Association of Nonionic Polymer with Hydrocarbon/Fluorocarbon Surfactant in Aqueous Solution

Takahiko Nojima, Kunio Esumi and **Kenjiro Meguro***
Department of Applied Chemistry, Institute of Colloid and Interface Science, Science University of Tokyo, Tokyo 162, Japan

The interaction between a nonionic polymer and a hydrocarbon or fluorocarbon surfactant has been investigated by means of surface tension, viscosity, electroconductivity, fluorescence probing, solubilization of a water-insoluble dye, and electron spin resonance (ESR). The systems studied consisted of polyvinylpyrrolidone (PVP) with lithium dodecyl sulfate (LiDS) or lithium perfluorooctane sulfonate (LiFOS). Surface tension measurements indicated that formation of PVP-surfactant complex is more favorable in the PVP-LiFOS system than in the PVP-LiDS system, and that the adsorbed amount of LiFOS is less than that of LiDS, although the CMCs of the surfactants are almost the same. In the PVP-LiFOS system, the relative viscosity and the solubilized amount of a water-insoluble dye showed a maximum at a certain concentration of LiFOS in the region between two transitions observed in the surface tension, where also a change in the slope of the electroconductivity is observed. These results indicate that shielding of effective charge of the PVP-LiFOS complex causes a conformational change of PVP wrapped around the aggregate of LiFOS with an increase of free surfactant in the bulk phase. The conformational change can be correlated with microenvironmental properties of PVP-surfactant complexes. The microviscosity estimated with ESR indicated that the headgroups of LiFOS adsorbed on PVP are less tightly packed than those of LiFOS micelles, while an opposite result was obtained in the PVP-LiDS system. In particular, the marked high viscosity at a low concentration of LiFOS in the PVP-LiFOS system can probably be attributed to rigidity of the fluorocarbon chain of LiFOS.

KEY WORDS: Lithium dodecyl sulfate, lithium perfluorooctane sulfonate, microenvironmental property, PVP-perfluorinated surfactant, solubilization of dye.

There have been many studies on interactions between nonionic water-soluble polymers and surfactants (1–25). Aqueous solutions containing mixtures of polymers and surfactants have been used in a wide variety of industrial applications, including enhanced oil recovery (4). Apart from being industrially important, there is much interest in the morphology of micelle-polymer complexes and in the nature of interactions involved in the complexation process.

Several investigators discussed the models of complexation (5–8): among them, Ruckenstein *et al.* (7) considered that the presence of polymer molecules in water changes the microenvironment of the surfactant molecules and alters particularly the interfacial free energy between the hydrocarbon core of the micellar aggregate and the water located in the "free space" of the coiled macromolecules.

*To whom correspondence should be addressed at Department of Applied Chemistry, Institute of Colloid and Interface Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan.

Factors influencing polymer-surfactant association, such as temperature, salt, surfactant chainlength, polymer structure, hydrophobicity, and a variety of surfactants have been studied (9–25). It is especially interesting that synthetic polymers have a stronger interaction or complex more favorably with anionic surfactants in an aqueous solution than with cationic or nonionic surfactants (23–25). Furthermore, Chari *et al.* (5) compared the behavior of a single-chained surfactant, SDS, with a double-chained surfactant, Aerosol-OT, and found that basic structures of the complexes are the same in both cases; these surfactant molecules are assembled in a micelle-like aggregate and polymer molecules are wrapped around the aggregate, shielding hydrocarbon groups on the surface of the micelle from contact with water.

Although various hydrocarbon surfactants have been used in studies of interactions between polymers and surfactants, there are no reports about interactions between polymers and perfluorinated surfactants. Complexation of a fluorocarbon surfactant with polymer can be expected to be different from that of a hydrocarbon surfactant, because the fluorocarbon chain has hydrophobic and lipophobic properties (26–29).

In this work, solution properties of polyvinylpyrrolidone (PVP)-lithium dodecyl sulfate (LiDS) and PVP-lithium perfluorooctane sulfonate (LiFOS) systems have been studied by means of various techniques. We will discuss association of PVP with hydrocarbon or fluorocarbon surfactant in aqueous solutions.

EXPERIMENTAL PROCEDURES

Materials. Lithium dodecyl sulfate (LiDS) was synthesized from 1-dodecanol by sulfonation with chlorosulfonic acid, followed by neutralization with lithium hydroxide. After recrystallization from ethanol, this surfactant was purified by extraction with ether. Lithium perfluorooctane sulfonate (LiFOS) was synthesized and purified by a published method (26). These surfactants were confirmed to be highly pure by the absence of a minimum in the surface tension.

Polyvinylpyrrolidone (PVP, K-90), obtained from Tokyo Kasei Co., Ltd., was purified by dialysis, followed by freeze-drying. The viscosity-average molecular weight of PVP was 2×10^5.

Pyrene was obtained from Wako Pure Chemical Industries (Osaka, Japan) and purified by passing through silica gel in cyclohexane and evaporation of the solvent. Pyrene-1-carboxaldehyde (PCA) obtained from Aldrich (Milwaukee, WI) was used without further purification. α-(o-tolylazo)-β-naphthylamine (Yellow-OB), obtained from Tokyo Kasei Co., Ltd., was purified by repeated crystallization from ethanol. 2,2,6,6-Tetramethylpiperidinyl-1-oxy (TEMPO) and 7-(4′,4′-dimethyl-oxazolidinyl-N-oxy-stearic acid (7NS) were obtained from Aldrich and used as received.

