

Solubilization of Octafluoronaphthalene by Mixed Micelles of Fluorocarbon and Hydrocarbon Surfactants in Aqueous Solutions

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ABSTRACT: Solubilization of octafluoronaphthalene (OFN) by fluorocarbon and hydrocarbon surfactants in aqueous solutions has been examined to investigate the effects of mixing surfactants and added salt. Diethylammonium perfluorononanoate (DEAPFN) micelles have the most solubilization power toward OFN. The difference in micellar solubilization power will be caused by the hydrophobicity of ionic groups and micellar size. Large positive synergistic effects on solubilization behavior were observed in the DEAPFN–diethylammonium tetradecyl sulfate mixed micellar systems. Solubilization of OFN depended on the concentrations of added salt and the aggregation number, that is, the micellar size.
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KEY WORDS: Added salt, diethylammonium perfluorononanoate, fluorocarbon and hydrocarbon surfactants, intrinsic viscosity, micellar growth, mixed micelles, mutual phobicity, octafluoronaphthalene, positive synergistic effect, solubilization.

Solubilization is an important phenomenon in many technical applications. A water-insoluble substance can be solubilized in a micellar aqueous solution because the micelle gives a hydrophobic environment. Solubilization behavior have been used to investigate the critical micelle concentration (CMC) of surfactant and micellar structure (1–3). Much of the literature focused on the location of a solubilize within the micelles (4–6). Previously, we investigated the solubilization of pyrene in aqueous lithium perfluorooctane sulfonate–lithium dodecyl sulfate (LiFOS–LiDS) mixed solutions (7). Solubilization power of LiFOS toward pyrene was extremely low because of the oil repellency of the fluorocarbon chain and the loosely packed micellar structure. However, the published information about solubilization of aromatic compound by fluorocarbon surfactants is sparse.

Recently, theoretical studies have been performed on the solubilization properties in nonideal mixed-surfactant solutions (8–11). Treiner *et al.* (11) found that the partition coefficient of 1-pentanol in fluorocarbon- and hydrocarbon-surfactant solutions had a maximum as a function of micellar com-

position. The regular solution theory was used to explain solubilization behavior of various mixtures of surfactants.

In this paper, we examine the solubilization power of fluorocarbon surfactants to investigate the properties of micelles and/or mixed micelles containing fluorocarbon surfactants. The dependence of solubility of octafluoronaphthalene on a surfactant's counterion was also investigated, which suggested the relationship between solubilization power and micellar size. The interactions between the solubilize and lipophobic fluorocarbon chains must be different from those between the solubilize and lipophilic hydrocarbon chains.

EXPERIMENTAL PROCEDURES

Materials. Lithium perfluorononanoate ($C_8F_{17}COOLi$, LiPFN), diethylammonium perfluorononanoate ($C_8F_{17}COONH_2(C_2H_5)_2$, DEAPFN), lithium perfluorooctanesulfonate ($C_8F_{17}SO_3Li$, LiFOS), lithium dodecylsulfate ($C_{12}H_{25}SO_4Li$, LiDS), lithium tetradecylsulfate ($C_{14}H_{29}SO_4Li$, LiTS), and diethylammonium tetradecylsulfate ($C_{14}H_{29}SO_4NH_2(C_2H_5)_2$, DEATS) were prepared by procedures similar to those reported previously (7). Octafluoronaphthalene ($C_{10}F_8$, OFN; Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan) and pyrene ($C_{16}H_{10}$; Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used as received. Cetylpyridinium chloride (CPC) was purified by repeated recrystallization from acetone/ethanol (4:1, vol/vol) mixture. The reagents were of guaranteed grade.

Measurements. Solubilization of OFN (pyrene) was performed by adding the solid sample to 2 mL surfactant solution in a test tube, sonicating for 1 h, and then shaking at 25°C for 12 h. After equilibrium was attained, the excess solid OFN remained in the test tube. The suspension was filtered through a Millipore filter of pore size 0.2 μm (W-13-2; TOSOH Co., Tokyo, Japan). Then the filtrate was accurately diluted more than fivefold with methanol to destroy the micelles. The absorption spectra of the diluted solution were measured to determine the solubility of OFN (pyrene). The molar extinction coefficients of OFN and pyrene in this water–methanol mixture were $\epsilon_{278} = 4.8 \times 10^3 \text{ L mol}^{-1}\text{cm}^{-1}$ and $\epsilon_{334} = 5.0 \times 10^3 \text{ L mol}^{-1}\text{cm}^{-1}$, respectively.

