Critical Demicellization Concentration of Diethylammonium Perfluorononanoate and Diethylammonium Tetradecyl Sulfate Mixture in Aqueous Solution

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The micellar pseudophase diagram of diethylammonium perfluorononanoate (DEAPFN) and diethylammonium tetradecyl sulfate (DEATS) was determined by both conductivity and fluorescence probe methods. The conductivity measurements gave unusually low dissociation degrees of counter ion for DEAPFN-rich regions in contrast to those for DEATS-rich region. The micelles in a DEAPFN-rich region have high microviscosities, suggesting a micellar growth. The existence of the second cmc indicated the presence of two types of mixed micelles, but the mutual solubility of fluorocarbon and hydrocarbon surfactants in micellar pseudophase showed significant differences between DEAPFN–DEATS and LiPFN–LiTS systems. Third inflection points on both conductivity and fluorescence intensity curves were observed for DEAPFN–DEATS system. This suggests the presence of a critical demicellization concentration (CDC).

The characteristics of mixed micelles composed of fluorocarbon and hydrocarbon surfactants have been studied.[1—8] The mixtures form two types of micelles; one rich in the fluorocarbon surfactant, the other rich in the hydrocarbon surfactant. Mysels predicted the presence of a critical demicellization concentration (CDC) if two micelles of limited mutual solubility form and if the mole fraction of one surfactant is higher in both micelles than in the system as a whole.[9] There are only a few findings of this behavior, because in most mixed systems the fluorocarbon and hydrocarbon surfactants did not satisfy the latter requirement.[10,11] Therefore, we have attempted to enhance the apparent mutual solubility in a micelle by the micellar growth with an intramicellar phase separation. That is to say, the fluorocarbon and hydrocarbon surfactants would each form islands in a large mixed micelle.

In this paper, the micellar miscibilities of fluorocarbon and hydrocarbon surfactants were evaluated by the micellar pseudophase diagrams. We shall give much attention to the influence of diethylammonium ion on the micellar miscibility and the presence of the CDC. The mixture cmc's were determined by both conductivity and fluorescence probe methods and were simulated by the group contribution method which included the contribution of diethylammonium group. The second cmc and CDC were also evaluated by both conductivity and fluorescence probe methods and were compared with the curves calculated for a hypothetical pseudophase separation. The micellar growth was evaluated by ^{1}H NMR line width of methylene signal and by the microviscosity sensed by auramine fluorescence.

Experimental

Materials. Fluorocarbon surfactants were prepared from perfluorononanoic acid (AG-118, Asahi Glass Co.) which had been recrystallized three times from carbon tetrachloride. The acids were neutralized with a methanol solution of lithium hydroxide. After the evaporation of methanol, the salts were recrystallized twice from a carbon tetrachloride–acetone (5 : 1) mixture. Diethylammonium perfluorononanoate (DEAPFN) was obtained by neutralizing the corresponding acid with a diethyl ether solution of diethylamine. The salts were recrystallized twice from a carbon tetrachloride–acetone (10 : 1) mixture.

Hydrocarbon surfactants was prepared from 1-tetradecanol (Tokyo Kasei Kogyo Co., Ltd.) by sulfation with chlorosulfonic acid in diethyl ether according to the procedure reported previously.[6] Lithium tetradecyl sulfate (LiTS) was recrystallized three times from a ethanol–water (6 : 1) mixture. Diethylammonium tetradecyl sulfate (DEATS) was recrystallized twice from a diethyl ether–acetone (2 : 1) mixture. Then, a diethyl ether–acetone mixture solution of the products was placed on Kiezel gel-60 (for column chromatography, Merck). The eluted solution was evaporated and the dried compound was recrystallized twice from acetone. All surfactants were dried over P_2O_5 in vacuo at room temperature. The melting points of $C_8F_{17}COOLi$ (LiPFN), $[NH_2(C_2H_5)_2]C_8F_{17}COO$ (DEAPFN), and $[NH_2(C_2H_5)_2]$-$C_{14}H_{29}SO_4$ (DEATS) were 244, 53, and 50 °C, respectively.