Water used in this study was purified by passing it

through a Milli-Q System (Nihon Millipore Co., Tokyo, Japan) until its specific conductivity fell below 0.1 $\mu S\ cm^{-1}$.

Measurements. The surface tension was measured as a function of surfactant concentration with a Wilhelmy plate apparatus (Shimadzu ST-1, Kyoto, Japan).

The viscosity was measured with a Haake Rotovisco RV100 concentric-cylinder rotational viscometer, Karlsruhe, Germany. The coaxial cylinder sensor system ME-30 was used, equipped with an outer cylinder that was temperature-controlled. The shear stress τ was measured at each shear rate D, and the viscosity η (D) at shear rate D was obtained from the following equation:

$$\tau = \eta\ (D) \times D \qquad [1]$$

The relative viscosity η_{rel} is given by

$$\eta_{rel} = \eta\ (D)/\eta_0 \qquad [2]$$

where η_0 is the viscosity of the solvent and is independent of the shear rate D.

Conductivity measurements were carried out at various concentrations of LiFOS in the presence of PVP with a conductivity meter model CM-30ET of TOA Electronics Ltd., Tokyo, Japan.

The fluorescence spectra being emitted by solubilized fluorescence probes (pyrene, PCA) were recorded on a Hitachi 650-10S fluorescence spectrophotometer, Tokyo, Japan. The excitation wavelength of pyrene and PCA were 335 and 356 nm, respectively. The concentrations of pyrene and PCA were 1×10^{-6} and 1×10^{-5} mol dm^{-3}, respectively.

The solubilized amount of Yellow-OB was determined as follows. PVP-surfactant or surfactant solutions containing an excess amount of Yellow OB were exposed to ultrasonic waves for 20 min and then shaken for 48 hr in order to reach saturation. Then, these mixtures were filtrated and diluted with ethanol. The optical density of the solutions at maximal absorption was measured with a Hitachi 220A double beam ultraviolet (UV) spectrophotometer. The amounts of solubilized dye were determined from calibration curves.

The electron spin resonance (ESR) spectra were measured on a JEOL JES FE 3-X spectrometer (X-band) (Tokyo, Japan) at modulation frequency of 100 KHz. The spin probe concentrations were 1×10^{-4} mol dm^{-3}.

All measurements were carried out at 25°C.

RESULTS AND DISCUSSION

Surface tension. Figure 1(a) shows the effect of PVP on the surface tension of aqueous solutions of LiDS. Two transition points, which are breaking points in the surface tension-concentration curves, are seen in the presence of PVP; one is located below and the other above the CMC of LiDS. The first transition point, T_1, is considered to be a concentration where association of LiDS and PVP in the bulk phase begins. The second one, T_2, corresponds to a concentration in which PVP is saturated with LiDS for complex formation. At concentrations greater than T_2, the regular micelles of LiDS and PVP-LiDS complex coexist in the bulk phase. T_1 is constant, 1.4 mmol dm^{-3}, and the concentration is independent of the

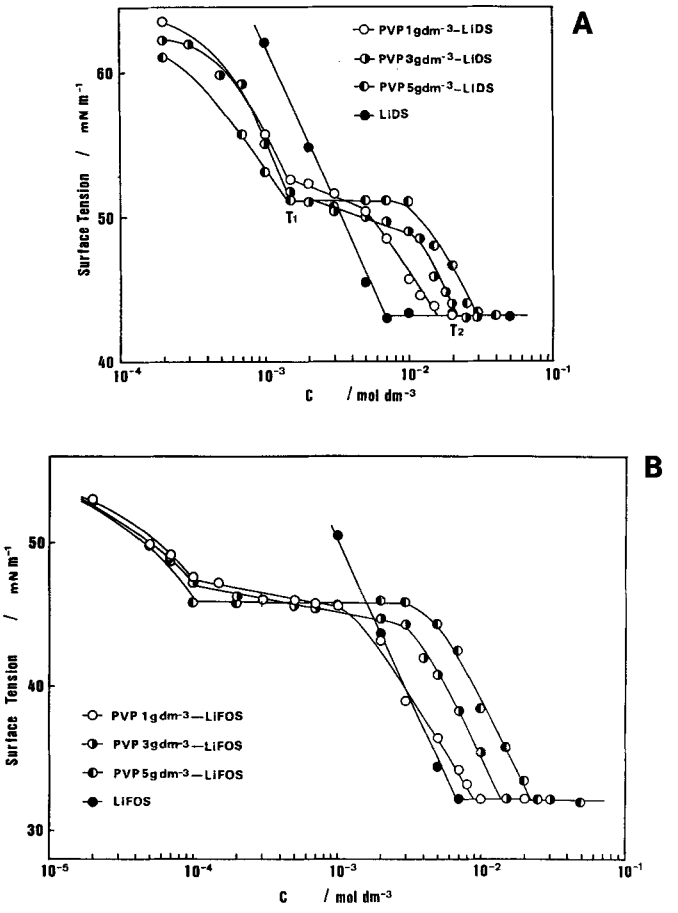

FIG. 1. Effect of PVP on surface tension of aqueous surfactant solutions: (a) PVP-LiDS system; (b) PVP-LiFOS system.

