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Selective Ion Transport across Monomeric or Reversed Micellar Liquid Membrane Containing an Open-Chain Polyether Surfactant

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The transport phenomena of salts across a liquid membrane containing a nonionic surfactant, polyoxyethylene *p*-nonylphenyl ether, as a carrier were investigated. The surfactant, complexing with metal cations selectively, functions as a monomeric carrier or a reversed micellar carrier of a self-assembly system depending on the concentrations of the carrier and the source phase salt. The fluxes of the hydrophobic salts were large in general, and potassium ion was selectively transported by the carrier containing 20 ethylene oxide units. The mole ratio of the salt to the carrier in the complex was 1 in the forms of both monomer and reversed micelle. The transport equation was derived from the complex formation, and its destruction rates and the diffusion resistance were found to be functions of the activities of the source phase salt and the carrier. The theoretical values agreed very well with the measured values. Both the reaction rate constant and the diffusion coefficient decreased significantly with the change of the carrier form from the monomer to the reversed micelle. Therefore, the increase of the flux with the increase of the concentrations of the source phase salt and the carrier was suppressed by the formation of the reversed micelle.

Introduction

Crown ethers have been studied for the specific complexation with metal ions[1] and used for the liquid membrane carrier to attain the specific transport characteristics.[2] Recently, it was reported that the synthesized surfactants of crown ether derivatives were used to be a self-assembly system of a monolayer lipid membrane.[3] However, conventional nonionic surfactants, the derivatives of polyethylene glycols, have characteristics of not only self-assembly systems but also open-chain crown compounds which can also complex with metal ions selectively.[4] The derivatives of polyethylene glycol can play the role of a liquid membrane carrier of the selective transport of alkali metal ions, although the selectivity was not so high as those of crown ethers.[5] The derivatives complexed with alkali and alkaline earth metal ions[6,7] and polyethylene glycol type nonionic surfactants can be determined by the complexing ability with barium ion.[8] Yanagida et al. reported that polyethylene glycols with more than seven ethylene oxide units have strong complexing ability with potassium ion as crown ether.[9] The polyoxyethylene chain forms a helical structure, and the oxygen atoms in the chain coordinate with metal ions. Polyethylene glycol derivatives are unusual carriers of liquid membranes which behave as monomeric carriers at low carrier concentration but turn out to be reversed micellar over the critical concentration.[10] A reversed micelle is a self-assembly system and is reported to function as an effective carrier in the selective transport of proteins.[11]

In this paper, the transport phenomena of the salts across a liquid membrane containing polyoxyethylene *p*-nonylphenyl ether as a carrier were investigated. The form of the carrier changes with the concentrations of the carrier and the source phase salt, and the transport characteristics depend to a great extent on the carrier form, that is, the monomer or the reversed micelle which is of interest as organized assemblies.[12] The mechanism of the salt transport in the membrane will be discussed, and the transport equation will be presented.

Experimental Section

Transport Experiments. For the transport experiments, a dialysis cell composed of a source phase, a liquid membrane phase, and a receiving phase was used and these phases were divided from each other by cellulose membranes, Visking dialysis membranes (Viskase Sales Corp.), as shown in Figure 1.[13] Both sides of the cell, the acrylic frames, were fastened to each other with bolts to seal the compartments of the three phases. The membrane area was 6.6 cm^2, and the thickness of each compartment was 3 mm. The solution in each compartment was circulated from each reservoir, respectively, by using tubing pumps at a rate of 15 cm^3 min^{-1}. The membrane phase was 1,2-dichloroethane containing a carrier of polyethylene glycol mono-(*p*-nonylphenyl) ether whose ethylene oxide unit was 20, the source phase was the solution of potassium thiocyanate, and the receiving phase was pure water, unless otherwise stated. The membrane phase solution was adjusted to be a solution with some molality concentration, and the molarity concentration was indicated in this paper after converting from the molality concentration with the density of the membrane phase solution, which was determined to be 1.22 g mL^{-1}.

The transport experiment was carried out at room temperature. The receiving phase solution was collected at regular time intervals, and the salt 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}.

