) and 1×10^{-2} mol dm^{-3} in phase(II), the respective mean activities, the transport numbers from membrane potentials and the membrane conductances in Table 2 were inserted into Eqs. 5 and 6. The results were shown in Table 3. The values of P_M were largely changed by the cationic valences while P_{Cl} showed almost constant values in three systems. For example, in the case of NaCl system, the membrane permeability coefficient of cation, P_{Na}, was approximately 20-fold larger than P_{Cl}. The large difference indicated that Na ion can be easily transported. In the case of $CaCl_2$, P_{Ca} decreased slightly. Contrary to former two cases, P_{La} in $LaCl_3$ was remarkably reduced, and as a result, Cl ion can be transported. The ratios, P_M/P_{Cl}, which were also given in Table 3, reflect the permselectivity of ions through membrane. The facts confirm again that membrane potential in the present system is determined by the difference of the membrane permeability coefficients for cation and anion. In other words, the membrane potentials strongly depend upon the cationic valences.

Here, it is interesting that the present result is compared with that of the previous paper at 10^{-2} mol dm^{-3} electrolyte solution.[6] The evaluated membrane permeabilities except for La ion in this study were almost the same order of magnitude as in previous one, but the membrane permeability ratios of cations to anions indicated large discrepancies between two kinds of the membranes. The values of present ratios were strongly dependent on the valency of electrolyte, and particularly, in the case of NaCl, the membrane indicated a high permselectivity to Na ion over Cl ion, while the permeability ratio of La ion to Cl ion was less than unity in the case of $LaCl_3$. On the other hand, the magnitude of cationic permeabilities exceeded that of anionic one as shown in Fig. 5 of previous paper though there is no result about $LaCl_3$. The reason is not clear at present, but it may be partly attributed to the difference of the membrane skeleton.

In the present electrodialysis and conductance experiments, the electrolyte solutions having the same concentration were placed at phase(I) and phase(II). Therefore, V, V_M, are V_{Cl} in Eqs. 5 and 6 are almost reduced to zero, and the potential terms can be dropped out. Furthermore, under the experimental conditions described above, $(a^{I}_{M}\cdot a^{II}_{M})^{1/2}$ and $(a^{I}_{Cl}\cdot a^{II}_{Cl})^{1/2}$ can be replaced by $a_{\pm M}$ and $a_{\pm Cl}$. Finally, taking account of $t_M G_m \delta = Z_M F^2 \bar{U}_M \bar{C}_M$, we can obtain Eqs. 7 and 8 as the alternative expression for P,

$$P_M = \frac{RT\bar{U}_M}{\delta}\cdot\frac{\bar{C}_M}{(a^{I}_{M}\cdot a^{II}_{M})^{1/2}}, \tag{7}$$

$$P_{Cl} = \frac{RT\bar{U}_{Cl}}{\delta}\cdot\frac{\bar{C}_{Cl}}{(a^{I}_{Cl}\cdot a^{II}_{Cl})^{1/2}}, \tag{8}$$

where δ denotes membrane thickness; $\bar{C}$, concentration of ion within membrane; $\bar{U}$, absolute mobility of ion within membrane. Equations of 7 and 8 are sufficiently applicable to the present systems in which the concentrations of electrolyte in both phases, I and II, were identical. The evaluated values of P were also shown in Table 3. The results were in good agreement with those obtained by means of Eqs. 5 and 6. Equations of 7 and 8 have the instructive expression for understanding of physicochemical meaning as to the membrane permeability coefficient, P. It is clear that P largely depends on a product of the mobility and the concentration within membrane under the present experimental conditions.

At present stage, it is possible to know the mobility of ion within membrane provided the ionic concentration within membrane, $\bar{C}$, is given. The ionic concentration, $\bar{C}$, was determined according to the method described in experimental section and given in Table 4. The ionic mobilities for three electrolyte systems examined were calculated in terms of Eqs. 7 and 8, and the results were summarized in Table 5 together with using mean activities. The mobilities indicated a similar tendency with membrane permeability coefficients. In the case of NaCl system, $\bar{U}_{Na}$ was larger than $\bar{U}_{Cl}$. In the system of $LaCl_3$ having tervalent cation, $\bar{U}_{La}$ was remarkably small. In this system, P_M and P_{Cl} could be mainly determined by the dynamic factor($\bar{U}$)

Table 4. Ionic Concentrations within Membrane

Salt	$\bar{C}_M$	$\bar{C}_{Cl}$
	mol dm^{-3}	mol dm^{-3}
NaCl	2.21	1.24
$CaCl_2$	5.76×10^{-1}	6.33×10^{-1}
$LaCl_3$	3.81×10^{-1}	5.81×10^{-1}

Table 5. Ionic Mobilities within Membrane, $\bar{U}_M$ and $\bar{U}_{Cl}$ Evaluated from Electrodialysis

Salt	$a_\pm$	$\bar{U}_M$	$\bar{U}_{Cl}$	$\bar{U}_M/\bar{U}_{Cl}$
	mol dm^{-3}	cm s^{-1} dyn^{-1}	cm s^{-1} dyn^{-1}	
NaCl	9.02×10^{-3}	5.81×10^{-12}	6.61×10^{-13}	8.79
$CaCl_2$	7.31×10^{-3}	4.34×10^{-12}	1.62×10^{-12}	2.69
$LaCl_3$	5.60×10^{-3}	4.08×10^{-14}	5.92×10^{-13}	0.07

rather than static factor($\bar{C}$). It is considered that La ion having large charge was trapped around the cation-exchange sites owing to the strong electrostatic attraction. It may be said that ionic permeability through membrane is controlled by the valence of cation.

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