concentration of PVP. A similar result is obtained in the PVP-LiFOS system [Fig. 1(b)]. However, T_1 for the PVP-LiFOS system is 0.1 mmol dm^{-3}, which is considerably different from T_1 for the PVP-LiDS system, although the CMC of LiFOS is almost the same as that of LiDS. It would appear that PVP influences the behavior of aqueous solutions of LiFOS to a much greater extent than that of aqueous solutions of LiDS. The fact that T_1 for the PVP-LiFOS system is much lower than that for the PVP-LiDS system implies that the polymer-surfactant aggregate is a more favorable energy state for LiFOS than for LiDS. Furthermore, T_2 for the PVP-LiFOS system is also lower than that for the PVP-LiDS system when the concentration of PVP is changed, suggesting that the adsorbed amount of LiFOS to PVP is less than that of LiDS.

Viscosity. The variation of relative viscosity as a function of LiDS concentration in the PVP-LiDS system is shown in Fig. 2(a). The relative viscosity of aqueous solutions of LiDS containing PVP increases with increasing concentration of LiDS. Such an increase in the viscosity occurs in the vicinity of 1 mmol dm^{-3} of LiDS, which is T_1 for this system. This result clearly implies the conformational change of PVP associated with LiDS. Alternatively, the increase in the viscosity is due to an expansion of the polymer coils on association with the charged surfactant. In the PVP-LiFOS system [Fig. 2(b)] an increase in the relative viscosity occurs at a concentration

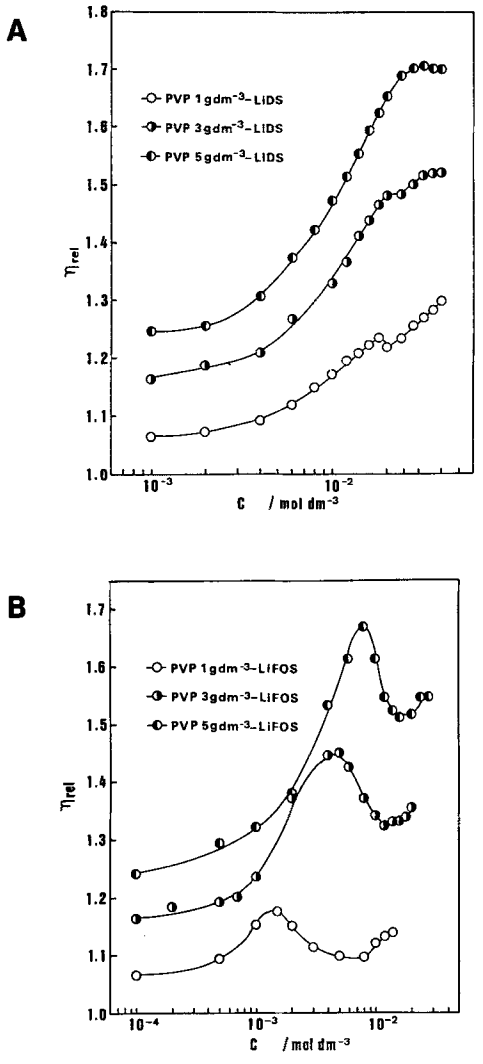

FIG. 2. Variation of relative viscosity in PVP-surfactant aqueous solutions: (a) PVP-LiDS system; (b) PVP-LiFOS system.

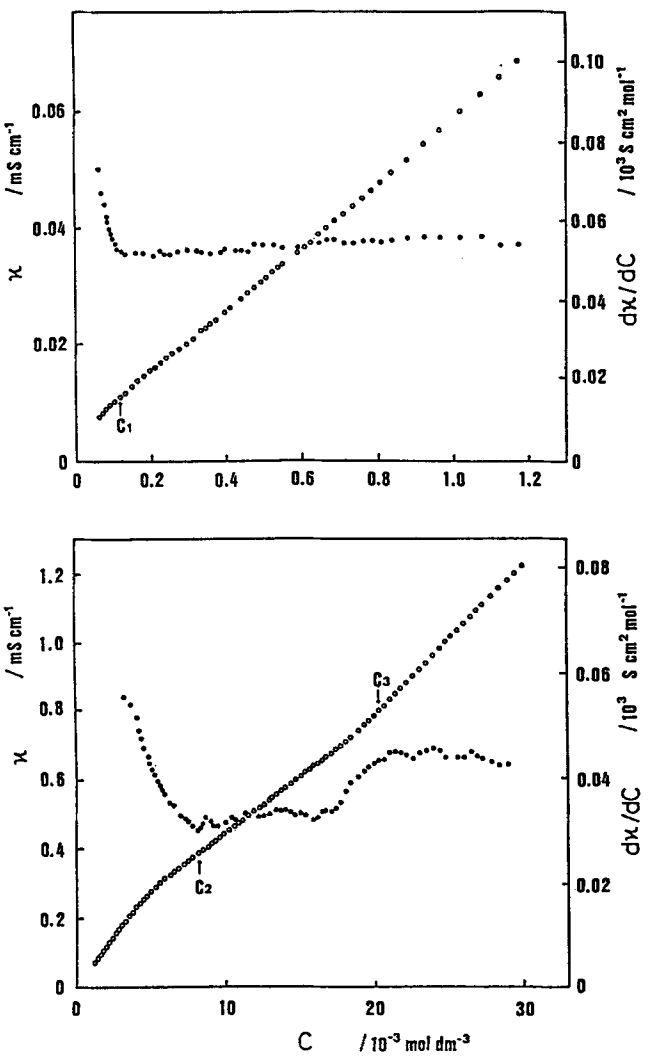

FIG. 3. Conductance variation of LiFOS-PVP (5g dm^{-3}) aqueous solutions as a function of LiFOS concentration.

