The Interaction Between Co-Polymer of Vinylpyrrolidone and Vinylacetate and Anionic Surfactants in Aqueous Solutions

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ABSTRACT: The interaction of co-polymers of vinylpyrrolidone–vinylacetate with anionic surfactants, such as lithium dodecyl sulfate (LiDS), lithium perfluorooctane sulfonate (LiFOS) in aqueous solution, has been studied. When the content of vinylacetate in the co-polymers increases, reduction in the surface tension of co-polymers alone becomes significant. In mixtures of co-polymers and surfactants, co-polymer–LiFOS complexes are formed at lower surfactant concentration than that of co-polymer–LiDS. The micropolarity of the co-polymers–surfactant complexes depends on the composition of co-polymers and is higher for co-polymer–LiFOS than that for co-polymer–LiDS. Further, the solubilization behavior of α-(o-tolylazo-)-β-naphthylamine (Yellow OB) (Tokyo Kasei Co., Ltd., Tokyo, Japan) in the co-polymer–surfactant complexes is almost independent of the co-polymer composition, but different from the surfactants, where a very low solubilized amount of Yellow OB is observed for co-polymer–LiFOS.

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KEY WORDS: Co-polymer of vinylpyrrolidone and vinylacetate, co-polymer–surfactant complex, fluorinated surfactant.

Nonionic water-soluble polymers have been shown to form association complexes with anionic surfactants in solution (1–3). The strength of these polymer and surfactant associations has been found to depend strongly on the properties of the polymers and surfactants. Most of the work done in this area has been focused on poly(ethylene oxide) (3–10), poly(ethylene glycol) (11), poly(vinylpyrrolidone)(PVP) (12,13), and poly(vinyl alcohol–acetate) (14). An anionic surfactant, sodium dodecyl sulfate, has been mainly used in these studies.

In a previous paper, we found (15) that PVP–surfactant complex is more favorably formed in the PVP–lithium perfluorooctane sulfonate (LiFOS) system than in the PVP–lithium dodecyl sulfate (LiDS) system, and the PVP–LiFOS complex causes a remarkable viscosity change because of the rigidity of the fluorocarbon chain of LiFOS. The interaction between these systems occurs mainly through hydrophobic bonding. It has also been reported (16) that co-polymers of vinyl alcohol–acetate show stronger hydrophobic interaction than poly(vinyl alcohol) with surfactant. Thus, it is expected that co-polymers exhibit different hydrophobic properties and interact differently with surfactants as compared to homopolymers.

In this work, interactions of co-polymers of vinylpyrrolidone–vinylacetate with anionic surfactants in aqueous solutions were investigated using several methods.

EXPERIMENTAL PROCEDURES

Materials. N-vinylpyrrolidone and vinyl acetate were purified by double distillation in vacuum. Co-polymerization of these monomers with various ratios was carried out in benzene using *t*-butyl perbenzoate as an initiator at 76°C for 2 h under nitrogen atmosphere. The co-polymers thus obtained were precipitated by pouring the solutions into *n*-hexane and purified by repeated precipitations from a chloroform system to a hexane system. The composition of the co-polymers was determined by H nuclear magnetic resonance (NMR). The molecular weight of the co-polymers was determined by a static light scattering. The compositions (vinylpyrrolidone/vinylacetate in mol) of co-polymers prepared were as follows: 92:8, 87:13, 66:34 and 20:80. Their corresponding molecular weights were 158000, 147000, 171000 and 128000, respectively. LiDS was synthesized from 1-dodecanol by sulfonation with chlorosulfuric acid, followed by neutralization with lithium hydroxide. After recrystallization from ethanol, this surfactant was purified by extraction with ether. LiFOS was synthesized and purified by a published method (17). These surfactants were confirmed to be highly pure by the absence of a minimum in the surface tension–concentration plots. Pyrene was obtained from Wako Pure Chemical Industries (Tokyo, 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 purification. α-(o-Tolylazo-)–β-naphthylamine(Yellow-OB), obtained from Tokyo Kasei Co. Ltd. was purified by repeated crystallization from ethanol. Water used

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in this study was purified using a Milli-Q-System (Nihon Milli Pore Co., Tokyo, Japan), where the specific conductivity fell below 0.1 μS cm^{-1}.