Ammonium 1-anilinonaphthalene-8-sulfonate ($C_{16}H_{16}N_2O_3S$, ANS, Wako Pure Chemical Ind., Ltd.) and auramine

($C_{17}H_{21}N_3$·HCl, Kanto Chemical Co., Inc.) were used as received. The reagents were of guaranteed grade.

Measurements.[6] Conductivity measurements were performed by using a conductivity meter MODEL CM-20E (Toa Electronics Ltd.). Fluorescence spectra of probes (ANS and auramine) were recorded on a Hitachi F-3010 fluorescence spectrometer. The probes were prepared as 6.3×10^{-5} M ANS and 1.0×10^{-5} M auramine in experimental conditions similar to those reported previously (1 M=1 mol dm^{-3}). The emission peaks of ANS and auramine were observed at 490 and 500 nm, with excitation at 385 and 440 nm, respectively. The emission peaks of ANS were shifted with the polarity of solvent. All experiments were performed at 25 °C. NMR spectra were obtained with a JEOL FX100S spectrometer by using freshly prepared surfactant solutions in D_2O (99.75%, Merck). The external reference for ^{1}H NMR was a D_2O solution of 2.5% sodium 2,2-dimethyl-2-silapentane-5-sulfonate contained in a coaxial capillary inside a 5 mm tube. The chemical shift of the long methylene chain signal was measured from an external reference signal.

Results and Discussion

The conductivities of surfactant aqueous solutions were measured at 25 °C to determine their cmc's. Figure 1 shows the conductivity curves of DEAPFN, DEATS, and their mixture at fixed composition $\alpha=0.85$ (α: mole fraction of DEAPFN in mixture). The cmc's of DEAPFN, LiPFN, DEATS, and LiTS were 3.0, 11.0, 1.0, and 2.2 mM, respectively; that is, the cmc of DEAPFN significantly decreased with the introduction of diethylammonium ion, in contrast to LiPFN. The mixture cmc at $\alpha=0.85$ was higher than the single surfactants systems. This means immiscibility between DEAPFN and DEATS in the micellar pseudophase. The slope of the conductivity curve of DEAPFN above cmc was much smaller than that of DEATS, which suggests preferential binding of diethylammonium ion to perfluorononanoate micelles.[12] The introduction of hydrophobic counter ion such as dimethylammonium to perfluoroalkanoate gave a micellar growth with a high counter ion binding of micelles.[13] Reeves et al. demonstrated by NMR method that dimethylammonium ion has more ability to penetrate and build structure in the electrical double layer interface than ammonium and tetramethylammonium ions.[14] It is suggested that the ammonium ion is hydrophilic and the tetramethylammonium ion is too bulky to penetrate into micellar surface. We expected that the diethylammonium ion could penetrate into the surface and hydrophobic regions of micelles.

The conductivity data of DEAPFN–DEATS mixtures are shown in Fig. 2, together with the differential conductivity of the equimolar mixture. The slopes of conductivity curves of DEAPFN-rich mixtures ($\alpha=0.8$—0.95) were much smaller than those of DEATS-rich mixtures ($\alpha=0.2$—0.7). The errors for the slopes of conductivity curves were less than ±0.6 S cm^2 mol^{-1}, as estimated by least-squares method. The differential conductivity curve indicated the three abrupt changes in the equimolar surfactant mixture. Similar behavior was observed in the region of $\alpha=0.5$—0.7. The $\Delta\kappa/\Delta C$ curve first shows an abrupt decrease in the mixture cmc, and then changed at the so-called second cmc well beyond the mixture cmc. Then, the $\Delta\kappa/\Delta C$ curve showed a third sudden drop, followed by a constant value. This