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Relative viscosity was measured at 25°C using an Ubbelohde-type capillary viscometer (Shibata Scientific Technology Ltd., Tokyo, Japan). Relative viscosity is given by $\eta_r = \rho t / \rho_0 t_0$, where t (t_0) is the flow time of surfactant solution (solvent), and ρ (ρ_0) is the density of solution (solvent). Density of solutions was measured by Ostwald pycnometers (Shibata Scientific Technology Ltd.) of 5 cm³ capacity.

The fluorescence spectra of pyrene were recorded by a Hitachi F-3010 spectrometer (Tokyo, Japan). The typical pyrene monomer spectra around 370 nm from dilute (10⁻⁶ M) pyrene solutions were observed by exciting at 334 nm. Fluorescence quenching of pyrene by cetylpyridinium chloride was used to determine the aggregation number of micelles. All experiments were performed at 25°C.

RESULTS AND DISCUSSION

The amount of a solubilize will depend on not only the CMC of surfactant and micellar size, but also on the nature of the fluorocarbon chain and the counterion. Figure 1 shows the solubility of OFN in aqueous surfactant solutions as a function of surfactant concentration. Solubilities of OFN increased above their CMC with increasing surfactant concentrations. OFN is a water-insoluble compound and can be solubilized into the hydrophobic region of micelles. The solubilization curve can be considered a linear dependence of solubilization on surfactant concentration. CMC determined by the solubilization method coincided with conductivity CMC. The difference of solubilization power between LiPFN and DEAPFN was very large compared with hydrocarbon surfactants. This suggests that the nature of micelles becomes

more hydrophobic by high micellar counterion binding of diethylammonium (12). Moreover, micellar growth must be induced by the diethylammonium ion. Kunieda and Shinoda (13) investigated the solubility of CCl₂FCClF₂ in aqueous solutions of perfluoroalkanoate having different counterions. They reported the dependence of the solubilization on the counterion and concluded that a well-balanced HLB may be essential for effective solubilization.

Measurements of solubilization of OFN or pyrene were performed at various mole fractions of DEAPFN-DEATS and LiPFN-LiTS. Solubilization power (S_a) is defined as

$$S_a = \frac{S - S_{\text{CMC}}}{C_t - \text{CMC}} \quad [1]$$

where S (S_{CMC}) is the concentration of solubilize in aqueous surfactant micellar (monomer) solution, C_t is the total surfactant concentration, and CMC is critical micelle concentration of mixed surfactant. Figure 2 shows the solubilization power toward OFN in aqueous mixed-surfactant solutions. S_a of LiPFN-LiTS mixed solutions was almost constant up to $X_F = 0.6$, whereas S_a of DEAPFN-DEATS mixed solutions had a maximum around $X_F = 0.8$. The large positive deviation from additivity may be ascribed to the structure of mixed micelles and micellar size. The increase in solubility of decane by surfactant mixture was observed for mixtures of anionic (sodium dodecylsulfate) and cationic (cetyltrimethylammonium chloride) surfactants (10). This behavior indi-