near T_1, 0.1 mmol dm^{-3}, which is due to a combination of electrical charging and attendant conformational effects. However, in the PVP-LiFOS system, a significant change in the relative viscosity, which shows a maximum at a certain concentration of LiFOS, is recognized by comparison with the PVP-LiFOS system. A marked high viscosity at low concentration of LiFOS in this system can probably be attributed to a rigidity of the fluorocarbon chain of LiFOS.

Conductivity. A change in the conductance curves at three different LiFOS concentrations for a constant PVP concentration is observed in Fig. 3: $C_1 = 0.12$, $C_2 = 8.09$, and $C_3 = 21.05$ mmol dm^{-3}. C_1 and C_3 correspond to the beginning of LiFOS fixation on PVP chains, and to the saturation of PVP and the formation of LiFOS micelles in the bulk, respectively. Fig. 1(b) shows that the values of C_1 and C_3 are in good agreement with T_1 and T_2 obtained by the surface tension measurement. C_2 corresponds to a LiFOS concentration at which the relative viscosity shows a maximum. Consequently, it is assumed that in a region between C_1 and C_2, LiFOS molecules bind sensibly to PVP while maintaining a constant concentration of free LiFOS, which equals to C_1. In a region between C_2 and C_3, the concentration of free LiFOS is assumed to increase from C_1 to the CMC. In the latter region, a shielding of the effective charge of PVP-LiFOS complex causes the conformational change in PVP associated with LiFOS by increasing free LiFOS in the bulk. The conformational change probably causes the micellization of LiFOS that is adsorbed on PVP along its chain.

Polarity of PVP-surfactant complexes. The I_1/I_3 ratio of pyrene is sensitive to the polarity of the microenvironment at the site of solubilization of pyrene, where I_1 and I_3 are the first and third vibrational peaks of monomeric pyrene (30). The fluorescence probe method also provides information on the solubilization mechanism, because the site of solubilization of the probe can be inferred.

Figure 4 shows the variation of I_1/I_3 ratios of pyrene as a function of surfactant concentration in the PVP-LiDS and PVP-LiFOS systems. The I_1/I_3 ratios of pyrene in aqueous solutions of both surfactants containing PVP

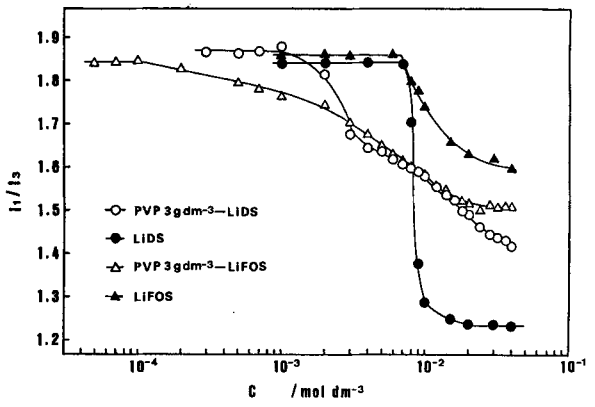

FIG. 4. Variation of I_1/I_3 ratio of pyrene in PVP-surfactant aqueous solutions.

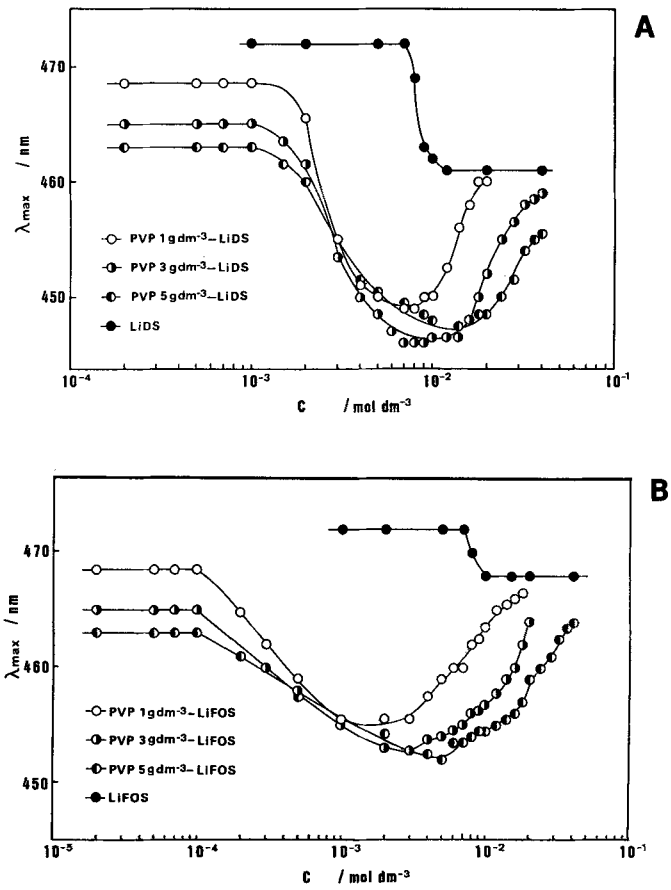

FIG. 5. Variation of λ_{max} of PCA in PVP-surfactant aqueous solution: (a) PVP-LiDS system; (b) PVP-LiFOS system.

