Extraction and Transport of Ions in a Liquid Membrane Containing Crown Ether

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The ion-transport mechanism through a liquid membrane containing dibenzo-18-crown-6 as a carrier was investigated by measuring the salt flux, the distribution coefficient to the membrane phase, and the membrane potential. The salt flux increased to a great extent with the activity of the source phase solution, but the effect of the activity on the distribution coefficient varied with the membrane solvent. The mobility ratio of cations to anions increased with an increase in the hydrophobicity of the membrane solvent. Although the selectivity of the cation transport is controlled mainly by the size of the crown ring, the hydrophobicity of the cation also influenced the salt flux and the flux of a slightly hydrated large cation, such as cesium ion, was high. The hydration degree of anions influenced the salt flux considerably since the stability constants of the crown ether complexes accompanied by a hydrophobic anions were very high. The salt flux correlated well with the lyotropic number of anions.

Crown ethers complex selectively with cations which have a similar diameter as the size of a crown ring[1] and have been applied for the separation and determination of various cations.[2] Especially in a separation with liquid membranes containing crown ethers as carriers, many reports have been presented up to now. Recently, some interesting applications have been attempted, such as ion transport driven by light energy,[3] by a redox potential,[4] or by a pH gradient.[5]

The basic theory of ion transport through a liquid membrane mediated by a crown ether has been constructed by Reusch and Cussler[6] and Lamb et al.[7] and salt transport equations have been reported. However, the extraction process of the most important process of salt transport has been investigated as solvent extraction separately against the investigation of the salt transport. There have been many reports regarding salt extraction with DB18C6;[8,9] however, extraction coefficients have not been measured in salt transport studies (with some exception).[10]

A membrane potential is also generated specifically during salt transport across the crown ether membrane; its principle is important for a specific determination of ions in ion electrodes.[11-13] However, the relationship between the salt transport and the membrane potential revealed in a liquid membrane containing a crown ether as a carrier has not yet been clarified and investigated.

In this paper, we will simultaneously analyze the extraction, the salt transport, and the membrane potential in a salt transport phenomenon of a liquid membrane containing a typical crown ether (dibenzo-18-crown-6) as the carrier with a flow cell.[14] We will attempt a preliminary clarification of the mutual relationship.

Experimental

Preparation of Membrane Phase and Source Phase Solutions. In this study, dibenzo-18-crown-6 (DB18C6) was used as the carrier of a liquid membrane. DB18C6 was obtained from Nippon Soda Co., as a commercial reagent and was used after recrystalization from benzene. Unless otherwise stated, the liquid membrane was a 0.1 mol dm^{-3} DB18C6 solution of tetrachloroethane and the source phase solution was a 0.1 mol dm^{-3} aqueous solution of KNO_3 (analytical grade reagent). For an investigation of the effect of a membrane solvent on ion transport, some solvents were examined; the solvents used in this study and their dielectric constants[15] were as follows: chloroform, 4.7; Chlorobenzene, 5.6; 1,1,1-Trichloroethane, 7.1; 1,1,2-Trichloroethane, 7.1; 1,1,2,2-tetrachloroethane, 8.0; Dichloromethane, 9.1 and 1,2-Dichloroethane, 10.5.

Measurements of Salt Flux and Distribution Coefficient. The salt flux was measured in a previously reported dialysis cell.[14] The cell comprised 3 compartments separated from each other by a Visking dialysis membrane (the membrane area was 6.6 cm^2, the thickness of each compartment was 3 mm; the source phase solution, membrane phase solution, and pure water of the receiving phase solution were circulated from respective reservoirs by using tubing pumps at a rate of about 15 cm^3 min^{-1}). The receiving phase solution was collected at regular time intervals and its concentration was measured by an atomic absorption spectrophotometer (Shimadzu AA-630-02). The salt flux was calculated from the concentration change with time in the receiving phase and was given in units of mol cm^{-2} min^{-1}. The distribution coefficient was measured with a cell (the same as that of a dialysis cell, except that the cell has only two compartments: a source phase compartment and a membrane phase compartment). A membrane phase solution of 0.10 cm^3 was collected at regular time intervals; each solution was diluted with both 0.9 cm^3 acetonitrile and 0.1 cm^3 pure water, and the metal concentration in it was measured using an atomic absorption spectrophotometer. Standard solutions for this determination were also prepared with the same type acetonitrile-water solution. The distribution coefficient was calculated from the salt activities in the membrane phase and in the salt solution during equilibrium.