Measurements. The surface tension was measured with a Wilhelmy plate apparatus (Shimadzu ST-1; Shimadzu, Kyoto, Japan).

The fluorescence spectra being emitted by solubilized fluorescence probe (pyrene, PCA) were recorded on a Hitachi 650-10S fluorescence spectrophotometer (Hitachi Co., Tokyo, Japan). The excitation wavelengths of pyrene and PCA were 335 and 356 nm, respectively. The experimental procedure for probing was as follows. A known volume of pyrene or PCA ethanol solution was put into a test tube and then evacuated by vacuum to remove ethanol. Then, aqueous solution of surfactant or co-polymer–surfactant was added into the test tube, followed by stirring. The final 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. Co-polymers–surfactant or surfactant solutions containing an excess amount of Yellow OB were exposed to ultrasonic waves for 20 min and then shaken for 48 h in order to reach equilibrium of solubilization. These mixtures were then filtered and diluted with ethanol. The optical density of the solution at maximal absorption was measured with a Hitachi 220A double beam ultraviolet-visible spectrophotometer. The amounts of solubilized Yellow OB were determined from calibration curves. All measurements were performed at 25°C.

RESULTS AND DISCUSSION

Figure 1 shows that the surface tension decreases with an increase in the concentration of the co-polymer and, in particular, the co-polymers with higher vinylacetate content provide a lower surface tension. As vinylpyrrolidone acts as the hydrophilic character and vinylacetate as the hydrophobic one, the reduction in the surface tension is controlled by the composition ratio of vinylpyrrolidone and vinylacetate. Figure 2 shows the effect of surfactants on the surface tension of co-polymers in aqueous solutions. These changes in the surface tension are very similar to that of PVP–LiDS and PVP–LiFOS systems (15)—two critical surfactant concentrations are seen in the presence of PVP, and the surface tension between the two concentrations is higher than that in the absence of PVP. However, the surface tension in the presence of the co-polymers (66:34 and 20:80) is lower compared to that of the respective surfactants at both below and above the critical micelle concentrations. This indicates that the co-polymers form complexes with the surfactants and their complexes show a greater surface tension reduction, especially for the co-polymers with higher vinylacetate content.

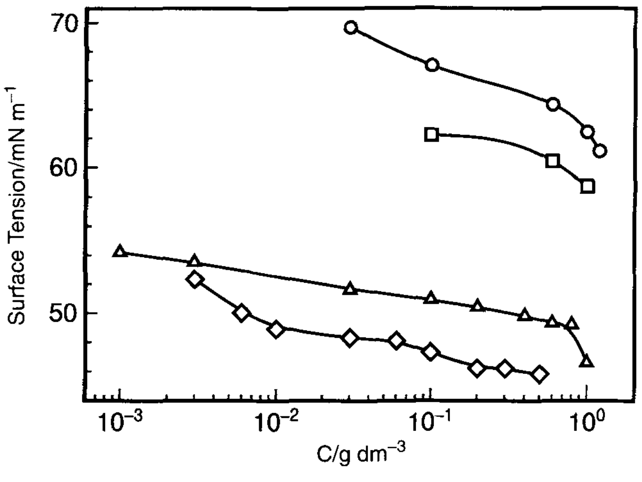

FIG. 1. Surface tension of co-polymers in aqueous solutions. Monomer ratio of vinylpyrrolidone/vinylacetate: (○) 92:8; (□) 87:13; (◇) 66:34; and (△) 20:80.