decrease with the formation of PVP-surfactant complexes. However, the average microenvironmental polarity experienced by pyrene is in the order H_2O>LiFOS micelle>PVP-LiFOS complex>PVP-LiDS complex>LiDS micelle. Muto *et al.* (31) reported that pyrene must be solubilized at the LiFOS micelle surface, close to or between the sulfonate head groups, where it undergoes extensive contact with water. It is thus possible that the average microenvironmental polarity experienced by pyrene is in the order LiFOS micelle>PVP-LiFOS complex, provided that the main binding site of LiFOS on PVP is in the neighborhood of the headgroup of LiFOS. On the other hand, this experimental result suggests that either the interior of the micelle-like aggregate of LiDS adsorbed on PVP is loose and polar, or the pyrene solubilizes at a more external site in the PVP-LiDS complex than in the LiDS micelle. Actually, Turro *et al.* (32) reported that the average environmental polarity by pyrene is in the order PVP-SDS complex>SDS micelle.

The fluorescence of PCA monomer depends on solvent polarity as does pyrene (33). The maximum fluorescence wavelength, λ_{max}, significantly shifts to the region of higher wavelength with increasing solvent polarity, which has a linear relationship with solvent dielectric constant above 10. Owing to the effect of solvation in the region of the aldehyde group, it is suggested that PCA solubilizes in the micellar Stern layer and exists in a more external region in the micelle than pyrene. Figure 5(a) and 5(b) shows the variation of λ_{max} as a function of surfactant concentration in the PVP-LiDS and -LiFOS systems. The λ_{max} gradually shifts to the region of lower wavelength with an increase of PVP concentration, suggesting that PCA becomes solubilized in more hydrophobic environments. Molyneux *et al.* (34) have attempted to explain the binding of PVP to anionic solutes on the basis of resonance of the pyrrolidone ring. Chari and Lenhart (5) discussed that it is difficult to accept this argument because the size of the sulfate or sulfonate group is comparable to that of the pyrrolidone ring, and the main driving force for attachment is a hydrophobic effect. In aqueous solutions of surfactant containing a constant amount of PVP, λ_{max} shifts to the region of lower wavelength, followed by shifts to the region of higher wavelength. The former shift is due to the association of surfactant with PVP and the latter shift to the micellization of surfactant adsorbed on PVP. The degree of shift in λ_{max} for complexation is larger than that in regular micellization. This result indicates that the main binding sites of surfactant adsorbed on PVP are near the head of the surfactant.

Solubilization of water-insoluble dye. Figure 6(a) shows the solubilized amount of Yellow-OB as a function of LiDS concentration in the PVP-LiDS system. The PVP-LiDS system shows different solubilization behavior than an aqueous solution of LiDS alone. This phenomenon has been ascribed to the formation of a water-soluble complex whose solubilization power is different from that of either polymer or surfactant. Solubilization in the PVP-LiDS mixtures occurs in two different species: complexes and regular micelles. Saito (35) concluded that the action of bound surfactants in solubilization by the complexes is to give the polymers a more lyophilic character by replacing the water layer around the polymers with the surfactants and thus to promote contact between the polymers and the solubilizates. In the PVP-LiFOS system [Fig. 6(b)], the solubilized amount of Yellow-OB shows a maximum at a certain concentration of LiFOS. Since PVP or LiFOS alone hardly shows any solubilizing power, Yellow-OB is regarded to be soluble in the PVP-LiFOS complex, and a change in the solubilized amount of Yellow-OB is due to the formation and the conformational change in the PVP-LiFOS complex. It is also suggested that Yellow-OB is soluble at the adsorption site of LiFOS on