Solvent-Extraction Experiments. The solvent extraction was also carried out by the same method as that for the transport experiment, except that the cell only had two compartments: the source phase compartment and the membrane phase compartment. A membrane phase solution of 0.10 cm^3 was collected at regular time intervals after the beginning of the extraction experiment. Each solution was diluted with both 0.90 cm^3 acetonitrile and 0.10 cm^3 pure water, and the metal ion concentration was measured by the atomic absorption spectrophotometer to obtain the equilibrium concentration of the salt in the membrane phase. The standard solution for this deter-

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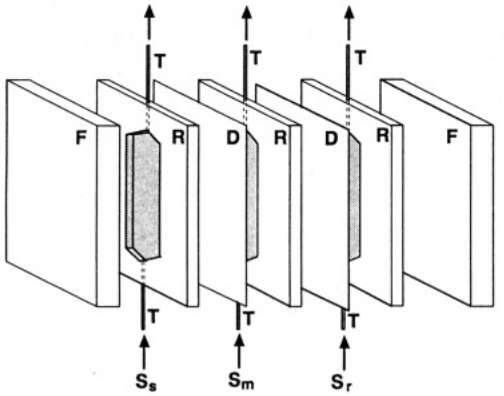

Figure 1. Dialysis cell: S_s, source phase solution; S_m, membrane phase solution; S_r, receiving phase solution; T, Teflon tubing; R, Viton rubber sheet; D, Visking dialysis membrane; F, acrylic frame.

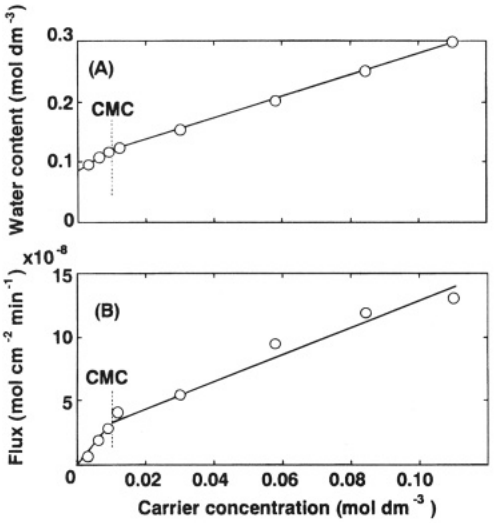

Figure 2. Effect of carrier concentration on the water content in the membrane phase (A) and the salt flux (B): source phase, 0.1 dm^3 of 0.1 mol dm^{-3} potassium thiocyanate; liquid membrane, 10 cm^3 of polyoxyethylene *p*-nonylphenyl ether in 1,2-dichloroethane; receiving phase, 0.1 dm^3 of pure water; cmc means the critical micelle concentration.

mination was also prepared in a manner similar to that for the sample solution to be the mixed solution of 1,2-dichloroethane, acetonitrile, and potassium thiocyanate aqueous solution. The extraction rate was also measured in this experiment by the initial linear change of the membrane phase concentration with time.

The water content in the membrane phase was also measured in some of the solvent extraction experiments. At regular time intervals, 0.1 cm^3 samples of the membrane phase solution were withdrawn and analyzed for water content to obtain the equilibrium value. The water content was measured by a moisturemeter (CA-05, Mitsubishi Chemical Industries Co. Ltd.), which works on the basis of Karl Fischer titration.

Reagents. The reagents used in this experiment were analytical grade. The carrier, polyethylene glycol mono-(*p*-nonylphenyl) ether, was obtained from Tokyo Chemical Industry Co., Ltd and used in this experiment without further purification. The chemical formula of the carrier is $HO(CH_2CH_2O)_nC_6H_4C_9H_{19}$, and n of the reagents used in this study was 2, 5, 10, 15, and 20.

Results and Discussion

Monomeric and Reversed Micellar Forms of Carrier. Figure 2 shows the effect of the carrier concentration on the water content in the liquid membrane and the ion flux, when

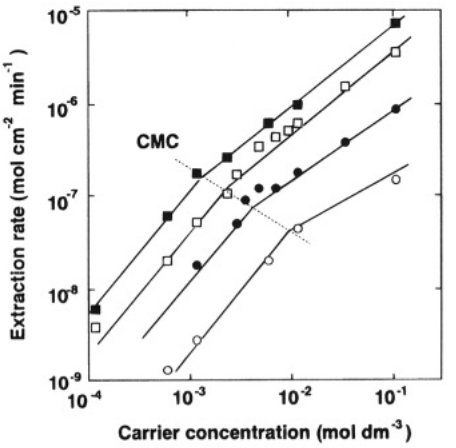

Figure 3. Effect of carrier concentration on extraction rate at some source phase concentration of potassium thiocyanate: source phase, 0.1 dm^3 of 3 mol dm^{-3} (■), 1 mol dm^{-3} (□), 0.3 mol dm^{-3} (●), and 0.1 mol dm^{-3} (○) potassium thiocyanate; liquid membrane, 10 cm^3 of polyoxyethylene *p*-nonylphenyl ether in 1,2-dichloroethane; cmc means the critical micelle concentration.