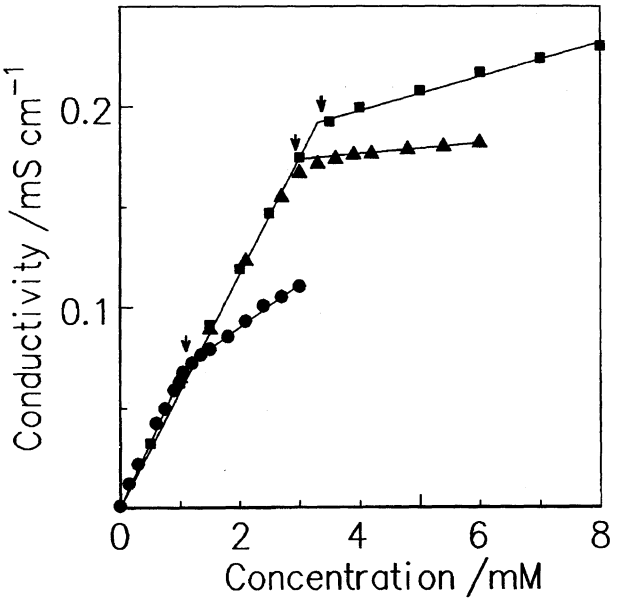

Fig. 1. The specific conductivity with the total concentration of DEAPFN, DEATS, and their mixture. α stands for the mole fraction of DEAPFN in mixture: (●) DEATS, (▲) DEAPFN, (■) $\alpha=0.85$.

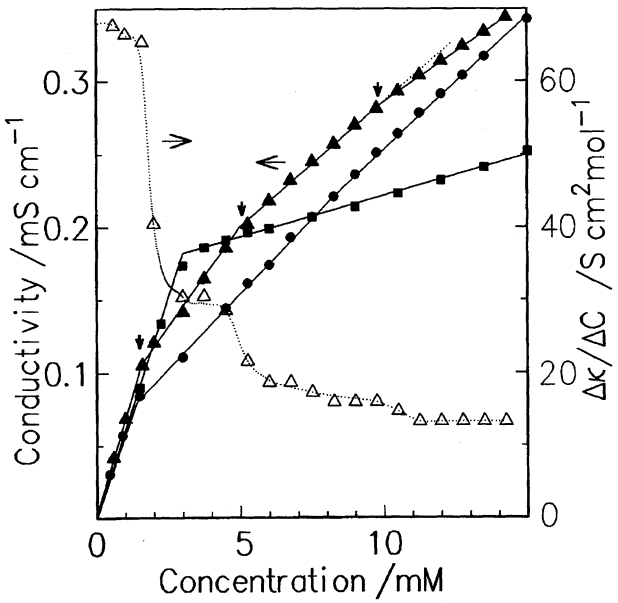

Fig. 2. The specific conductivity with the total concentration of DEAPFN–DEATS mixtures: (●) $\alpha=0.2$, (▲) $\alpha=0.5$, (■) $\alpha=0.9$, (△) differential conductivity at $\alpha=0.5$.

behavior can be explained as follows. At this composition, the DEATS-rich micelles form first at the mixture cmc because of the low cmc of DEATS. As the total concentration increases at fixed composition, the monomer concentrations of DEAPFN increase and become high enough at second cmc to form other micelles which are composed of DEAPFN. Above the third inflection point, the size, shape and/or composition of mixed micelles may change due to an unusually high counter ion binding of micelles.

The miscibility of fluorocarbon and hydrocarbon surfactants would be affected by the nature of the counter ion. First we evaluated the micellar miscibility of DEAPFN–DEATS and LiPFN–LiTS systems by the mixture cmc curves (Fig. 3). The mixture cmc curves were well simulated by a group contribution method, which suggested the presence of two types of mixed micelles.[15] The predicted pseudophase separation regions were $\alpha=0.19$—0.95 for LiPFN–LiTS and $\alpha=0.22$—0.91 for DEAPFN–DEATS, respectively. The mutual solubility of fluorocarbon and hydrocarbon surfactants was slightly enhanced by the introduction of diethylammonium group because of the penetration of diethylammonium group into micellar surface and hydrophobic regions. The limited mutual solubility would change with both the nature and concentration of counter ion.

