March, 1988] © 1988 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 61, 793—797 (1988)

A Behavior of Donnan Salt within Membrane

Akira YAMAUCHI,* Masashi DATE, Yukiko YAMAMOTO, Yutaka HIRATA,
and Hideo KIMIZUKA
Department of Chemistry, Faculty of Science, Kyushu University 33,
Hakozaki, Higashi-ku, Fukuoka 812

(Received September 11, 1987)

In an amphoteric ion exchange membrane-electrolyte system, three independent experiments were carried out, that is, the membrane potential, membrane conductance and concentration of ions within membrane were measured, respectively. The electrolytes adopted in the systems were NaCl, $CaCl_2$, $LaCl_3$. From the analysis of the results, the specific conductance attributed to Donnan salt within membrane was separated. As a result, it was pointed out that the dynamic state of Donnan salt is obviously different from that of salt in aqueous solution. Furthermore, the comparison between the ions constituting Donnan salt and the counterions which interact with the ion-exchange sites suggested us the existance of two different dynamic states on the ions within membrane.

Up to the present, a number of investigations concerning ion transport phenomena in membrane–electrolyte solution system have been reported.[1–3] We have also studied the membrane phenomena in systems using an ion-exchange membrane or an amphoteric ion-exchange membrane.[4–10] There may be several factors controlling the membrane phenomena, such as ion flux through the membrane, distribution coefficient at the interface between the membrane and electrolyte solution, the ionic concentration within membrane and etc. Of these, the ions within membrane may play an important role in the transport phenomena. The ions may exist in two different states, that is, due to ion exchange with sites and due to Donnan adsorption. It would be interesting to separate the two states experimentally, and in particular, to compare the behavior of Donnan salt with that of free ion in solution. Moreover, it is predicted that in the amphoteric membrane having the cationic and anionic exchange sites, the ions within membrane behave differently from usual monotonic ion-exchange membrane.[6,11]

Unfortunately, the detailed investigation has not been done concerning the mobilities of Donnan salt within membrane. Therefore, in this work, first, it was tried to separate the two states, and second, the behavior of Donnan salt was discussed. In order to satisfy a story mentioned above, the measurements of membrane potential and membrane conductance, and the determination of ionic concentration within membrane were carried out.

Experimental

Materials. An amphoteric membrane used in this study was supplied by Tokuyama Soda Co. Ltd., of which the characterestics were described already elsewhere.[7–10] The electrolytes (NaCl, $CaCl_2$, $LaCl_3$) of extra pure reagents were used without further purification.

Apparatus. The cell for membrane potential and conductance was made of glass, and consisted of 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 3.14 cm^2. The details for the measurements were described elsewhere.[7–10]

The Determination of Ionic Concentration within Membrane. After the membrane (5×5 cm^2) was equilibrated with the sample solutions from 10^{-3} to 10^0 mol dm^{-3} for 72 h, the membranes were transferred into the distilled water and stood for 72 h in order to remove the electrolytes due to Donnan adsorption. Then, the ions within membrane due to ion exchange with sites were eluted by 1.0 mol dm^{-3} HNO_3. The two different concentrations $\bar{C}^E$ and $\bar{C}^D$, were determined by the atomic absorption spectroscopy (Hitachi Co., Ltd., Model 180-50). In the case of La ion, the calorimetric method with arsenaso III reagent was employed because the sensitivity of the atomic absorption was insufficient.

During the course of this experiment, the solution phases were sufficiently stirred by the magnetic stirrers and temperature was kept at 25 °C.

Theoretical

The consideration[12] based on the nonequilibrium thermodynamics gives us the equation concerning the specific conductance of membrane, $\bar{\kappa}$,

$$\begin{aligned}\bar{\kappa} &= \nu_1 Z_1 \bar{C} F(\bar{U}_1 + \bar{U}_2)\\ &= \nu_1 Z_1 \bar{C} F(\bar{U}_{11} + 2\bar{U}_{12} + \bar{U}_{22}),\end{aligned} \tag{1}$$

where

$$\bar{U}_1 = \frac{Z_1^2 l_{11}}{\nu_1 Z_1 \bar{C}} F + \frac{Z_1 Z_2 l_{12}}{\nu_1 Z_1 \bar{C}} F \equiv \bar{U}_{11} + \bar{U}_{12}, \tag{2}$$