the source phase was 0.10 mol dm^{-3} KSCN. The ion flux and the water content increased with the increase of the carrier concentration, but the slope changes at the concentration of about 0.010 mol dm^{-3}, which we interpret to be the critical reversed micelle concentration (cmc). The cmc's of some surfactants in nonaqueous media have been reported, although the data are limited. For example, the cmc and aggregation number of n-$C_{13}H_{27}(OC_2H_4)_6OH$ in benzene are reported to be 2.6×10^{-3} mol dm^{-3} and 99,[14] respectively, and cmc is affected by the length of the polyoxyethylene group and the hydrophobic chain length.[15] Konno and Kitahara reported the cmc of polyethylene glycol mono-(*p*-nonylphenyl) ether containing 2−10 ethylene oxide units to be 0.011−0.0069 mol dm^{-3} in cyclohexane,[10] which agreed with the result shown in Figure 2. In the concentration range over the cmc, ion was transported by not only monomeric carrier but also the carriers of the reversed micelle. The relationship between the ion flux and the water content and the surfactant concentration was also studied for polyethylene glycol mono-(*p*-nonylphenyl) ether with the ethylene oxide unit numbers of 2, 5, 10, and 15. All of the critical concentrations of these surfactants were about 0.010 mol dm^{-3}, and the critical point was not affected by the length of the polyoxyethylene group.

It is well-known that the cmc changes with the salt concentration.[15] Then, the dependence of the extraction rate of potassium thiocyanate on the surfactant concentration was measured for some salt concentrations in the aqueous phase. There were also critical points which correspond to the cmc's as shown in Figure 3. We obtained cmc from the critical points of the slopes to be the function of the source phase salt concentration as follows.

$$\text{cmc} = 0.0024[\text{KSCN}]^{-0.65} \quad (1)$$

The cmc of a nonionic surfactant in an aqueous phase decreased with the increase of the salt concentration in the source phase because of the salting-out effect of the hydrophobic group of the surfactant by the electrolyte,[16,17] which may also explain the depression of the critical concentration of reversed micelle by the electrolyte.

Selective Permeation Properties. Figure 4A shows the relationships between the fluxes of alkali metal ions and their ion radii[18] in the lower carrier concentration range (0.0030 mol dm^{-3}) and in the high carrier concentration range (0.11 mol dm^{-3}), which correspond to the monomer and reversed micelle, respectively. The flux of potassium ion was the highest, and

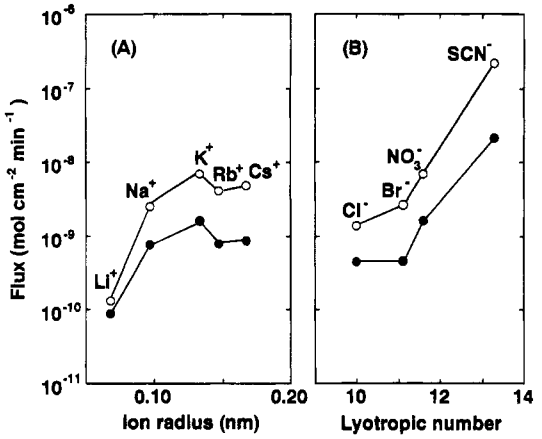

Figure 4. Selective permeabilities of alkali metal ions (A) and effect of anions on the salt flux (B): source phase, 0.1 dm^3 of 0.1 mol dm^{-3} chloride salt or potassium salt; liquid membrane, 10 cm^3 of 0.0030 mol dm^{-3} (●) or 0.11 mol dm^{-3} (○) polyoxyethylene *p*-nonylphenyl ether in 1,2-dichloroethane; receiving phase, 0.1 dm^3 of pure water.