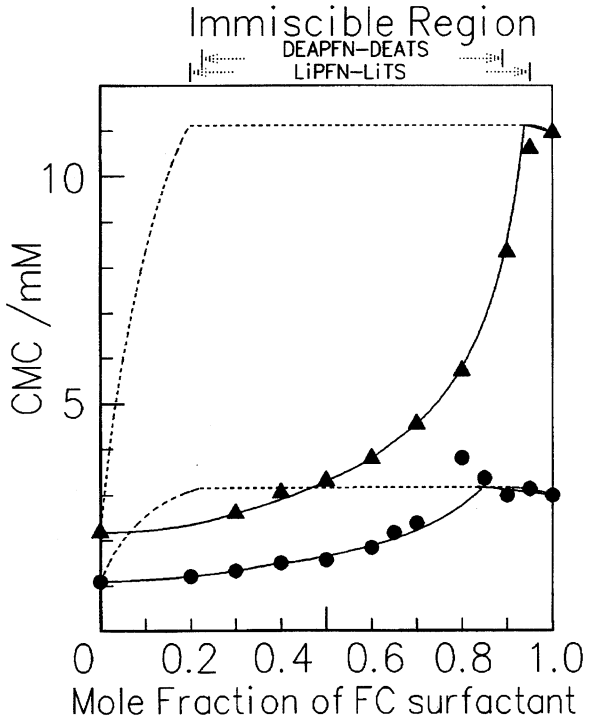

Fig. 3. Comparison of mixture cmc's of DEAPFN–DEATS and LiPFN–LiTS. The plotted points are experimental values. The solid line and the dotted line are the cmc curves and the micellar composition curves, respectively, from the group contribution method: (●) DEAPFN–DEATS, (▲) LiPFN–LiTS.

The hydrophobic probe, ammonium 1-anilinonaphthalene-8-sulfonate, was used to determine the formation of hydrocarbon-rich micelles, which was accompanied by an abrupt increase in fluorescence intensity and a shift of emission peak.[6] Figure 4 shows the variation of fluorescence intensity in single surfactant systems as a function of the surfactant concentration. The intensity in water (I_0) was used as a standard. The intensity increased above the cmc's with increase in the surfactant concentrations, while the intensity in both LiPFN and DEAPFN increased very little above the cmc's. The DEATS micelles became more hydrophobic with the introduction of diethylammonium group. However, the fluorocarbon micelles would have far less hydrophobic environment suggesting an appreciable water contact around the solubilization site of ANS.[6]

The fluorescence probe method was utilized to confirm the presence of the third inflection point. Figure 5 shows the variation of fluorescence intensity in mixed systems as a function of hydrocarbon surfactant concentration. The intensity increased above the mixture cmc's with increase in the hydrocarbon surfactant concentrations, corresponding to the formation of hydrocarbon-rich micelles. Moreover, the intensities of mixtures were increased compared with the intensities for pure hydrocarbon surfactants. This suggests that pure hydrocarbon micelles do not form in a mixed system, i.e., the hydrocarbon-rich micelles solubilize fluorocarbon surfactants to a certain extent, resulting in more

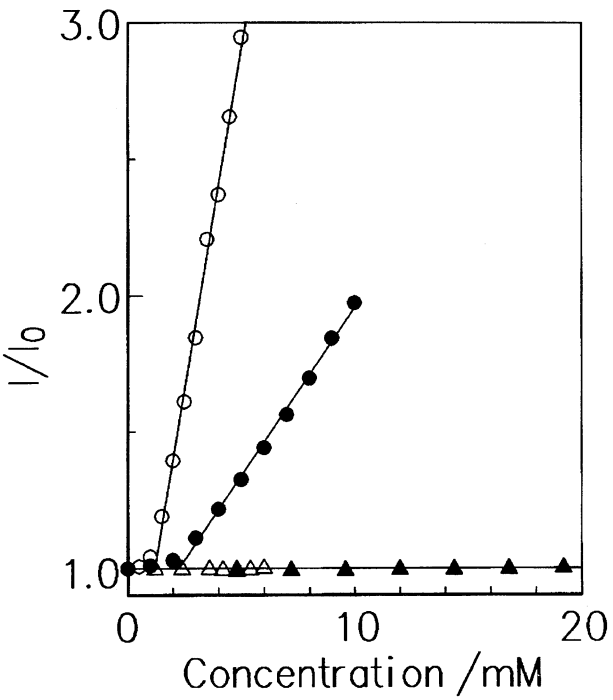

Fig. 4. The relative fluorescence intensity of ANS with surfactant concentration of single surfactant systems. I_0 is the fluorescence intensity in water. (○) DEATS, (△) DEAPFN, (●) LiTS, (▲) LiPFN.