and

$$\bar{U}_2 = \frac{Z_1 Z_2 l_{21}}{\nu_1 Z_1 \bar{C}} F + \frac{Z_2^2 l_{22}}{\nu_1 Z_1 \bar{C}} F \equiv \bar{U}_{12} + \bar{U}_{22}, \tag{3}$$

where the subscripts 1 and 2 refer to cation and anion; ν, Z, $\bar{C}$, and F, the stoichiometric number, the ionic charge, the concentration of electrolyte within membrane, and Faraday constant, respectively; $\bar{U}_1$ and $\bar{U}_2$ are the ionic mobilities within membrane defined by Eqs. 2 and 3; l's are the phenomenological coefficients involving the interactions between ions and it is assumed that Onsager's reciprocal relation is held among l's. Accordingly, the mobilities, $\bar{U}_1$ and $\bar{U}_2$, are also the quantities involving the effect of interactions between different ionic species, $\bar{U}_{12}$.

On the other hand, the concentration of electrolyte whthin membrane may be shared into two terms due to ion exchange with site and Donnan adsorption as

$$\bar{C} = \bar{C}^E + \bar{C}^D. \tag{4}$$

Corresponding to two kinds of concentrations in Eq. 4, there may be presumably two different transport processes which are characterized by the mobilities, $\bar{U}^E$ and $\bar{U}^D$. Each process may be described by means of Eq. 1. Provided the additivity between the processes can be assumed, the total specific conductance, $\bar{\kappa}^T$, is given as sum of the two processes. Therefore, one can write the following equation,

$$\begin{aligned}\bar{\kappa}^T &= \bar{\kappa}^E + \bar{\kappa}^D \\ &= \nu_1 Z_1 F \bar{C}^E(\bar{U}_1^E + \bar{U}_2^E) + \nu_1 Z_1 F \bar{C}^D(\bar{U}_1^D + \bar{U}_2^D),\end{aligned} \tag{5}$$

where $\bar{\kappa}^E$ and $\bar{\kappa}^D$ represent the contributions due to ion exchange and Donnan adsorption, and $\bar{U}^E$ and $\bar{U}^D$ also express the mobilities in the corresponding states, respectively. Under the experimental conditions that the concentrations of Donnan salt are nearly equal to zero, Eq. 5 is reduced to Eq. 6,

$$\bar{\kappa}^T_{\bar{C}^D\to 0} \simeq \bar{\kappa}^E. \tag{6}$$

Assuming that $\bar{\kappa}^E$ $(=\bar{\kappa}^T_{\bar{C}^D\to 0})$ can be separated into cationic and anionic contributions, the transport numbers, t_1 and t_2 may be defined as

$$t_1 = \bar{\kappa}_1^E/\bar{\kappa}^E, \tag{7a}$$

and

$$t_2 = \bar{\kappa}_2^E/\bar{\kappa}^E, \tag{7b}$$

where $\bar{\kappa}_1^E$ and $\bar{\kappa}_2^E$ denote respectively the specific conductances of cation and anion, which can not be directly obtained from the experiments. However, $\bar{\kappa}_1^E$ and $\bar{\kappa}_2^E$ may be easily separated by means of Eq. 7 provided t_1 and t_2 can be measured experimentally.

Moreover, when $\bar{C}^D$ is not zero but the finite value, $\bar{\kappa}^D$ in Eq. 5 is evaluated as the difference between the total specific conductance and that due to ion exchange. If the additivity for $\bar{\kappa}^T$ is assumed in the same manner as Eq. 7, the transport numbers, t_1' and t_2' may be described as

$$t_1' = (\bar{\kappa}_1^E + \bar{\kappa}_1^D)/\bar{\kappa}^T, \tag{8a}$$

and

$$t_2' = (\bar{\kappa}_2^E + \bar{\kappa}_2^D)/\bar{\kappa}^T. \tag{8b}$$

Generally, the apparent transport number, which can be obtained by the membrane potential, is approximately independent of the concentration of outer electrolyte solution.[4,10] Then, t_1' and t_2' may be equal to t_1 and t_2, respectively.