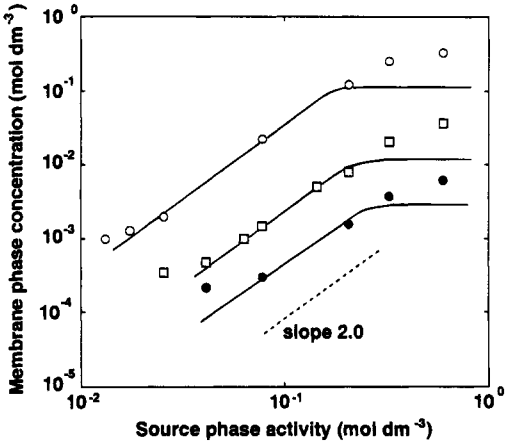

Figure 5. Effect of source phase activity on equilibrium concentration in membrane phase: source phase, 0.1 dm^3 of potassium thiocyanate; liquid membrane, 10 cm^3 of 0.0030 mol dm^{-3} (●), 0.012 mol dm^{-3} (□), or 0.11 mol dm^{-3} (○) polyoxyethylene *p*-nonylphenyl ether in 1,2-dichloroethane; the solid line was the calculated value from eq 6.

the hydrophobic salts were transported effectively in both cases, although the selectivity is not so high as that of a crown ether. This selective permeability must be controlled by the stability constant of the salt. The transport rate of lithium salt was very small, and the difference between the lithium ion fluxes in the low and the high carrier concentrations was also very small. The flux of lithium ion which was not mediated by any carrier was around 10^{-10} mol cm^{-2} min^{-1},[13] and the contribution of the complex formation to the transport of lithium salt in Figure 4A must be very small.

Figure 4B shows the effect of the lyotropic number of some anions[19] on their potassium salt flux at the carrier concentrations of 0.0030 and 0.11 mol dm^{-3}. The hydrophobicity increases with the increase of the lyotropic number, and the flux increases with the increase of hydrophobicity of the anion. It is also the case for the crown ethers because of the high stability of hydrophobic salts in nonaqueous media.[13]

The selective permeability of cations also increased with increasing hydrophobicity of the counteranions. When the carrier concentration was 0.11 mol dm^{-3} and the source phase salt concentration was 0.10 mol dm^{-3}, the flux ratio of potassium thiocyanate to sodium thiocyanate was 8.6, while the flux ratio of potassium nitrate to sodium nitrate was 5.9.

Complexation Properties of Carrier. Figure 5 shows the effect of the source phase salt activity on the equilibrium concentration in the membrane phase obtained by using a two compartment cell. The concentration in the membrane phase became a constant value in 2 h, and the value was used as the equilibrium concentration. Potassium thiocyanate was used as the salt, and the concentration in the membrane phase increased with the increase of the source phase salt activity. The equilibrium salt concentration in the liquid membrane phase can be derived as follows.

The *n* mol of potassium ion reacts with a carrier molecule, polyethylene glycol mono-(*p*-nonylphenyl) ether (L), with counteranion, thiocyanate ion, to be a complex at the interface of the membrane phase adjacent to the source phase as follows

$$n\mathrm{K}^+ + n\mathrm{SCN}^- + \mathrm{L}_m = \mathrm{L}{\cdot}n\mathrm{KSCN}_m \quad (2)$$

where the subscript m means the chemical species in the membrane phase. The solute is transported as an ion pair complexed with a neutral carrier like a crown ether,[2] and then the formation constant of the complex is defined as follows.

$$K = \frac{[\mathrm{L}{\cdot}n\mathrm{KSCN}]_m}{[\mathrm{K}^+]^n[\mathrm{SCN}^-]^n[\mathrm{L}]_m} \quad (3)$$

Since some of the carriers turn out to be the complex and the rest is the free carrier, the total carrier concentration in the membrane phase, $[L_0]$, can be defined as follows.

$$[\mathrm{L}_0]_m = [\mathrm{L}]_m + [\mathrm{L}{\cdot}n\mathrm{KSCN}]_m \quad (4)$$

Since the concentration of potassium thiocyanate free from the carrier in the membrane phase was negligible, the complex concentration can be described by the concentration of potassium thiocyanate in the membrane phase, which was measured in this study.

$$[\mathrm{L}{\cdot}n\mathrm{KSCN}]_m = [\mathrm{KSCN}]_m/n \quad (5)$$

From these equations, the potassium thiocyanate concentration in the membrane phase can be derived as follows.