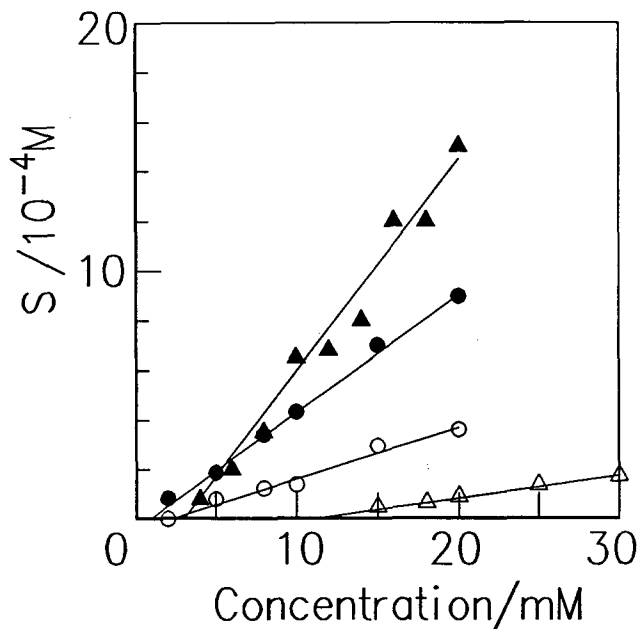


FIG. 1. Solubility of octafluoronaphthalene (OFN) against surfactant concentration in aqueous solutions: ○, lithium tetradecylsulfate (LiTS); △, lithium perfluorononanoate (LiPFN); ●, diethylammonium tetradecylsulfate (DEATS); ▲, diethylammonium perfluorononanoate (DEAPFN).

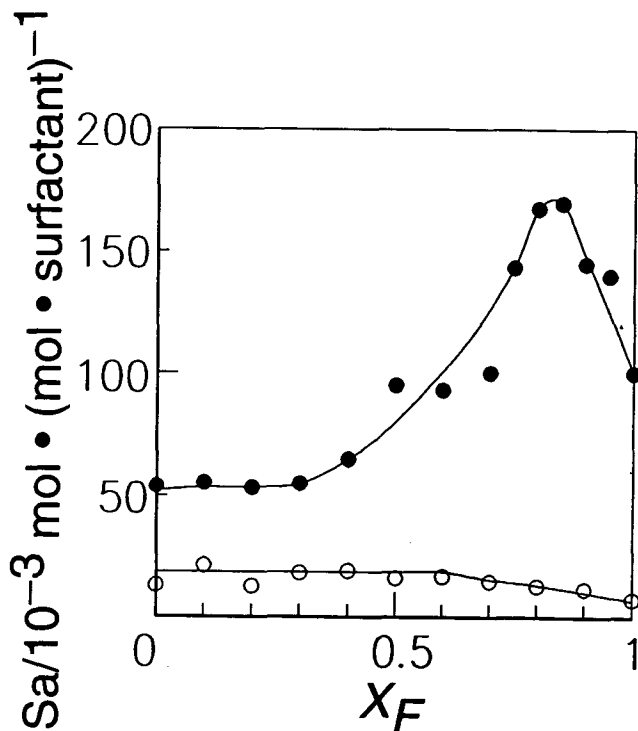


FIG. 2. Solubilization power of surfactant toward OFN as a function of the mole fraction of fluorocarbon surfactant (X_F) in mixed micellar solutions: ○, 20 mM LiPFN-LiTS; ●, 20 mM DEAPFN-DEATS. Abbreviations as in Figure 1.

cated a good correlation between the solubility of decane and the aggregation number.

Figure 3 shows the solubilization power toward pyrene in aqueous mixed-surfactant solutions. The negative deviations from the additivity were observed for both LiPFN-LiTS and DEAPFN-DEATS mixtures. The negative deviations would occur as a result of the interaction of pyrene with surfactant in mixed micelles. Water-insoluble pyrene solubilized into the palisade region of the micelles of hydrocarbon surfactant (14). However, fluorocarbon surfactants have a low solubilization power toward pyrene. Therefore the solubilization power of hydrocarbon surfactants decreased by incorporating fluorocarbon surfactants, which have a lipophobic nature. The reduction effect by the fluorocarbon chain would overcome the preferred solubilization effect by micellar growth, much like OFN for the DEAPFN-DEATS mixture.

Addition of salt is a very efficient method for increasing micellar size. The correlation between solubilization power and micellar size of fluorocarbon surfactants should be investigated in terms of the effects of added salt and surfactant mixture. Figure 4 shows the solubilization power of LiPFN, LiFOS, and LiDS micelles toward OFN as a function of LiCl concentration. Solubilization power increased with increasing LiCl concentration. However, inflection points were observed at LiCl concentrations of about 0.3, 1.0, and 1.0 M for LiPFN, LiFOS, and LiDS, respectively. Small micelles would have a loosely packed structure and a water penetration in the