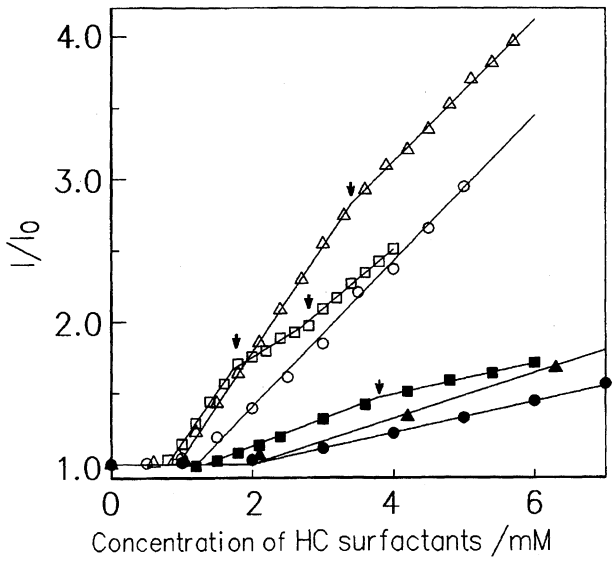

Fig. 5. The relative fluorescence intensity of ANS with concentration of hydrocarbon surfactant at fixed compositions for DEAPFN–DEATS and LiPFN–LiTS mixtures. (○) DEATS, (△) α=0.4, (□) α=0.6 for DEAPFN–DEATS, (●) LiTS, (▲) α=0.3, (■) α=0.7 for LiPFN–LiTS.

hydrophobic micelles. At α=0.4 for DEAPFN–DEATS, the DEATS-rich micelles form first at mixture cmc and then the DEAPFN-rich micelles form beyond the second inflection point. The third inflection point was observed at α=0.6 for DEAPFN–DEATS.

Next, we examined the influence of counter ion on the microviscosity of micelles. Figure 6 shows the variation of fluorescence intensity of auramine with the mole fraction of fluorocarbon surfactant at fixed total surfactant concentration. The intensity in water (I_0) was used as a standard. The dependence of fluorescence intensity of auramine on solvent has been shown to be sensitive to the viscosity of the probe's environment but not to the polarity.[16,17] The microviscosity in the solubilization site of auramine for DEAPFN micelles was much higher than that for DEATS and LiPFN micelles. Auramine would be solubilized in the anionic micellar surface due to the cationic group. The DEAPFN micelles would form a compact micellar surface in a large micellar size due to the unusually high counter ion binding of micelles. Abrupt increases in microviscosity of DEAPFN–DEATS mixtures were observed in the region of α=0.5—1.0. Therefore, the mixed micelles rich in DEAPFN would give a larger size at higher concentrations above the third inflection point (see Fig. 9).

The dissolution characteristics of surfactants have often been investigated by the changes in chemical shift of methylene signal.[18,19] Figure 7 shows the variation of chemical shifts and line width of the long methylene chain signal of DEATS molecule with the mole fraction of DEAPFN in 10 mM DEAPFN–DEATS mixture. Generally, the chemical shift changes are caused

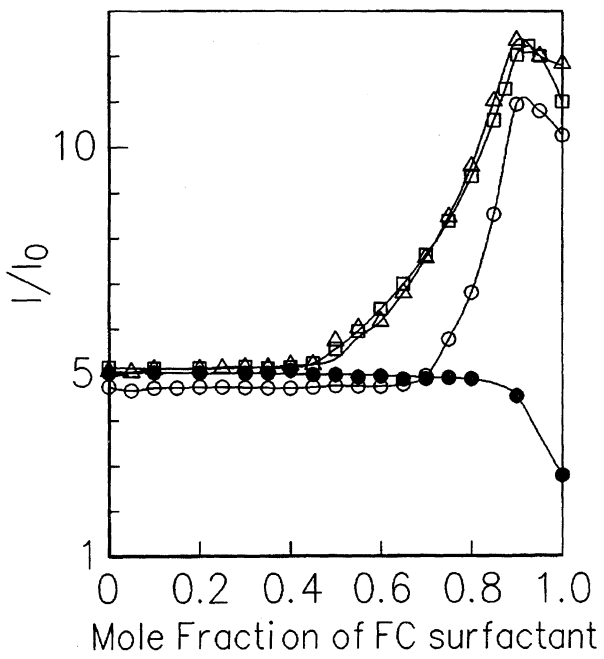

Fig. 6. Comparison of auramine fluorescence intensity of DEAPFN–DEATS and LiPFN–LiTS mixtures. I_0 is the fluorescence intensity in water. (○) 5 mM DEAPFN–DEATS, (△) 8 mM DEAPFN–DEATS, (□) 15 mM DEAPFN–DEATS, (●) 15 mM LiPFN–LiTS.