Measurement of Membrane Potential. The membrane potential was measured with a cell (the same as that of the dialysis cell, except that both sides of the cell were bored and a salt bridge was set at the vicinity of the each outside surface

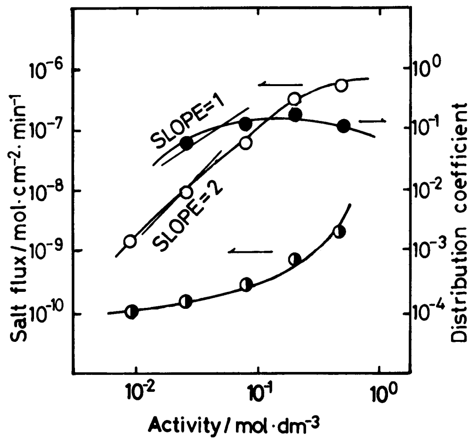

Fig. 1. Salt flux and distribution coefficient vs. KNO_3 activity in carrier-mediated transport in 1,1,2,2-tetrachloroethane solvent.
Source phase: 0.1 mol dm^{-3} KNO_3 aq soln. Liquid membranes: 0.1 or 0 mol dm^{-3} dibenzo-18-crown-6(DB18C6) in 1,1,2,2-tetrachloroethane. ●: Distribution coefficient, ○: Salt flux through membrane containing DB18C6, ◑: Salt flux through membrane containing no carrier.

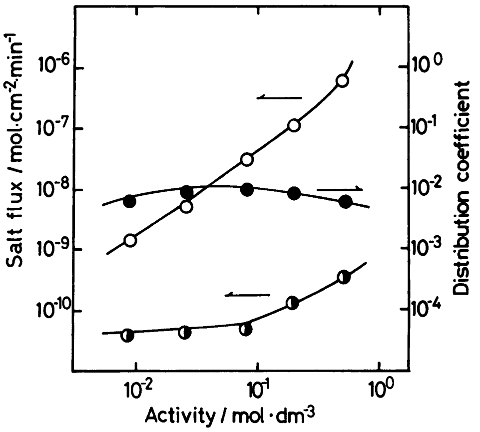

Fig. 2. Salt flux and distribution coefficient vs. KNO_3 activity in carrier-mediated transport in chloroform solvent.
Source phase: 0.1 mol dm^{-3} KNO_3 aq soln. Liquid membranes: 0.1 or 0 mol dm^{-3} DB18C6 in chloroform. ●: Distribution coefficient, ○: Salt flux through membrane containing DB18C6, ◑: Salt flux through membrane containing no carrier.

of the liquid membrane). Circulating the salt solution, the membrane phase solution, and the receiving phase solution with tubing pumps, the membrane potential was measured using a potentiometer (Toa IM-20E) connected to a recorder (Yanagimoto YR-101). The potential changed with time; after an appropriate time it approached a constant value, from which the ion mobility ratio, u_+/u_- or u_-/u_+, was calculated with

$$E = (u_+ - u_-)/(u_+ + u_-) \times \mathrm{RT/F} \times \ln a_s/a_r. \qquad (1)$$

Here, u_+ and u_- are the mobilities of the cation and anions; R, T, and F are the gas constant, absolute temperature, and the Faraday constant; and a_s and a_r are the salt activities of the source phase solution and the receiving phase solution, respectively.

Results and Discussion

Effects of Salt Activities and Membrane Solvent on Salt Transport. The salt flux depends on the salt activity of the source phase solution. Figures 1 and 2 show the relationship between the permeation characteristics and the salt activity in the cases of liquid membranes of DB18C6 in 1,1,2,2-tetrachloroethane and DB18C6 in chloroform. In the figures, the salt flux, the distribution coefficient, and the salt flux across the liquid membrane containing no carrier are shown together. These permeation characteristics depending on the salt activity can be expressed by the following equations. The distribution coefficient of the salt between the membrane phase and the source or receiving phase, k, is

$$k = a_m/a, \qquad (2)$$

where a_m and a are the salt activity in the liquid membrane and that in the source or receiving phase, respectively. The salt flux, J_s, can be expressed by