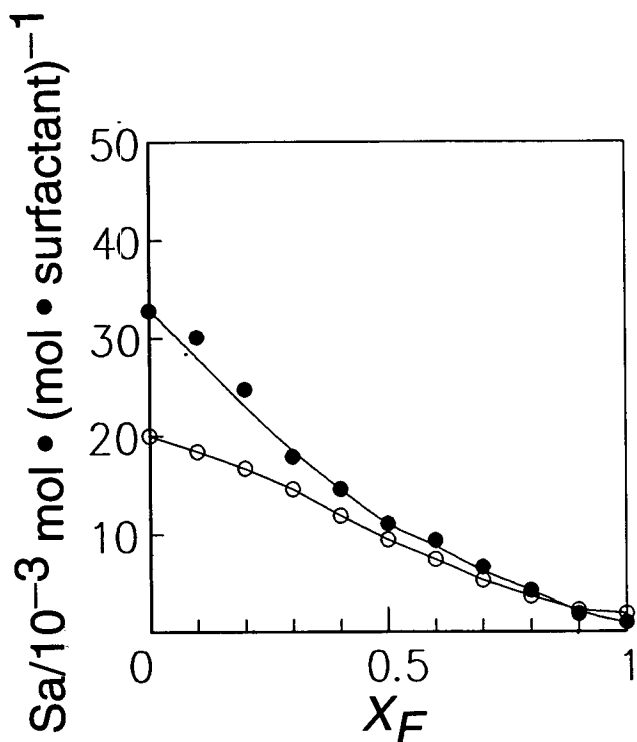


FIG. 3. Solubilization power of surfactant toward pyrene as a function of the mole fraction of the fluorocarbon surfactant (X_F) in mixed micellar solutions: ○, 20 mM LiPFN-LiTS; ●, 20 mM DEAPFN-DEATS. Abbreviations as in Figure 1.

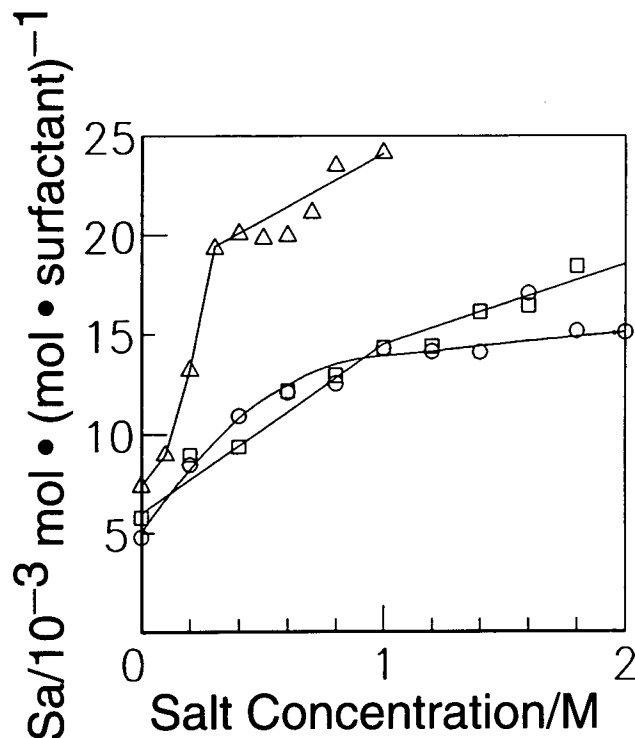


FIG. 4. Solubilization power of the surfactant toward OFN as a function of LiCl concentration in aqueous solutions: ○, 20 mM LiDS; △, 20 mM LiPFN; □, 20 mM LiFOS. Abbreviations as in Figure 1.

absence of salt. Bendedouch and Chen (15) reported that the aggregation numbers of LiDS increased with increasing LiCl concentration (63 in water, 109 in 1.0 M LiCl, 155 in 1.5 M LiCl). Solubilization power of LiDS micelles was proportional to its aggregation number with up to 1 M LiCl. Small angle neutron scattering measurements also indicated that the aggregation number of sodium perfluorooctanoate (SPFO) was 23; that is, the micellar size of SPFO was smaller than that of LiDS (16). SPFO micelles possessed a small, loose, and open structure (17). Head-group area per fluorocarbon surfactant would be larger than that of the hydrocarbon surfactant because of the small aggregation number and the bulkiness of the fluorocarbon chain. LiPFN micelles also have similar micellar characteristics to SPFO. The added salt for the solubilization power of LiPFN was effective probably due to the remarkable increase in aggregation number.