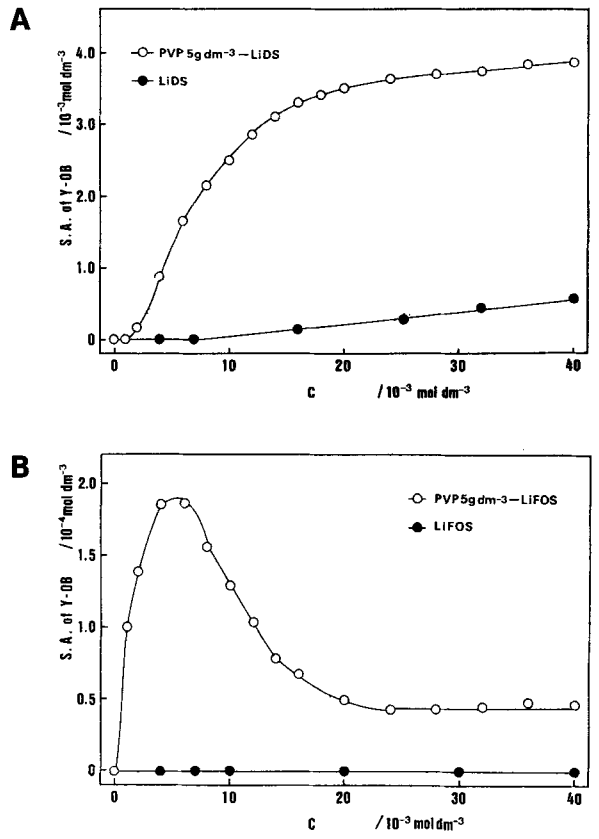

FIG. 6. Solubilized amount of Yellow-OB in PVP-surfactant aqueous solutions: (a) PVP-LiDS system; (b) PVP-LiFOS system.

PVP, and it is thus recognized that a change occurs in the condition of LiFOS adsorbed on PVP.

ESR. The ESR spectrum of TEMPO in water exhibits the usual three line pattern (A_N = 17.2 gauss), and is closely identical with that in the presence of surfactant, such as LiDS or LiFOS, below their CMCs. Above their CMCs, TEMPO is solubilized in the micelles as evidenced by broadening of the high-field line. However, a change in A_N, which can be correlated to the reduced micropolarity at the binding site in the micellar aggregates, is hardly observed. From the TEMPO data, the external microenvironment of micelle and polymer-surfactant complex can be estimated. Similarly, when TEMPO is solubilized into the PVP-LiDS complex and PVP-LiFOS complex, the A_N also shows a constant value (17.1~17.2 gauss), which can be compared to that in water. In fact, Ramachandran *et al.* (36) reported that most of the TEMPO solubilized in the micelles is located at the micelle-water interface. The relative anisotropy observed in an ESR spectrum is directly related to the rotational mobility of the probe, *i.e.*, a term that can be correlated with the microviscosity of the probe. The rotational correlation time (37) can be calculated from

$$\tau_c = 6.6 \times 10^{-10} W_{+1}((h_{-1}/h_{+1})^{1/2}-1) \text{ sec} \qquad [3]$$

where W_{+1} is the peak-to-peak line width of the low-field line (in gauss) and h_{-1} and h_{+1} are the peak-to-peak heights of the low- and high-field lines, respectively. In an aqueous solution of PVP (5g dm^{-3}) in the absence of LiDS or LiFOS, τ_c is hardly affected. Figure 7(a) shows the variation of rotational correlation time as a function of LiDS concentration in the PVP-LiDS system. In the absence of PVP, τ_c of TEMPO in aqueous solutions of LiDS increases above 7 mmol dm^{-3}, which corresponds to the CMC of LiDS. On the other hand, in aqueous solutions of LiDS containing PVP (5g dm^{-3}), τ_c increases with an increase of LiDS concentration, suggesting that TEMPO is located at polar sites of the PVP-LiDS complex. At about 30 mmol dm^{-3} of LiDS, where the regular micellization of free LiDS in the bulk begins, τ_c is almost constant, where the τ_c value in the PVP-LiDS complex is greater than that in the regular micelles of LiDS. This result suggests that the headgroups of LiDS adsorbed on PVP are more tightly packed than those in the LiDS micelle. A similar behavior of τ_c in the PVP-LiFOS system is observed, except that τ_c in the PVP-LiFOS system is smaller than that in LiFOS alone. It is likely that the headgroups of LiFOS adsorbed on PVP are less tightly packed than those in LiFOS micelles. Witte and Engerts (6) reported that the more hydrophobic polypropylene oxide binds more strongly to the micelles than polyoxyethylene and suggested that the headgroups of the micelles adsorbed on the polymers are presumably less tightly packed, leading to a more "open" structure of the polymer-complexed micelle. However, the packing

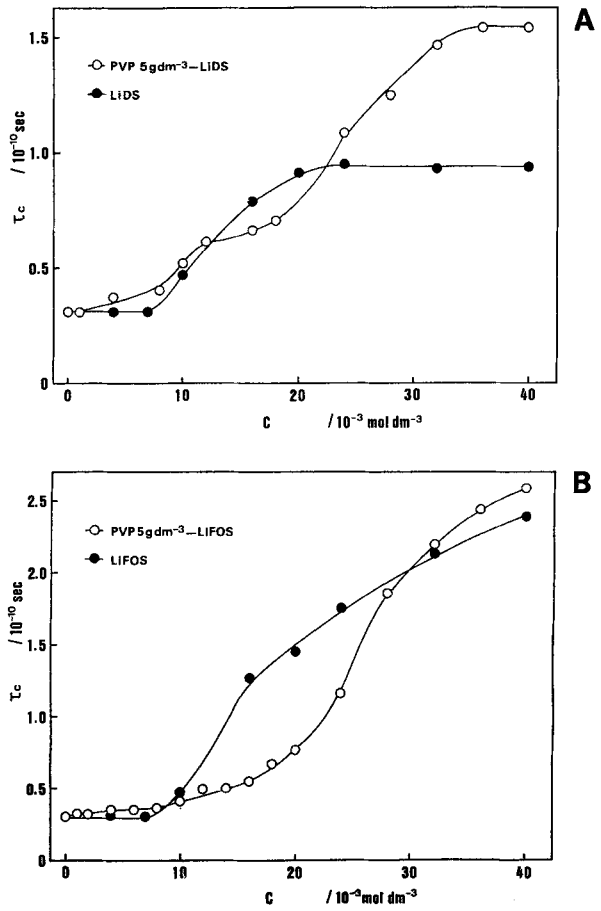

FIG. 7. Variation of rotational correlation time, τ_c of TEMPO in PVP-surfactant aqueous solutions: (a) PVP-LiDS system; (b) PVP-LiFOS system.