Thus, one can finally get to the following equations,

$$\bar{\kappa}_1^D = t_1'\bar{\kappa}^T - \bar{\kappa}_1^E = t_1(\bar{\kappa}^T - \bar{\kappa}^E), \tag{9a}$$

and

$$\bar{\kappa}_2^D = t_2'\bar{\kappa}^T - \bar{\kappa}_2^E = t_2(\bar{\kappa}^T - \bar{\kappa}^E). \tag{9b}$$

The specific conductance of Donnan salt, $\bar{\kappa}^D$, can be obtained from Eq. 9 as

$$\bar{\kappa}^D = \bar{\kappa}_1^D + \bar{\kappa}_2^D = \bar{\kappa}^T - \bar{\kappa}^E, \tag{10}$$

which is obviously the same as Eq. 5.

Results and Discussion

In Fig. 1, logarithms of the specific conductance of membrane, $\bar{\kappa}^T$ were given against logarithm of outer aqueous electrolyte solutions in the case of NaCl, $CaCl_2$, and $LaCl_3$, respectively. $\bar{\kappa}^T$ values increased with the concentrations of outer electrolyte solution which were equilibrated with the membrane. The order was $\bar{\kappa}^T(NaCl) > \bar{\kappa}^T(CaCl_2) > \bar{\kappa}^T(LaCl_3)$ in all the range of concentration examined in this study.

$\bar{C}^E$ and $\bar{C}^D$ obtained separately were given as the functions of the concentrations of outer electrolyte solution in Fig. 2 in which $\bar{C}^E$'s were constant within experimental errors, and $\bar{C}^D$'s increased with the concentration of outer electrolyte solution in the same manner as $\bar{\kappa}^T$. The difference of $\bar{C}^E$ between cation and anion may be neglected in this study. Taking allowance for Eq. 5, the increase of $\bar{\kappa}^T$ may be attributed to the Donnan salt, $\bar{C}^D$ as indicated later. Accordingly, $\bar{\kappa}^E$ can be determined from the values of

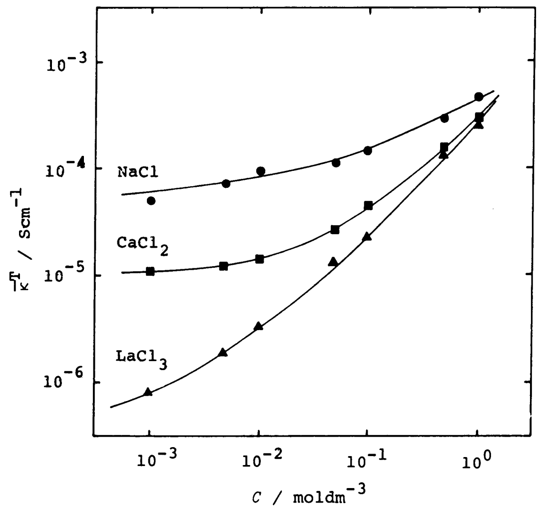

Fig. 1. Specific membrane conductance against the concentration of outer electrolyte solution equilibrated with membrane. ●: NaCl, ■: $CaCl_2$, ▲: $LaCl_3$.

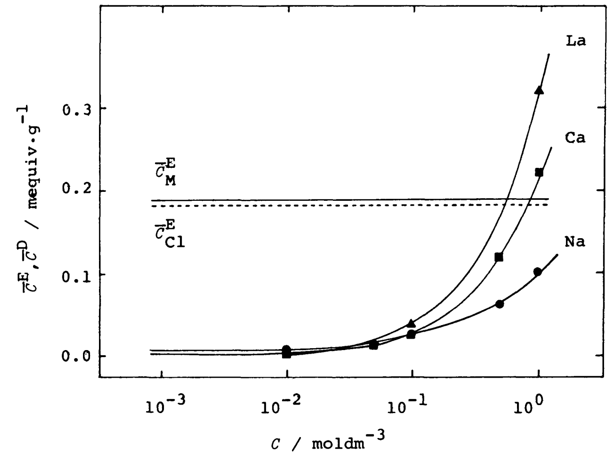

Fig. 2. Concentration of ion within membrane. Horizontal lines (solid and broken) denote the concentration due to ion exchange with sites, $\bar{C}^E$. Curved lines denote the concentration of Donnan salt, $\bar{C}^D$. ●: NaCl, ■: $CaCl_2$ ▲: $LaCl_3$. The abscissa is the same as in Fig. 1.