Light-scattering method has been used to determine micellar size. This method, however, is difficult for fluorocarbon surfactants because the refractive indexes of fluorocarbons are close to that of water. Therefore the salt-induced micellar growth was investigated by a viscosity measurement of aqueous surfactant solutions. Figure 5 shows the relative viscosity of LiPFN, LiFOS, and LiDS as a function of LiCl concentration. Viscosity of LiPFN solutions markedly increased at concentrations above 0.5 M LiCl. The measured intrinsic viscosities (η) of LiPFN were 2.7 cm³/g in 0.1 M LiCl and 16.3 cm³/g in 1.0 M LiCl, respectively. A spherical micelle would be formed in low LiCl concentration, while the size and shape

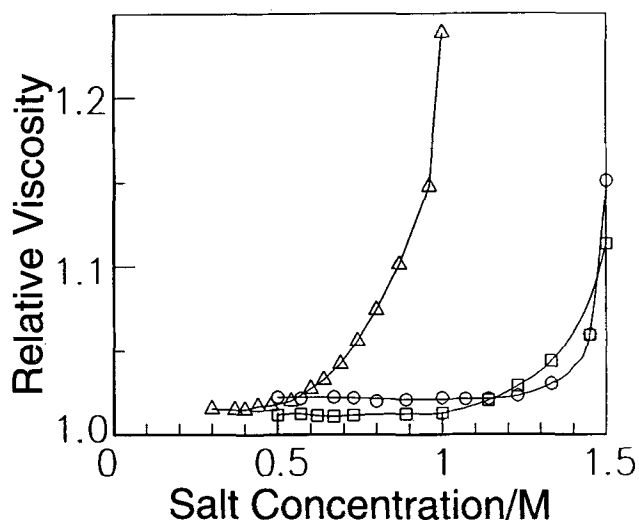


FIG. 5. Relative viscosity of aqueous surfactant solutions as a function of LiCl concentration: ○, 20 mM LiDS; △, 20 mM LiPFN; □, 20 mM LiFOS. Abbreviations as in Figure 1.

of LiPFN micelles in 1.0 M LiCl would depart from small, spherical micelles. Abrupt increases in viscosity were observed for LiFOS and LiDS solutions above 1.2 M LiCl. The measured intrinsic viscosities (η) of LiFOS and LiDS in 0.1–1.0 M LiCl were 2.5 and 4.2 cm³/g, respectively, while those of LiFOS and LiDS in 1.6 M LiCl were 12.0 and 5.0 cm³/g, respectively. Bendedouch and Chen (15) indicated that the LiDS micelles in aqueous LiCl solutions could be represented as a prolate ellipsoid according to small angle neutron scattering experiments. Thus the salt-induced increase in viscosity could be caused by the variation from sphere to ellipsoid. Such micellar growth induced the increase in the solubilization power of micelles. Solubilization power of spherical micelles would be proportional to micellar volume. Ozeki and Ikeda (18) reported that solubilization power of spherical micelles toward Sudan III increased with increasing micellar aggregation number, but solubilization power of rodlike micelles was independent of the micellar aggregation number. Sudan III would be only partly buried in the spherical micelle, while it is located deeper in the rodlike micelle. Solubilization power could be used to evaluate the sphere–rod transition.

The value of solubilization power of various surfactants toward OFN and pyrene is summarized in Table 1. The average numbers of solubilized OFN per a LiDS micelle were about 0.3 in water and 1.7 in 1.2 M LiCl, respectively. Added salt for solubilization power for OFN was more effective compared with that for pyrene. Solubilization power of LiFOS micelles toward OFN was comparable to that of LiDS micelles, whereas that of LiFOS micelles toward pyrene was remarkably small, even with the sufficient addition of LiCl. Thus low solubilization power of fluorocarbon micelles toward pyrene is due to mutual phobicity between the fluorocarbon chain and pyrene. Introduction of the diethylammonium ion induced the increase in solubilization power toward OFN, as seen in DEAPFN and DEATS micelles. Conversely,