$$[\mathrm{KSCN}]_m = \frac{nK[\mathrm{L}_0]_m[\mathrm{KSCN}]^{2n}}{1 + K[\mathrm{KSCN}]^{2n}} \quad (6)$$

where $[KSCN] = [K^+] = [SCN^-]$. When the salt activity in the source phase was low and $1 \gg K[KSCN]^{2n}$, the equation was simplified as follows.

$$\log([\mathrm{KSCN}]_m) = \log(nK[\mathrm{L}_0]_m) + 2n \log([\mathrm{KSCN}]) \quad (7)$$

When the salt activity was high and $1 \ll K[KSCN]^{2n}$, the equation was as follows.

$$[\mathrm{KSCN}]_m = n[\mathrm{L}_0]_m \quad (8)$$

We can obtain the values of *n* and *K* from the experimental values of the salt concentration in the membrane phase depending on the source phase salt activity in the low salt activity range by using eq 7. Even when the carrier concentration was 0.0030 mol dm^{-3}, the surfactant forms reversed micelle in a high salt concentration range, which is expected to be higher than ca. 0.7 mol dm^{-3} by eq 1. Then, the carrier was dissolved only as the form of the monomer, when the surfactant concentration was 0.0030 mol dm^{-3} and the salt concentration was lower than 0.7 mol dm^{-3}. In the low concentration range, the values of *n* and *K* were obtained from the data shown in Figure 5 to be 1 and 17.8 dm^6 mol^{-2}, respectively. On the other

hand, when the reversed micelle was formed, some of the surfactants were present as the form of the monomer. Then, the equilibrium concentration of salt in the reversed micelle was obtained from the difference between the equilibrium salt concentration in the membrane phase and that of the dissolved salt complexed with the monomeric surfactant. The concentration of the salt complexed with the monomer was calculated by substituting the cmc value obtained by eq 1 for $[L_0]_m$, the values n and K obtained above, and the salt activity, [KSCN], into eq 6. The characteristic values for reversed micelle were obtained in the case of the carrier concentration of 0.11 mol dm^{-3} by the same method as that for the monomeric carrier, using eq 7. In the calculation, $[KSCN]_m$ was the equilibrium concentration of the salt in the reversed micelle. The values of n and K were obtained to be 1 and 39.6 dm^6 mol^{-2}, respectively, on the assumption that the equilibrium of the complexation of the reversed micellar carrier was independent of the complexation of the monomeric carrier.

The mole ratio of potassium thiocyanate to the carrier in the complex did not depend on the form of carrier in the membrane phase, but the stability constant of the reversed micellar complex was more than 2 times larger than that of the monomeric complex. It is known that a reversed micelle contains a water pool in the center, which has the specific water structure with a high proton-transfer rate.[20] In this reversed micelle, however, the water pool does not seem to provide a suitable hydrophilic field for the complexation because the mole ratio, n, was constant and only 1.

This was also supported by the dependence of the water content on the carrier form shown in Figure 2A. In the monomeric concentration range of 0−0.010 mol dm^{-3} of the carrier, the slope of water content was 3.1 mol per 1 mol of the carrier, while in the reversed micellar concentration range of 0.010−0.11 mol dm^{-3}, the slope was 1.7 mol per 1 mol of the carrier. The mole ratio of the water molecule to the carrier is dependent on the form of the carrier. The concentration ratio of potassium thiocyanate to the carrier can also be calculated by eq 6. At the carrier concentration of 0.11 mol dm^{-3} and the salt concentration of 0.1 mol dm^{-3}, the concentration ratio of the total potassium thiocyanate complexed with the reversed micellar carrier to the carrier in the membrane phase was 0.21 and that with the monomeric carrier was 0.10, while the mole ratio of the salt to the carrier was constant, 1. It is reported that water molecules were extracted by the derivatives of polyethylene glycols in an organic phase and metal ions were exchanged with the water molecules coordinated by the oxygen atoms of the polyethylene chain.[7] The amount of the water molecules decreased with the increase of the amount of the metal ions complexed with the derivatives. In the monomeric carrier, the surroundings were hydrophobic solvents and the salt with electric charge was less stable than the water molecule in the complex of the open-chain crown compound. In the reversed micelle, the carrier was aggregated to decrease the number of water molecules coordinated by the carrier but the potassium thiocyanate was extracted to be a stable form in the hydrophilic field formed in the inner part of the reversed micelle.