$$J_s = D_s/l \times (a_{m,s} - a_{m,r}), \qquad (3)$$

where D_s is the diffusion coefficient, l is the membrane thickness, and $a_{m,s}$ and $a_{m,r}$ are the activity at the liquid membrane interface adjacent to the source phase solution and that adjacent to the receiving phase solution. If the salt activity of the receiving phase is much lower than that of the feed solution, $a_{m,r}$ becomes much smaller than $a_{m,s}$ and can be ignored. Using Eq. 2, the salt flux in Eq. 3 therefore becomes

$$J_s = D_s/l \times a_{m,s} = D_s ak/l. \qquad (4)$$

The crown ether compex is considered to be formed in the liquid membrane phase from the crown ether and the ion pair to be formed in the aqueous phase and distributed to the membrane phase. The formation constant of the ion pair, K_i, is

$$K_i = a_i/a^2, \qquad (5)$$

and the distribution coefficient of the ion pair, D_i is

$$D_i = a_{i,m}/a_i. \qquad (6)$$

Here, a_i and $a_{i,m}$ are the activity of the ion pair in the aqueous phase and that in the membrane phase, respectively. The salt flux and the distribution coefficient can be correlated with the salt activity in the source phase solution with these equations. For a derivation of the salt flux and the distribution coefficient, the total carrier activity, L_T and the formation constant of the crown ether complex in the liquid membrane phase, K_c can be defined as follows:

$$L_T = L + a_L, \qquad (7)$$

and

$$K_c = a_L/(a_{i,m} \times L). \qquad (8)$$

Here, L and a_L are the activities of the free crown ether and that of the complex in the liquid membrane phase. Then, a_m is correlated with $a_{i,m}$ and a_L as

$$a_m = a_{i,m} + a_L. \tag{9}$$

If $a_{i,m}$ can be ignored compared to a_L, the distribution coefficient, k, becomes

$$k = a_m/a = a_L/a. \tag{10}$$

From these equations, k can be derived as a function of the salt activity of the source phase solution as

$$k = K_{ex}L_T a/(1 + K_{ex}a^2), \tag{11}$$

where K_{ex} is an extraction coefficient defined by

$$K_{ex} = a_L/(a^2 L) = K_c K_i D_i. \tag{12}$$

From Eqs. 4 and 12, the salt flux, J_s, can be derived as

$$J_s = D_s K_{ex} L_T/l \times a^2/(1 + K_{ex}a^2). \tag{13}$$

This is the same equation reported by Reusch and Cussler.[6] In Fig. 1, both the distribution coefficient and the salt flux increased enormously with the salt activity when the salt activity was lower than 0.1 mol dm^{-3} (while the distribution coefficient was initiated to decrease and the salt flux became constant when the activity was higher than 0.1 mol dm^{-3}). These permeation phenomena can be expected from Eqs. 11 and 13. When the value of K_{ex} a^2 becomes much lower than 1 (that is, the salt activity becomes very low), Eqs. 11 and 13 can be transformed into

$$k = K_{ex}L_T a, \tag{14}$$

and

$$J_s = D_s K_{ex} L_T a^2/l, \tag{15}$$

where k and J_s are proportional to the first power and the second power of the salt activity, respectively. When the value of K_{ex} a^2 becomes much higher than 1 (that is, the salt activity becomes very high), Eqs. 11 and 13 can be transformed into

$$k = L_T/a, \tag{16}$$

and

$$J_s = D_s L_T/l, \tag{17}$$

where k is proportional to the reciprocal of the salt activity and J_s is constant.

In the figure, the salt flux through a liquid membrane containing no carrier is also shown. By using Eqs. 2—6, the flux can be expressed as

$$J_s = D_s D_i K_i a^2/l. \tag{18}$$

The salt flux, J_s, is derived to be proportional to the second power of the salt activity in this equation; however, in Fig. 1 this is true only in a high activity range and the J_s becomes a constant with a decrease in the salt activity. The transport of salt in a low-activity range may be mainly caused by leakage through the membrane; This is probably due to the microquantity of the microvolume droplets of water dispersed in the membrane. By comparing Eq. 15 and Eq. 18, the J_s ratio of Eq. 15 to Eq. 18 is found to be $K_c L_T$ when the diffusion coefficient of the crown complex can be assumed to be almost the same to that of the ion pair. As L_T is 0.1 mol dm^{-3}, K_c can be estimated to be about three orders of magnitude from Fig. 1.