TABLE 1
Solubilization Power of Various Fluorocarbon and Hydrocarbon Surfactants in Aqueous Solutions at 25°C^a

	Cs (M)	Critical micelle concentration (mM)	Sa (10 ⁻³ mol/mol surfactant)	
			OFN	Pyrene
C ₁₂ H ₂₅ SO ₄ Na (SDS)	0.0 0.5 ^b	8.1 0.57 ^d	4.3 12.1	13.6 18.8
C ₁₂ H ₂₅ SO ₄ Li (LiDS)	0.0 1.2 ^c	8.7 0.23 ^d	4.7 14.3	13.3 18.1
C ₈ F ₁₇ SO ₃ Li (LiFOS)	0.0 1.2 ^c	7.1 0.15 ^d	5.8 14.5	1.5 1.1
C ₈ F ₁₇ COOLi (LiPFN)	0.0 0.5 ^c	11.0 —	7.6 36.0	1.9 —
C ₈ F ₁₇ COONH ₂ (C ₂ H ₅) ₂ (DEAPFN)	0.0	3.0	98.9	1.0
C ₁₄ H ₂₉ SO ₄ Li (LiTS)	0.0	2.2	13.5	20.0
C ₁₄ H ₂₉ SO ₄ NH ₂ (C ₂ H ₅) ₂ (DEATS)	0.0	1.0	54.5	28.3

^aSDS, sodium dodecyl sulfate; OFN, octafluoronaphthalene. ^bNaCl. ^cLiCl. ^dDetermined by surface tension method.

the measured solubilization powers of LiPFN and DEAPFN toward naphthalene were 10.3 × 10⁻³ and 5.6 × 10⁻³ mole/ (mole surfactant), respectively. That is, solubilization power toward OFN increased by diethylammonium counterion, while the solubilization power toward naphthalene decreased by diethylammonium counterion. DEAPFN micelles would have a large, compact structure compared to LiPFN micelles due to high counterion binding of diethylammonium. Thus mutual phobicity between the fluorocarbon chain and naphthalene would reduce solubilization power.

As described above, solubilization behavior of OFN was sensitive to micellar sizes. Changes in micellar size and compactness of micelles can be attained by adding salts and mixing surfactants. Figure 6 shows solubilization power of LiFOS–LiDS mixed micelles in 1.2 M LiCl toward OFN and pyrene as a function of mole fraction of LiFOS. Solubilization power toward pyrene decreased with increasing mole fraction of LiFOS, while solubilization power toward OFN increased with increasing mole fraction of LiFOS up to $X_F = 0.6$. We reported micellar growth with mixing LiFOS and LiDS in 1.2 M LiCl by both self-diffusion coefficients and line-width measurements of methylene signal using Fourier transform-NMR (19). Negative deviation from additivity on solubilization power is due to the phobicity of the fluorocarbon chain for pyrene. However, the positive synergistic effect toward OFN occurs as a result of micellar growth by mixing surfactants. Segregation between fluorocarbon and hydrocarbon surfactants in micelles would occur and induce the increase in solubilization amount of OFN.

The steady-state fluorescence quenching method can be used to evaluate the surfactant aggregation number. The pair of pyrene (fluorescence probe) and cetylpyridinium chloride (CPC, quencher) has been used for various surfactant aggregates (20). The fluorescence intensity ratio (I/I_0) is given by