The solid line in Figure 5 shows the calculated total concentrations of the salt complexed with the monomeric and reversed micellar carrier in the membrane phase. The concentrations were obtained by eq 6 for the cases of the carrier concentrations of 0.0030, 0.012, and 0.11 mol dm^{-3}, and the calculated values agreed very well with the experimental values for each carrier concentration. In a very high source phase activity range, the equilibrium concentration was a little higher than the predicted values. This was caused by the following reasons: the surfactant can complex with more than one potassium ion after the saturation of the 1:1 complex of the surfactant with potassium ion because the surfactant has 20 ethylene oxide units and only 7 ethylene oxide units can complex with a potassium ion in a helical structure;[9] the liquid membrane phase turned out to be turbid in a high salt concentration range, which shows the emulsion formation, and the emulsion can contain much salt in its water phase. In a very low source phase activity range, the equilibrium concentration was also a little higher than the predicted values, which may be caused by the concentration of the salt free from the carrier in the membrane phase[13] ignored in eq 5.

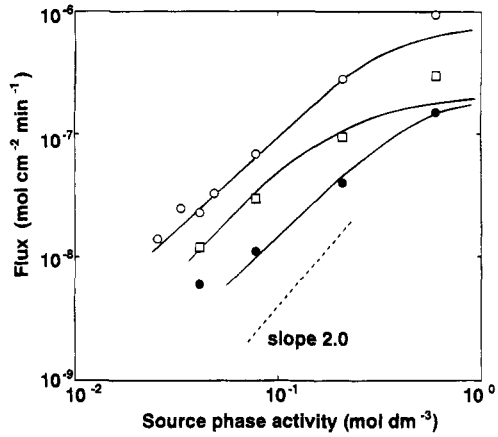

Figure 6. Effect of source phase activity on salt flux: source phase, 0.1 dm^3 of potassium thiocyanate; liquid membrane, 10 cm^3 of 0.0030 mol dm^{-3} (●), 0.012 mol dm^{-3} (□), or 0.11 mol dm^{-3} (○) polyoxyethylene p-nonylphenyl ether in 1,2-dichloroethane; receiving phase, 0.1 dm^3 of pure water; the solid line was the calculated value from eq 13.

Transport Rate Equation. Figure 6 shows the effect of the source phase activity on the flux. The flux increased with the increase of the activity. The permeation process of potassium thiocyanate across the membrane was composed of the reaction process and the diffusion process. In most of the studies on the liquid membrane, the diffusion process has been regarded as the rate-limiting step and the reaction rate of the complex formation of the carrier with salt has not been considered.[21] In this study, however, the reaction rate should be considered because the reaction rate was small, the membrane phase layer was thin, and the diffusion rate was fast for the fast circulating rate of the liquid membrane phase solution; the circulating rate of each solution was 15 cm^3 min^{-1}, which corresponds to 42 cm min^{-1} of the linear velocity in the cell. The diffusion resistance across the Visking dialysis membrane was small and can be ignored. Then, the flux can be derived as a function of the source phase salt and carrier activities as follows.

The rate constants, k_1 and k_{-1}, in the complex formation reaction can be defined as follows.

$$K^+_s + SCN^-_s + L_m \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} L{\cdot}KSCN_m \qquad (9)$$

At the interface of the membrane phase and the source phase, the salt flux can be described as the difference between complex formation and its destruction rates.

$$J = k_1[K^+]_s[SCN^-]_s[L]_{m,s} - k_{-1}[L{\cdot}KSCN]_{m,s} \qquad (10)$$

At the interface of the membrane phase and the receiving phase, the salt flux can be described as the difference between the destruction and the complex formation rates.

$$J = k_{-1}[L{\cdot}KSCN]_{m,r} - k_1[K^+]_r[SCN^-]_r[L]_{m,r} \qquad (11)$$

In both equations, the subscripts s and r mean the species in source phase and in receiving phase and the subscripts m,r and m,s mean the species in the membrane phase adjacent to the receiving phase or the source phase, respectively. The second term on the right side in eq 11 can be ignored, because $[K^+]_r$ and $[SCN^-]_r$ were very small at the initial period of the permeation experiment when the flux was measured.