Table 1. Apparent Transport Numbers Evaluated from Membrane Potentials

Salt	t_M	t_{Cl}
NaCl	0.95	0.05
$CaCl_2$	0.91	0.09
$LaCl_3$	0.13	0.87

$\bar{\kappa}^T$ at $\bar{C}^D=0$ (Eq. 6). In general, $\bar{\kappa}^E$ should be constant independent of the concentration of outer electrolyte solution because it interacts strongly with ion-exchange sites having constant exchange capacity. The values were estimated as 5.37×10^{-5} (NaCl), 1.14×10^{-5} ($CaCl_2$), and 3.39×10^{-6} S cm^{-1} ($LaCl_3$) in this study, respectively. Inserting $\bar{\kappa}^E$ values into Eq. 5 or 10, $\bar{\kappa}^D$ can be obtained. The results as to 3 couples of electrolytes were given in Fig. 3.

On the other hand, the transport numbers in the system of NaCl, $CaCl_2$, and $LaCl_3$ were evaluated from the membrane potential measurements, and summarized in Table 1. As discussed in theoretical section, the experimental facts show that t's are approximately constant independent of the concentration of outer electrolyte solution.[9,10] Therefore, using the values in Table 1 and Eqs. 7 and 9, the cationic and anionic conductances of $\bar{\kappa}^E$ and $\bar{\kappa}^D$ were separately calculated. The results were given in Fig. 4 in which the broken lines indicate the constant $\bar{\kappa}^E$ originated from ion-exchange capacity, and the solid lines indicate $\bar{\kappa}^D$ due to Donnan adsorption.

Here, taking into account the electroneutrality for Donnan salt, and that the cationic and anionic exchange capacities are nearly equal, we can obtain the next relations,

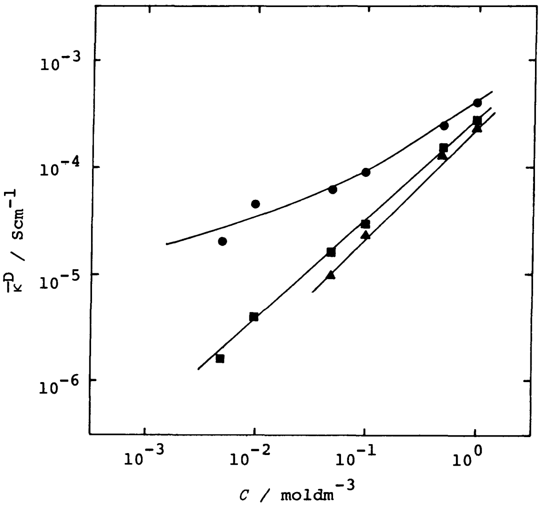

Fig. 3. Specific conductance originated from Donnan salt, $\bar{\kappa}^D$. Symbols and the abscissa are the same as in Fig. 2.

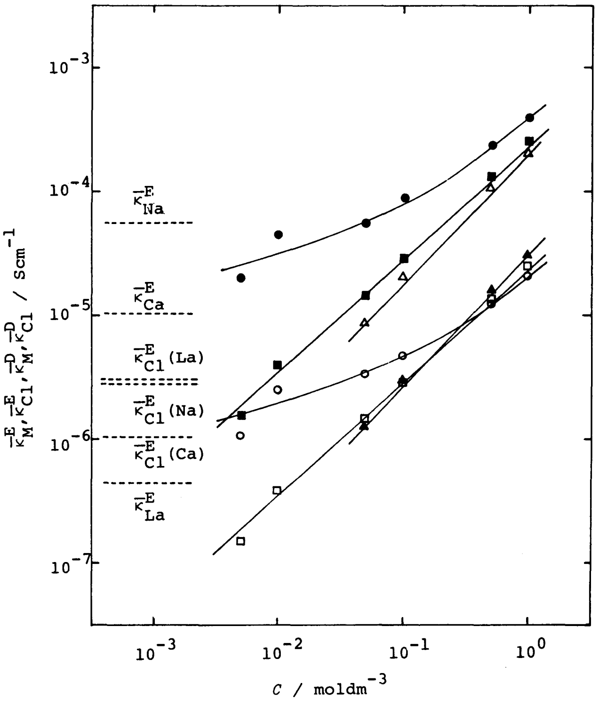

Fig. 4. Specific conductances of the respective ions. The broken lines are $\bar{\kappa}^E$ and indicate constant values in range of concentration examined though not seen in Fig. The solid lines are $\bar{\kappa}^D$. ●:Na, ■: Ca, ▲: La, ○: Cl(Na), □: Cl(Ca), △: Cl(La). The abscissa is the same as in Fig. 2.