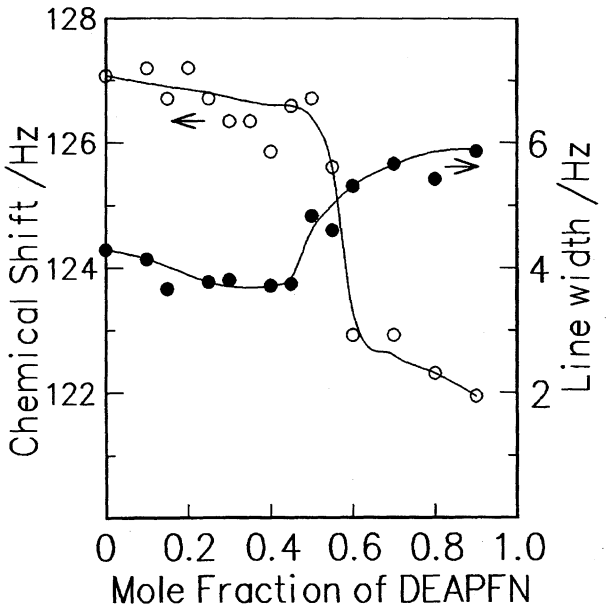

Fig. 7. Chemical shift and line width of long methylene chain signal with the mole fraction of DEAPFN in 10 mM DEAPFN–DEATS mixtures. (○) chemical shift, (●) line width.

by the changes in polarity and/or conformation. The abrupt drop of chemical shift around α=0.5 suggests the significant changes in micellar structure with the high microviscosity.

The presence of large micelles has been known to

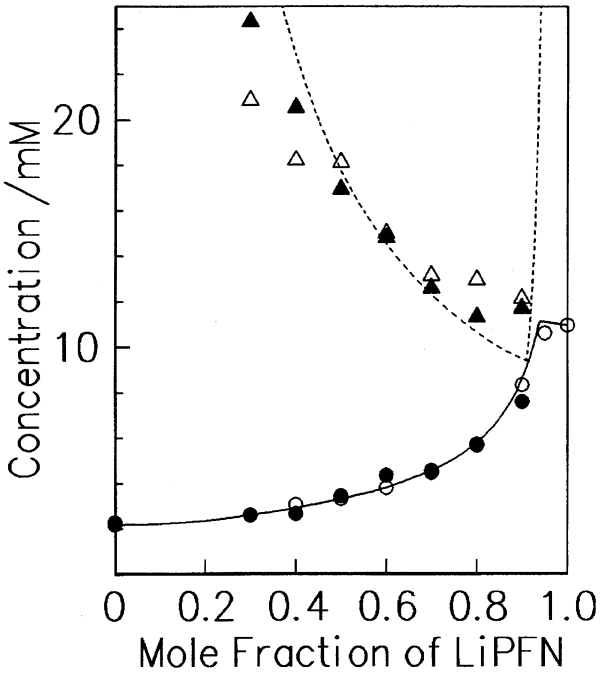

Fig. 8. The micellar pseudophase diagram of LiPFN–LiTS mixture. The dashed lines are calculated second cmc curves by material balances with $X_H=0.05$, $X_F=0.95$, $X_{AZ}=0.90$, and $C_{AZ}=9.4$ mM. X_H and X_F are the composition of LiPFN in fluorocarbon-rich and hydrocarbon-rich micelles, respectively.: (○) mixture cmc's by conductivity method, (●) mixture cmc's by ANS fluorescence method, (△) second cmc's by conductivity method, (▲) second cmc's by ANS fluorescence method.