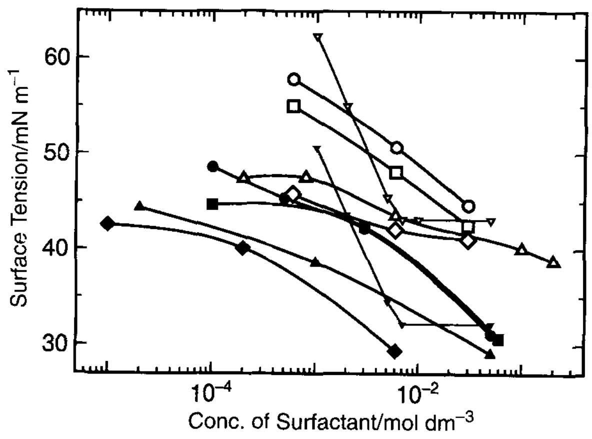

FIG. 2. Effect of lithium dodecyl sulfate LiDS, (open marks)/lithium perfluorooctane sulfonate LiFOS, (closed marks) on surface tension of co-polymers in aqueous solutions. Monomer ratio of vinylpyrrolidone/vinylacetate and feed concentration: (○, ●) 92:8, 1 g dm^{-3}; (□, ■) 87:13, 1 g dm^{-3}; (◇, ◆) 66:34, 0.5 g dm^{-3}; (△, ▲) 20:80, 1 g dm^{-3}. Surfactant alone: (▽) LiDS; (▼) LiFOS.

The fluorescence of PCA monomer depends on solvent polarity (18). The maximum fluorescence wavelength shifts to higher wavelength with increasing solvent polarity, which has a linear relationship with solvent dielectric constant above 10. Accordingly, this PCA method can provide a micropolarity of co-polymers and co-polymer–surfactant complex where PCA resides. Figure 3 shows that the maximum fluorescence wavelength shifts to the region of lower wavelength with an increase of the co-polymer concentration. In particular, the co-polymers (66:34, 20:80) have break points; the maximum fluorescence wavelength in the co-polymer (66:34) decreases remarkably at about 0.2 g dm^{-3} and then almost keeps constant with the concentration, whereas that in the co-polymer (20:80) decreases gradually and then keeps constant at above 1.0 g dm^{-3}. These break points may correspond to the critical micelle concentration of these co-polymers. On the other hand, no break points were observed for the other co-polymers, which had higher vinylpyrrolidone content. These results can be understood by a view that micellization of the co-polymers occurs by a balance between hydrophobicity and

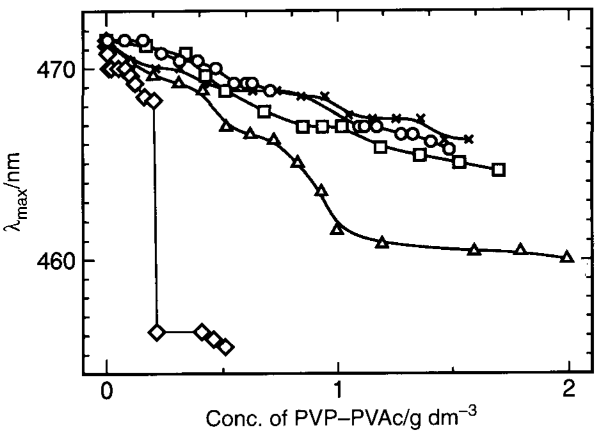

FIG. 3. Variation in maximum fluorescence wavelength of pyrene-1-carboxaldehyde in co-polymer aqueous solutions. Monomer ratio of vinylpyrrolidone/vinylacetate: (○) 92:8; (□) 87:13; (◇) 66:34; and (△) 20:80. (x) Poly(vinylpyrrdidone) (PVP), molecular weight = 360000.

hydrophilicity of the co-polymers. It is interesting to note that the micropolarity of co-polymer (66:34) micelles is quite low compared with that of the others.