The diffusion process can also be derived as follows by using the diffusion constant, D

$$J = \frac{D}{d}([L{\cdot}KSCN]_{m,s} - [L{\cdot}KSCN]_{m,r}) \quad (12)$$

where d was the thickness of the membrane layer in the dialysis cell, 3 mm. From these equations and eq 4, we can obtain the salt flux as a function of the activities of the source phase salt and the carrier as follows.

$$J = \frac{k_1[KSCN]_s^2[L_0]_m}{1 + (k_1[KSCN]_s^2 + k_{-1})(d/D + 1/k_{-1})} \quad (13)$$

The value of k_1 can be obtained experimentally, and the value of k_{-1} was calculated from the k_1 value and the complex formation constant, K, as $k_{-1} = k_1/K$. The value of k_1 was obtained by the extraction experiment. At the initial stage of the experiment when the complex in the membrane phase was very low, the destruction rate was negligible in eq 10 and the extraction rate can be described as follows.

$$J = k_1[KSCN]_s^2[L_0]_m \quad (14)$$

By the experiments with the carrier concentration of 0.0030 mol dm^{-3}, k_1 and k_{-1} for monomeric carrier were obtained to be 2.0×10^6 cm^7 mol^{-2} min^{-1} and 0.22 cm min^{-1}, respectively. When the carrier concentration is 0.11 mol dm^{-3}, the carrier at the cmc obtained by eq 1 functions as monomer and the rest functions as reversed micelle. On the assumption that the monomer and the reversed micelle functioned independently, the extraction rate by the reversed micelle can be obtained by the difference between the experimental value and the rate calculated for the monomer carrier, and k_1 and k_{-1} for the reversed micelle were obtained to be 1.3×10^5 cm^7 mol^{-2} min^{-1} and 6.8×10^{-3} cm min^{-1}, respectively. Then, $[L{\cdot}KSCN]_{m,s}$ and $[L{\cdot}KSCN]_{m,r}$ were calculated for each case from eqs 4, 10, and 11 and D was obtained by eq 12 to be 3.8×10^{-2} cm^2 min^{-1} for monomer and 1.1×10^{-2} cm^2 min^{-1} for reversed micelle. It is well-known that the diffusion coefficient is inversely proportional to the cube root molar mass in the case of the spherical macromolecules, while for a nonspherical particle the molar mass is smaller than the value calculated from the diffusion coefficient on the assumption of the spherical particle.[22] Then, the aggregated number of the spherical reversed micelle from the nonspherical monomers was estimated to be over 41.

The reaction rate constant of the reversed micellar complex was much smaller than that of the monomeric complex, although the stability constant of the reversed micellar complex was larger than that of the monomeric complex. The diffusion coefficient of the reversed micellar complex was also smaller than that of the monomeric complex. These differences were caused by the characteristics of the aggregated structure of the reversed micelle.

The theoretical fluxes were derived from substituting the characteristic values obtained above into eq 13. In the carrier concentration range of the reversed micelle, the flux should be estimated as the sum of the calculated fluxes for monomeric carrier and reversed micelle. Figure 6 shows the experimental values, and they agreed very well with the calculated values (solid line) except in the very high and very low salt activity ranges. The equation for the diffusion-limited process was derived from eq 6 as follows, when the salt concentration in the receiving phase was negligible.

$$J = \frac{D}{d}\frac{K[L_0]_m[KSCN]_s^2}{1 + K[KSCN]_s^2} \quad (15)$$

The diffusion coefficient was assumed to be 2.2×10^{-2} cm^2 min^{-1} for monomer and 8.2×10^{-4} cm^2 min^{-1} for reversed micelle, which were obtained by the measured ion flux for 0.10 mol dm^{-3} KSCN solution. The slope for the calculated values for the diffusion-limited process of both monomeric and reversed micelle complexes was 2 (dotted line), which was steeper than the slope of the measured values, and the diffusion coefficients were much smaller than those obtained in this study by considering not only the diffusion process but also the reaction process. In the very high salt activity range, the experimental values were larger than the solid line because of the emulsion formation, whereas in the very low salt activity range, the transport of the salt which was not mediated by the carrier was not negligible and the experimental values were also larger than the solid line. Microemulsion can be a carrier of the liquid membrane, although there existed a little selectivity for the ion transport.[23] The theoretical values of the fluxes and the extraction rates also can be obtained as a function of the carrier concentration by using eqs 13 and 14, and they agreed well with the experimental values in Figures 1 and 2. Then, the characteristic values obtained above are the self-consistent values.

Both the reaction rate constant and the diffusion coefficient decreased significantly with the change of the form from the monomer to the reversed micelle, and the increase of the flux with the increase of the concentrations of the source phase salt and the carrier was suppressed by the formation of the reversed micelle.

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