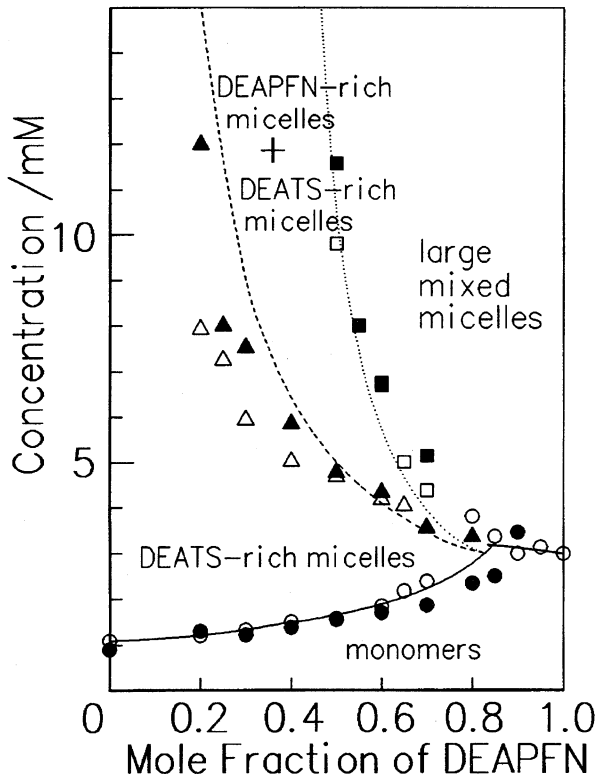

Fig. 9. The micellar pseudophase diagram of DEAPFN–DEATS mixture. The dashed line is calculated second cmc curve by material balances with $X_H=0.05$, $X_{AZ}=0.83$, and $C_{AZ}=3.0$ mM. The dotted line is calculated curve by Eqs. 5 and 6 with $\sigma_1=0.57$, $\sigma_2=0.80$, $X_{AZ}=0.83$, and $C_{AZ}=3.0$ mM: (○) mixture cmc's by conductivity method, (●) mixture cmc's by ANS fluorescence method, (△) second cmc's by conductivity method, (▲) second cmc's by ANS fluorescence method. (□) third inflection points of conductivity curves, (■) third inflection points of ANS fluorescence intensity curves.

give broad NMR signals, owing to the decrease in magnetic relaxation of the surfactant molecules.[20,21] The increase in NMR line width between $\alpha=0.5$ and 0.9 corresponds to an increase in the micellar size, because the abrupt signal broadening could be explained by sphere-rod transition. Both the microviscosity and NMR data indicated the micellar growth at $\alpha=0.5$—0.9. Burkitt et al. observed micellar growth by mixing perfluorooctanoate and decanoate.[22] Such a micellar growth by mixing surfactants was also observed for lithium perfluoro-1-octanesulfonate and lithium dodecyl sulfate in 1.2 M LiCl.[23] The ordered packing of surfactant in micelles may be induced by high counter ion binding and the incorporation of rigid fluorocarbon chains. The increased packing would give rise to growth in micellar size. The segregation between fluorocarbon and hydrocarbon surfactants would occur while minimizing the interfacial area between the two hydrophobic chains. The micellar composition would be affected by such a condition.

Above the second cmc, two types of mixed micelles form with limited mutual solubility. Above the third inflection point, the micellar growth would enhance the solubility of DEAPFN-rich micelles toward DEATS, resulting in the formation of large mixed micelles. That is, the third inflection points may correspond to the critical demicellization concentration (CDC). The mutual solubility in micelles would be increased by a favorable segregation between fluorocarbon and hydrocarbon chains with phobic interactions. Each of the two surfactants would form islands in a mixed micelle. In such a situation, a single kind of mixed micelles would exist, consisting of two different intramicellar sites. Kamogawa and Tajima already proposed plausible models of intramicellar phase separation.[24]

Based on the conductivity and ANS fluorescence data, the micellar pseudophase diagram of LiPFN–LiTS system is shown in Fig. 8. The LiTS-rich micelles first appear at mixture cmc's due to the low cmc of LiTS. As the total surfactant concentration increases, the monomeric LiPFN increases until the second cmc, at which the LiPFN-rich micelles appear. The observed second cmc's were simulated by the demixing of micelles as described previously.[12]