$$\bar{C}^E = Z_1\bar{C}^E_1 \simeq Z_2\bar{C}^E_2, \tag{11}$$

and

$$\bar{C}^D = Z_1\bar{C}^D_1 \simeq Z_2\bar{C}^D_2. \tag{12}$$

On the other hand, rearranging Eqs. 6 and 10, we obtain,

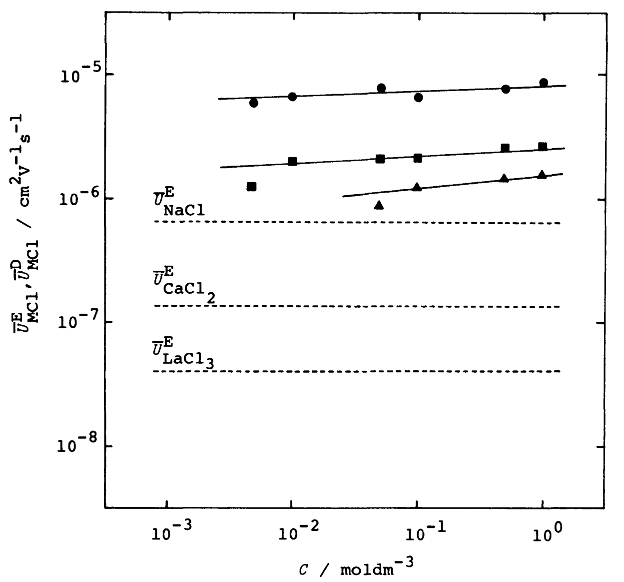

Fig. 5. Mobilities of salt within membrane. The broken lines denote $\bar{U}^E_{MCl}$. The solid lines denote $\bar{U}^D_{MCl}$. Note the difference between $\bar{U}^E_{MCl}$ and $\bar{U}^D_{MCl}$ depending upon ionic charges.

$$\bar{U}^E_{MCl} = \bar{U}^E_M + \bar{U}^E_{Cl} = \bar{\kappa}^E/F\,|Z_M|\,\bar{C}^E_M, \qquad (13)$$

and

$$\bar{U}^D_{MCl} = \bar{U}^D_M + \bar{U}^D_{Cl} = \bar{\kappa}^D/F\,|Z_M|\,\bar{C}^D_M, \qquad (14)$$

where the subscript, MCl refers to the electrolyte, and M and Cl correspond to 1 and 2 mentioned before, respectively. According to the relations, Eqs. 11, 12, 13, and 14, we can calculate the mobility of the salt at each state. A comparison of $\bar{U}^D_{MCl}$ with $\bar{U}^E_{MCl}$ was given in Fig. 5, in which the difference of mobilities is evident. In contrast to $\bar{\kappa}^D$, the values of $\bar{U}^D_{MCl}$ indicated approximately constant independent of the concentration of outer electrolyte solution. The facts take out the following important conclusion: the increase of the specific conductance, $\bar{\kappa}^T$ is attributed to the increase of Donnan salt within membrane. The $\bar{U}^D_{MCl}$ increased slightly in concentrated range of outer electrolyte solution, but it is not clear at present whether the cause comes from the experimental errors or the variation of the water content within membrane. As for $\bar{U}^E_{MCl}$, the values are constant and obviously were less than $\bar{U}^D_{MCl}$. It can be therefore pointed out that there exist two different ionic states in the membrane from the results in Fig. 5.