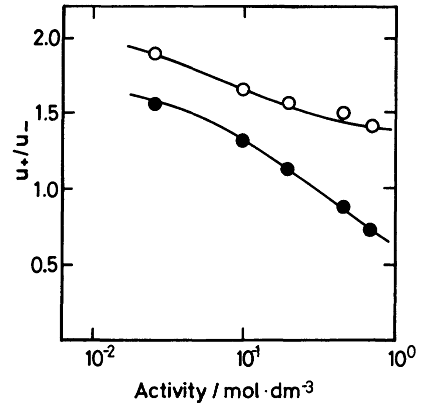

Fig. 3. Effect of salt activity on mobility ratio. Liquid membrane:0.1 mol dm^{-3} DB18C6 in 1,1,2,2-tetrachloroethane (●), chloroform (○). Ratio of salt (KNO_3) concentration: 10 to 1. The abscissa show the activity of the solution of the higher concentration side.

The salt transport characteristics depend not only on the salt activities, but also on many other conditions, such as cation species, anion species, and membrane solvents.[16,17] Figure 2 shows the effect of the salt activity on the salt flux and the distribution coefficient in a different membrane solvent, chloroform membrane containing DB18C6. In this case, the salt fluxes were smaller than those given in Fig. 1 and the dependency of the distribution coefficient on the salt activity was very small; However, the difference between the magnitude of the carrier-mediated transport in this case and that in Fig. 1 was especially small in the range of high salt activity. The independence of the distribution coefficient on the activity can not be explained on the basis of the theory described above. It is reported that in the case of chloroform the solubility of DB18C6 is high but decreases enormously by complexing[1] since the complex is more hydrophilic than DB18C6 alone and chloroform is a hydrophobic solvent. This may be the reason for the low and constant distribution coefficient. Although the distribution coefficient is constant, the ratio of the flux of the complex to that of the ion pair was larger than that in the case of Fig. 1 and must have been caused by a high formation constant of the DB18C6 complex in the hydrophobic solvent, chloroform.

In order to clarify the reason for the effect of the activity on the salt flux and the difference of the effect between the case of 1,1,2,2-tetrachloroethane and the case of chloroform, the mobility ratio of the cation to anion in the liquid membrane phase was measured; values were shown in Fig. 3. When the cation is more

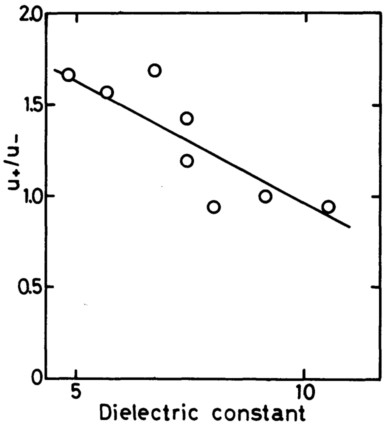

Fig. 4. Mobility ratio vs. dielectric constant of liquid membrane solvent.
Liquid membrane: 0.01 mol dm^{-3} DB18C6 organic soln. Salt concentration: 0.1—0.01 mol dm^{-3}.

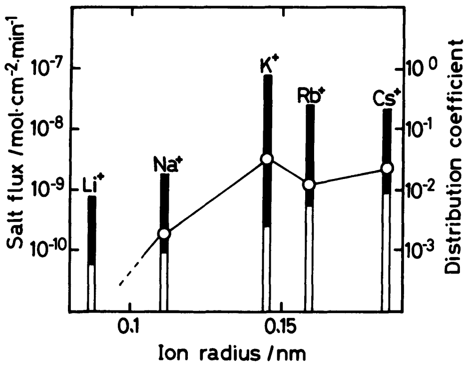

Fig. 5. Effect of cation radius on salt flux and distribution coefficient.
Liquid membrane: 0.1 mol dm^{-3} DB18C6 in 1,1,2,2-tetrachloroethane soln. ○: Distribution coefficient, ■: Salt flux through membrane containing DB18-C6, □: Salt flux through membrane containing no carrier.