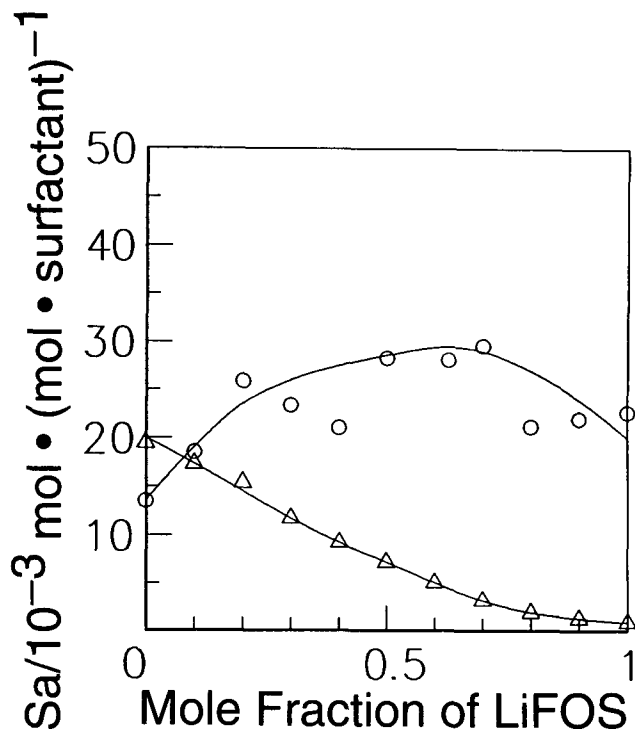


FIG. 6. Solubilization power as a function of the mole fraction of LiFOS (X_F) in 20 mM LiFOS-LiDS in the presence of 1.2 M LiCl: ○, OFN; △, pyrene. Abbreviations as in Figure 1.

$$\frac{I}{I_0} = \exp\left[-\frac{Q}{M}\right] \quad [2]$$

where I/I_0 is the fluorescence intensity of pyrene in the presence (absence) of CPC, Q is the concentration of CPC (quencher), and M is the micelle concentration. The plot of $\ln(I_0/I)$ vs. Q plot gave a linear dependence and the aggregation number of DEAPFN-DEATS mixed micelles. Figure 7 shows the dependence of aggregation numbers as a function of the mole fraction of DEAPFN at various fixed total-surfactant concentrations. The aggregation number remained almost constant up to $X_F = 0.3$, but it increased sharply at $X_F = 0.7 \sim 0.8$. The curve passed through a maximum at $X_F = 0.8$ of 20 mM DEAPFN-DEATS, similar to the solubilization power curve (Fig. 2). That is, solubilization power of mixed micelles toward OFN was markedly dependent on micellar size.

Thus solubilization power of fluorocarbon micelles toward aromatic compounds depends not only on micellar size but also on lipophobicity of the fluorocarbon chain. Solubilization behavior of OFN corresponded to micellar size and shape in contrast to that of pyrene. The large positive synergistic effect on solubilization of OFN was observed for DEAPFN-DEATS and LiFOS-LiDS in 1.2 M LiCl. The effect was interpreted from the micellar growth due to mixing surfactants. The decreased hydrophilic characteristics by diethylammonium counterion led to an increase in aggregation number, resulting in high solubilization power for perfluorinated aromatic compounds such as OFN.

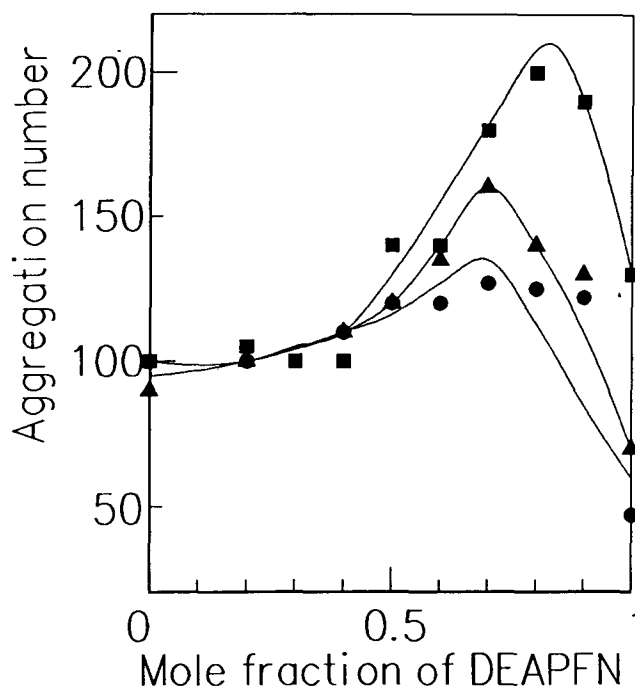


FIG. 7. Aggregation number of DEAPFN-DEATS mixed micelles as a function of the mole fraction of DEAPFN (X_F): ●, 7 mM; ▲, 10 mM; ■, 20 mM. Abbreviations as in Figure 1.

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