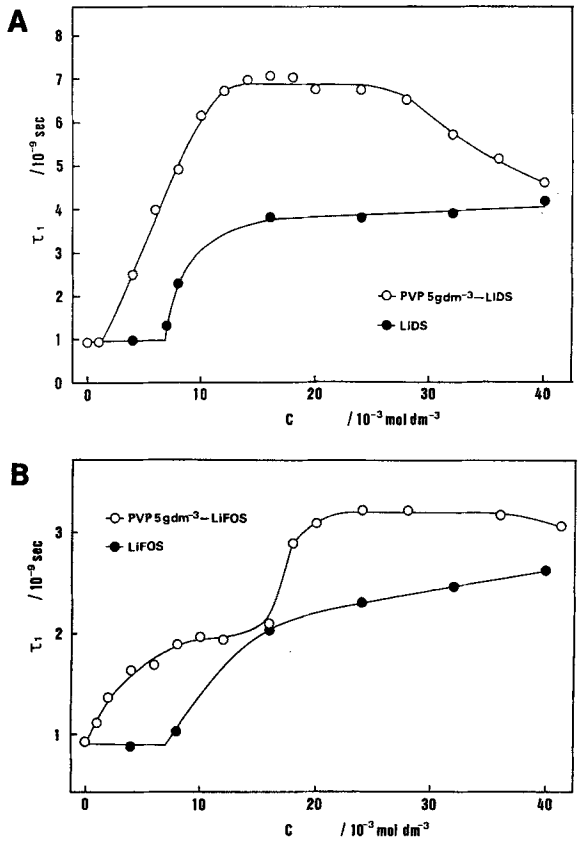

FIG. 8. Variation of rotational correlation time, τ_1 of 7NS in PVP-surfactant aqueous solutions: (a) PVP-LiDS system; (b) PVP-LiFOS system.

degree of the headgroups of the micelle-like aggregates adsorbed on the polymer is probably dependent on the strength of the interaction between polymer and surfactant on the polymer, and on the structure of polymer or surfactant. Also, Esumi *et al.* (38) reported that there is a substantial difference between LiFOS and LiDS on the magnitude in the rotational correlation time of TEMPO.

On the other hand, 7NS is an amphiphilic spin probe. The ESR spectra of 7NS yield information on the internal microenvironments in micelles (39,40) and polymer-surfactant complexes. The expression presented by Cannon *et al.* (41) for calculation of the correlation time can be written:

$$\tau_1 = 6.5 \times 10^{-10} W_0((h_0/h_{-1})^{1/2}+(h_0/h_{+1})^{1/2}-2) \text{ sec} \quad [4]$$

where τ_1 is the correlation time and W_0, h_0, h_{-1}, and h_{+1} represent the peak-to-peak linewidth of the ESR mid-field line (in gauss) and the peak-to-peak heights of mid-, low-, and high-field lines, respectively. In the PVP-LiDS system [Fig. 8(a)], τ_1 of 7NS in aqueous solutions of LiDS containing PVP (5 g dm^{-3}) is larger than in aqueous solutions of LiDS alone. This implies that the internal microviscosity of the micelle-like aggregate of LiDS, which is wrapped around by PVP, is greater than that of the regular micelle of LiDS. This result is consistent with that of the solubilization of Yellow-OB. In a region of the complexation, τ_1 increases with an increase of LiDS concentration from 1 mmol dm^{-3}, while that value is almost constant to about 30 mmol dm^{-3}. In the PVP-LiFOS system [Fig. 8(b)], τ_1 increases with an increase of LiFOS concentration in a region of complexation until 21 mmol dm^{-3} of LiFOS. In particular, τ_1 tends to increase remarkably above 8 mmol dm^{-3} of LiFOS. These phenomena are due to the micellization of LiFOS adsorbed on PVP. Furthermore, the microviscosity of the interior of the micelle-like aggregate, consisting of LiFOS molecules adsorbed on PVP, is greater than that of the regular LiFOS micelle, while the head groups of the former are less tightly packed than the latter. This suggests that LiFOS molecules initially adsorb on PVP along its chain and then form the micelle-like aggregate wrapped around by PVP. This complexation causes a remarkable viscosity change assisted by the rigidity of the fluorocarbon chain of LiFOS.

The results above show that a PVP-surfactant complex is more favorably formed in the PVP-LiFOS system than in the PVP-LiDS system and that the adsorbed amount of LiFOS is less than that of LiDS, although their CMCs are almost the same. The PVP-LiFOS complex causes a remarkable viscosity change because of the rigidity of the fluorocarbon chain of LiFOS. Furthermore, it was found that the head groups of LiFOS adsorbed on PVP are less tightly packed than those in the LiFOS micelle, while the headgroups of LiDS adsorbed on PVP are more tightly packed than those in the LiDS micelle.