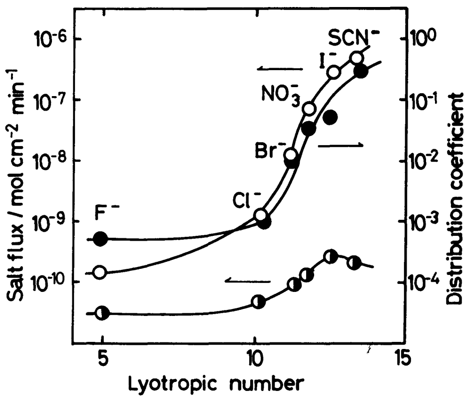

Fig. 6. Effect of lyotropic number of anion on salt flux and distribution coefficient.
Liquid membrane: 0.1 mol dm^{-3} DB18C6 in 1,1,2,2-tetrachloroethane soln. ●: Distribution coefficient, ○: Salt flux through membrane containing DB18-C6, ◑: Salt flux through membrane containing no carrier.

stable than the anion and the permeability of the cation is larger than that of the anion in the membrane phase, the value of u_+/u_- becomes larger than 1. The cations complexed with crown ether, whose hydrophobic group was arranged outside of it, were more stable than naked anions, and the mobility ratio became greater than 1 (with some exceptions). In the case of the 1,1,2,2-tetrachloroethane solution, the values of u_+/u_- decreased with an increase in the salt activity and became smaller than 1 for a high salt activity. In the case of the chloroform solution, the values of u_+/u_- were constant, except within a low salt activity range and were higher than those of a 1,1,2,2-tetrachloroethane solution. These differences between two membrane solvents are considered to be caused by differences in the hydrophobicity of the solvent. The ratio was higher for chloroform than for 1,1,2,2-tetrachloroethane since chloroform is more hydrophobic than 1,1,2,2-tetrachloroethane. In 1,1,2,2-tetrachloroethane, the naked anions were more stable than in chloroform and their stability increased with the ionic strength of the aqueous solution on either side of the membrane.

The relationship between u_+/u_- and the dielectric constant is shown in Fig. 4 in order to investigate the effect of the hydrophobicity of the membrane solvent using chlorinated hydrocarbons for the membrane solvents. As predicted in the prior paragraph, the mobility ratio of the complexed cation to that of the naked anion increased with an increase in the hydrophobicity of the membrane solvent; also, the mobility ratio decreased, on the whole, with an increase in the dielectric constant (an indication of the hydrophilicity of the solvent).

Selective Transport of Salts. The relationship between the salt flux or the distribution coefficient and the ion radius for alkaline cations is shown in Fig. 5 in order to investigate the mechanism of the selective transport. The distribution coefficient is maximum for potassium ions since the stability constant of a DB18C6 complex is maximum for potassium ions in alkaline metal ions.[1] The value of lithium was not plotted in this figure because its concentration in the membrane phase was very low and could not be detected. The salt flux changes with a change in the distribution coefficient and the flux was also maximum for potassium salt. The salt flux through the liquid membrane with no carrier was also measured. This transport was caused by a concentration difference of ion pairs in the membrane without a carrier. Since the hydrophobicity of the ions increases with an increase in the cation radius and hydrophobic ions are easy to be transported in a hydrophobic membrane,[18,19] the flux of ion pairs increased with an increase in the ion radius. The relationship between the salt flux or the distribution coefficient and the lyotropic number[20] of anions is also shown in Fig. 6. The

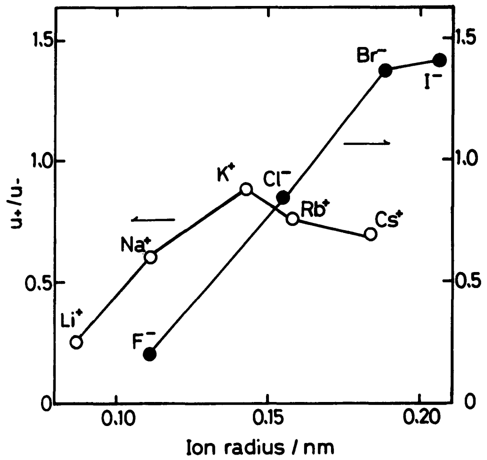

Fig. 7. Mobility ratio vs. ion radius.
Liquid membrane: 0.1 mol dm^{-3} DB18C6 organic soln. Salt concentration: 0.1—0.01 mol dm^{-3}. Counter anion is NO_3^-. Counter cation is K^+.