When the demixing of micelles occurs, the critical

concentrations can be given by material balance with the assumption of pseudophase separation micelles.[9] The total concentration of surfactant 1 can be given by

$$C_{1t} = \alpha C_t = C_{1m} + M_1 + S_1, \quad (1)$$

$$C_{1m} = x_1 C_1, \quad C_{2m} = x_2 C_2, \quad (2)$$

where C_t is the total concentration, α is the mole fraction of surfactant 1, C_{1m} is the monomer concentration of surfactant 1 (fluorocarbon), M_1 is that of micellized surfactant 1 in fluorocarbon-rich micelles, S_1 is that of surfactant 1 solubilized in hydrocarbon-rich micelles, x_1 is the micelle composition and C_1 is the cmc of surfactant 1. The subscripts 1 and 2 refer to surfactants 1 and 2.

The surfactant 2 (hydrocarbon) in fluorocarbon-rich micelle is in equilibrium with monomeric surfactant 2 in bulk water. The mole fraction of surfactant 2 in fluorocarbon-rich micelle can be related to the ratio C_{2m}/C_2. Hence,

$$x_1 = M_1/(M_1+S_2) = 1 - S_2/(M_1+S_2) = 1 - \sigma_2 C_{2m}/C_2, \quad (3)$$

where σ_2 is a proportionality constant. The same condition is set up for the micelle composition x_2 of hydrocarbon-rich micelles; that is,

$$x_2 = M_2/(M_2+S_2) = 1 - S_1/(M_2+S_1) = 1 - \sigma_1 C_{1m}/C_1. \quad (4)$$

When two types of mixed micelle coexist, the constant mole fraction of surfactant 1 in mixed micelles, X_{HF}, can be given by Eqs. 2, 3, and 4.

$$X_{HF} = (1-\sigma_2)/(1-\sigma_1\sigma_2), \quad (5)$$

that is, the micelle composition is independent of concentration and mole fraction above the second cmc.

One type of mixed micelles disappears at the CDC, hence, CDC can be given by a similar relation with the conditions of the second cmc.[12]

$$\mathrm{CDC} = C_{AZ}(X_{AZ} - X_{HF})/(\alpha - X_{HF}), \quad (6)$$

where C_{AZ} and X_{AZ} are the concentration and composition of surfactant 1 in azeotropic condition. The third inflection points of DEAPFN–DEATS can be fitted by σ_1=0.57 and σ_2=0.80 resulting in X_{HF}=0.37, as shown in Fig. 9. This suggested that hydrocarbon-rich micelle significantly solubilized fluorocarbon surfactant above the third inflection point.

The micellar pseudophase diagram of DEAPFN–DEATS system (Fig. 9) can be interpreted as follows. The DEATS-rich micelles first appear at the left side of the cusp of the mixture cmc curve. Both DEAPFN-rich and DEATS-rich micelles coexist above the second cmc curve. As the total surfactant concentration increased further, one type of mixed micelles disappears due to the formation of large mixed micelles having a large solubilization capacity. The third inflection points can be fitted by X_{HF}=0.37, i.e., the formation of mixed micelles rich in DEATS surfactant. The presence of CDC was derived from the introduction of diethylammonium counter ion, which affected the mutual solubility in micelles and the micellar size due to the high counter ion binding of diethylammonium to micellar surface. The high counter ion binding would give access to the hydrophobic chains. Therefore, DEAPFN and DEATS would each form islands in one large mixed micelle due to the phobic interaction between fluorocarbon and hydrocarbon chains. The increase in mutual solubility with the intramicellar phase separation would result in the presence of CDC. On the other hand, LiPFN micelles would not cause such a significant intramicellar phase separation due to the small micellar size. The low mutual solubility of LiPFN and LiTS would result in the intermicellar phase separation.

Conclusion

The introduction of diethylammonium counter ion gave high microviscosity of perfluorononanoate micelles, suggesting a micellar growth. The micellar pseudophase diagram was affected by the counter ion, due to the change in cmc and micellar immiscibility. The third inflection points of conductivity curves can be explained by the presence of CDC. Above the CDC, the segregation in a large aggregate would be promoted with minimizing the interfacial area between fluorocarbon and hydrocarbon chains. Under such a condition, the mutual solubility of mixed micelles significantly enhanced in DEAPFN–DEATS system in contrast to the results for LiPFN–LiTS system.

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