REFERENCES

1. Fishman, M.L., and F.R. Eirich, *J. Phys. Chem. 75*: 3135 (1971).
2. Lewis, K.E., and C.P. Robinson, *J. Colloid Interface Sci. 32*:539 (1970).
3. Kresheck, G.C., and I. Constantinidis, *Anal. Chem. 56*:152 (1984).
4. Robb, I.D., *Anionic Surfactants-Physical Chemistry of Surfactant Action*, edited by E.H. Lucassen-Reinders, Marcel Dekker, New York, NY, 1981, p. 109.
5. Chari, K., and W.C. Lenhart, *J. Colloid Interface Sci. 137*:204 (1990).
6. Witte, F.M., and J.B.F.N. Engerts, *J. Org. Chem. 53*:3085 (1988).
7. Ruckenstein, E., G. Hurber and H. Hoffmann, *Langmuir 3*:382 (1987).
8. Nagarajan, R., *Colloids Surf. 13*:1 (1985).
9. Goddard, E.D., and G.C. Benson, *Can. J. Chem. 35*:986 (1957).
10. Arai, H., M. Murata and K. Shinoda, *J. Colloid Interface Sci. 54*:450 (1976).
11. Shirahama, K., and N. Ide, *Ibid. 54*:450 (1971).
12. Lang, H., *Kolloid Z.Z. Polym. 243*:101 (1971).
13. Murata, M., and H. Arai, *J. Colloid Interface Sci. 46*:528 (1974).
14. Arai, H., and S. Horin, *Ibid. 30*:372 (1969).
15. Horin, S., and H. Arai, *Ibid. 32*:547 (1970).
16. Witte, F.M., P.L. Buwalda and J.B.F.N. Engerts, *Colloid and Polym. Sci. 265*:42 (1987).
17. Witte, F.M., and J.B.F.N. Engerts, *Colloids Surf. 36*:417 (1989).
18. Tokiwa, F., and K. Tsujii, *Bull. Chem. Soc. Jpn. 46*:2684 (1973).
19. Saito, S., *J. Colloid Interface Sci. 15*:283 (1960).
20. Zana, R., J. Lang and P. Lianos, *Poly. Prepr. Am. Chem. Soc. Div. Polym. Chem. 23*:39 (1982).
21. Francois, J., J. Dayantis and J. Sabbadin, *Eur. Polym. J. 21*:165 (1985).
22. Arai, H., M. Murata and K. Shinoda, *J. Colloid Interface Sci. 37*:223 (1971).
23. Cabane, B., *J. Phys. Chem. 81*:1639 (1977).
24. Goddard, E.D., *Colloids Surf. 19*:255 (1986).
25. Fishman, M.L., and F.R. Eirich, *J. Phys. Chem. 79*:2740 (1975).
26. Suzuki, T., K. Esumi and K. Meguro, *J. Colloid Interface Sci. 93*:205 (1983).
27. Meguro, K., M. Ueno and T. Suzuki, *J. Japan Oil Chem. Soc. 31*:909 (1982).

28. Muto, Y., M. Asada, A. Takasawa, K. Esumi and K. Meguro, *J. Colloid Interface Sci. 124*:632 (1988).
29. Meguro, K., Y. Muto, F. Sakurai and K. Esumi, *Phenomena in Mixed Surfactant Systems*, edited by J. F. Scamehorn, ACS Symposium Series, No. 31, American Chemical Society, Washington, DC, 1986, p. 61.
30. Kalyanasundaram, K., and J.K. Thomas, *J. Am. Chem. Soc. 99*:2039 (1977).
31. Muto, Y., K. Esumi and K. Meguro, *J. Colloid Interface Sci. 120*:162 (1987).
32. Turro, N.J., B.H. Baretze and J.P. Kuo, *J. Am. Chem. Soc. 106*:1321 (1984).
33. Kalyanasundaram, K., and J.K. Thomas, *J. Phys. Chem. 81*:2176 (1977).
34. Molyneux, P., and G.S. Ahmed, *Kolloid Z.Z. Polym. 251*:310 (1973).
35. Saito, S., *J. Colloid Interface Sci. 24*:227 (1967).
36. Ramachandran, C., R.A. Pyter and P. Mukerjee, *J. Phys. Chem. 86*:3198 (1982).
37. Martine, J., J. Michon and A. Rassat, *J. Am. Chem. Soc. 97*:818 (1975).
38. Esumi, K., H. Otsuka and K. Meguro, *J. Colloid Interface Sci. 136*:224 (1990).
39. Schreier, S., J.R. Ernandes, I. Cuccova and H. Chaimovich, *J. Magn. Reson. 30*:283 (1978).
40. Baglioni, P., and L. Kevan, *J. Phys. Chem. 91*:1516 (1987).
41. Cannon, B., C.F. Polnaszek, K.W. Bulter, L.E.G. Eriksson and I.C.P. Smith, *Arch. Biochem. Biophys. 167*:505 (1975).

[Received April 12, 1991; accepted August 29, 1991]