salt flux through a membrane containing DB18C6 as a carrier can be related well to the lyotropic number (as in the case of anion chromatography on silica gel coated with crown ether polymer;[21] Lamb et al. related the salt transport phenomena to the dehydration energies of anions).[22] The salt flux through a membrane containing no carrier also increased with increasing lyotropic number, but the degree was much smaller for the latter than for the former. The distribution coefficient increased with the salt activity in the same manner as the salt flux. Figure 7 shows the relationship between u_+/u_- and cation radius for the salt of alkaline metal ions and that between u_-/u_+ and anion radius for halogenide ions. The ratio of the mobility of a cation to that of NO_3^- was maximum for potassium ions (all the values were lower than 1). In anions, the mobility ratios increased with an increase in the anion radius and the mobilities of Br^- and I^- were much higher than that of a complexed potassium ion. It is clear that the selectivity for anions was caused by the hydrophobicity of the ions and that for cations was mainly caused by the selective complexation of DB18C6.

References

1) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).

2) M. Igawa, *Kagaku Koujou*, **25**, 49 (1981).

3) S. Shinkai, T. Nakaji, T. Ogata, K. Shigematsu, and O. Manabe, *J. Am. Chem. Soc.*, **103**, 111 (1981).

4) S. Shinkai, K. Inuzuka, K. Hara, T. Sone, and O. Manabe, *Bull. Chem. Soc. Jpn.*, **57**, 2150 (1984).

5) T. M. Fyles, V. A. M. Diemer, and D. M. Whitfield, *Can. J. Chem.*, **59**, 1734 (1981).

6) C. F. Reusch and E. L. Cussler, *AIChE J.*, **19**, 736 (1973).

7) J. D. Lamb, J. J. Christensen, S. R. Izatt, K. Bedke, M. S. Astin, and R. M. Izatt, *J. Am. Chem. Soc.*, **102**, 3399 (1980).

8) H. K. Frensdorf, *J. Am. Chem. Soc.*, **93**, 4684 (1971).

9) Y. Takeda, "Host Guest Complex Chemistry III," Springer-Verlag, (1984), p. 1.

10) S. Yoshida and S. Hayano, *J. Am. Chem. Soc.*, **108**, 3903 (1986).

11) G. A. Rechuitz and E. Eyal, *Anal. Chem.*, **44**, 370 (1972).

12) K. Kimura, T. Maeda, H. Tamura, and T. Shōno, *Anal. Chem.*, **95**, 91 (1979).

13) K. Kimura, K. Kumami, S. Kitazawa, and T. Shōno, *Anal. Chem.*, **56**, 2369 (1984).

14) M. Igawa, K. Saitou, F. Monoe, K. Nishida, M. Tanaka, and T. Yamabe, *Nippon Kagaku Kaishi*, **1985**, 826.

15) "Kagaku-Binran (Kisohen)," ed by Chem. Soc. Jpn., rev. 3, Maruzen (1982).

16) M. Igawa, M. Tanaka, S. Izumi, Y. Kaneko, and T. Yamabe, *Nippon Kagaku Kaishi*, **1980**, 135.

17) M. Igawa, K. Matsumura, M. Tanaka, and T. Yamabe, *Nippon Kagaku Kaishi*, **1981**, 625.

18) I. Satake, H. Nakajima, and H. Noguchi, *Membrane*, **2**, 225 (1977).

19) M. Igawa, K. Torii, M. Tanaka, and M. Senō, *J. Appl. Polym. Sci.*, **29**, 117 (1984).

20) K. Miyajima, Kagaku no Ryoiki, Zokan 106, Nankōdō (1974), p. 83.

21) M. Igawa, K. Saitō, J. Tsukamoto, and M. Tanaka, *Anal. Chem.*, **53**, 1942 (1981).

22) J. D. Lamb, J. J. Christensen, J. L. Oscarson, B. L. Nielsen, B. W. Asay, and R. M. Izatt, *J. Am. Chem. Soc.*, **102**, 6820 (1980).