For the comparison, the mobilities of salts in solution were calculated by means of the molar conductances, Λ_{MCl} in literature[13] as follow,

$$U_{MCl} = \Lambda_{MCl}/|Z_M|\,F. \qquad (15)$$

In Fig. 6, $\bar{U}^D_{MCl}$ and U_{MCl} were plotted against the concentrations of Donnan salt and solution, $\bar{C}^D$ and C, respectively. It is shown in Fig. 6 that $\bar{U}^D_{MCl}$ which is about 10^{-6}cm^2 v^{-1} s^{-1}, reduces by three orders than U_{MCl} in solution. A comparison between the electrolytes examined in this study shows that the order of mobility of Donnan salts is $\bar{U}^D$(NaCl)>$\bar{U}^D$(CaCl$_2$)>$\bar{U}^D$(LaCl$_3$) corresponding to that in concentrated electrolyte solution. Contrary to our prediction, the experimental facts indicated that Donnan salt within membrane and salt in solution are in different states distinctly. One of the reasons is that Donnan salt is affected by the pore size in membrane matrix and is partly attributed to electric field around the exchange sites. Consequently, it is considered that the domains of membrane pores have an influence owing to the strong electric field produced by cation- and anion-exchange sites.[6]

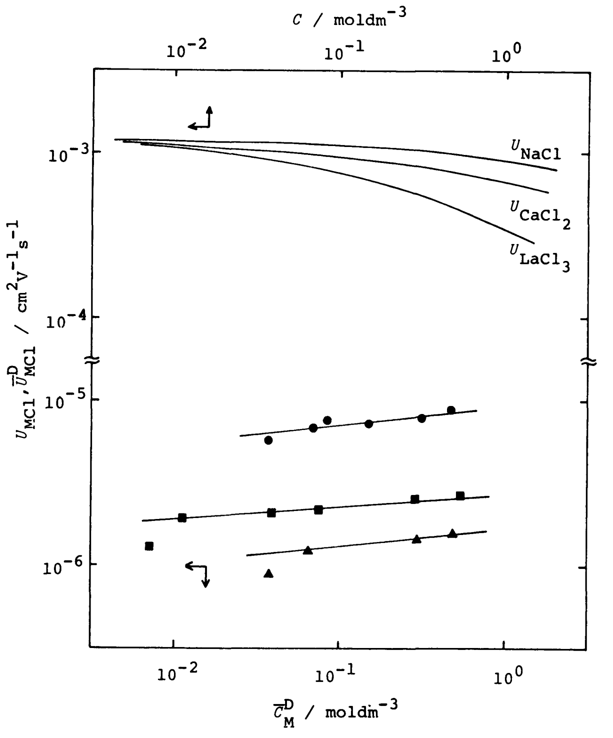

Fig. 6. A comparison between the mobility of Donnan salt and that of salt in solution. Lower abscissa indicates the concentration of Donnan salt. Symbols are the same as in Fig. 1.

Though the mobilities of salts have been discussed, so far, ionic mobility can be also estimated from the results in Fig. 4. The results were essentially the same as the case of salt. Therefore, the discussion as to the ionic form was excluded in this paper.

References

1) N. Lakshminarayanaiah, "Transport Phenomena in Membranes," Academic Press, New York, NY (1969).

2) O. Kedem and A. Katchalsky, *Trans. Faraday Soc.*, **59**, 1918, 1931, 1941 (1963).

3) C. R. Gardner, J. N. Weinstein, and S. R. Caplan, *Desalination*, **12**, 19 (1973).

4) A. Yamauchi and H. Kimizuka, *J. Theor. Biol.*, **30**, 285 (1971).

5) A. Yamauchi, S. Tsuruyama, H. Masumori, Y. Nagata, K. Kaibara, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **55**, 3297 (1982).

6) Y. Nagata, K. Kohara, W. K. Yang, A. Yamauchi, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **59**, 2689 (1986).

7) M. Shinoda, Y. Hirata, A. Yamauchi, and H. Kimizuka, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **15**, 195 (1986).

8) A. Yamauchi, H. Shinohara, M. Shinoda, M. Date, Y. Hirata, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **60**, 1645 (1987).

9) Y. Hirata, M. Date, Y. Yamamoto, A. Yamauchi, and H. Kimizuka, *Bull. Chem. Soc. Jpn.*, **60**, 2215 (1987).

10) A. Yamauchi, Y. Okazaki, R. Kurosaki, Y. Hirata, and H. Kimizuka, *J. Membr. Sci.*, **32**, 281 (1987).

11) M. J. Hach, J. A. Dillon, and H. B. Smith, *Ind. Eng. Chem.*, **49**, 1812 (1957).

12) A. Katchalsky and P. F. Curran, "Nonequilibrium Thermodynamics in Biophysics," Harvard Univ. Press, Cambridge, Massachusetts (1965).

13) "Kagaku Binran," ed by Chemical Society of Japan, (1966), p. 1034.