Figure 4 shows the variation of maximum fluorescence wavelength as a function of surfactant concentration in the presence of the co-polymers. The maximum fluorescence wavelength shifts to the region of lower wavelength, followed by shifts to the region of higher wavelength with increasing surfactant concentration for the co-polymer–LiDS and co-polymer–LiFOS system, except the co-polymer (66:34). The former shift is due to the association of surfactant with co-polymer and the latter one to the micellization of surfactant adsorbed on co-polymer or micellization of surfactant alone. The degree of shift in the maximum fluorescence wavelength for complexation is larger than that in regular micellization, indicating that the main binding sites of the surfactant adsorbed on the co-polymer are near the head group of the surfactant. On the contrary, the co-polymer (66:34)–surfactant system shows relatively higher polarity, similar to that of the surfactants alone. This suggests that LiDS or LiFOS molecules adsorb on the external surface of the co-polymer micelles, orienting its hydrophilic groups to aqueous solution and resulting in a high polarity at the micelle co-polymer surface. These explanations would be consistent with a physical picture of the reduced mobility of the segments in the backbone of the polymer obtained with ^{13}C NMR spectroscopy (19). The concentration at which the maximum fluorescence wavelength starts to shift to the region of lower wavelength is lower for the co-polymer–LiFOS system than for the co-polymer–LiDS system. A similar behavior has been observed in PVP–LiDS and PVP–LiFOS systems (15). Accordingly, for the co-polymer–surfactant system, the co-polymer–surfactant aggregate is also a more favorable energy state for LiFOS than for LiDS. In addition, the I_1/I_3 ratio of pyrene is sensitive to the polarity of the microenvironment at the sites of solubilization of pyrene, where I_1 and I_3 are the first and third vibrational peaks of monomeric pyrene. Figure 5 shows the variation of I_1/I_3 ratio of pyrene as a function of surfactant concentration in the presence of co-polymers. The I_1/I_3 ratios decrease with an increase in the concentration of the surfactant. The average microenvironmental polarity experienced by pyrene for the co-polymer–LiDS system is in the order 66:34 < 20:80 < 92:8 < 87:13. Above 8 mmol dm^{-3} of LiDS, the micropolarity of the co-polymer–LiDS is greater than that of LiDS alone. It seems likely that either the interior of the micelle-like aggregate of LiDS adsorbed on the co-polymer is loose and polar, or the pyrene solubilizes at a more external site in the co-polymer–LiDS complex than in the LiDS micelle. It has also been reported (20) that the average environmental polarity by pyrene is in the order PVP–SDS complex > SDS micelle. On the other hand, in the co-polymer–LiFOS-system the average environmental polarity in the co-polymer (92:8)–LiFOS system provides the lowest I_1/I_3 value at higher LiFOS concentration. Furthermore, the co-polymer–LiFOS system shows a higher average environmental polarity compared to that of the co-polymer–LiDS system. This result may indicate that the main binding site of LiFOS on the co-polymers is in the neighborhood of the head group of LiFOS.

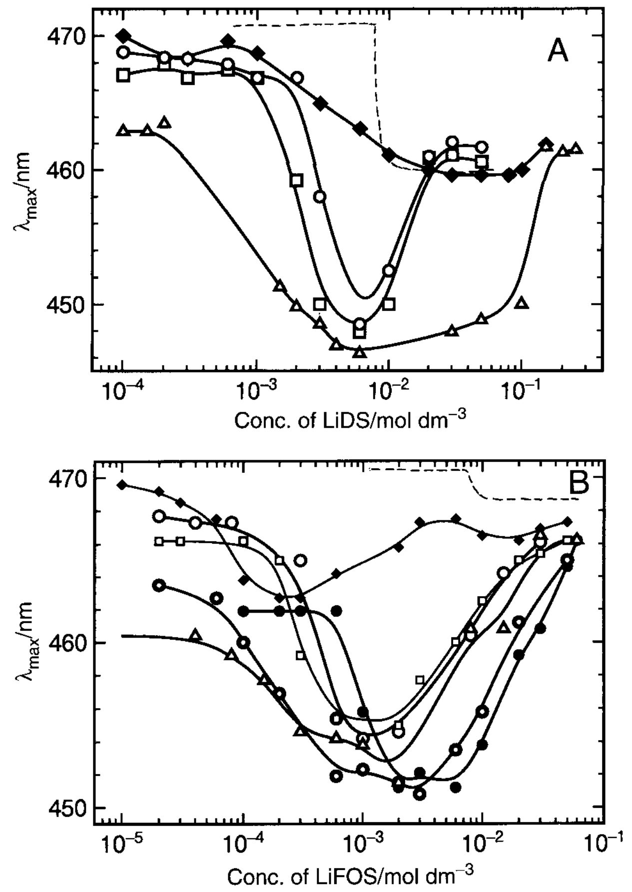

FIG. 4. Effect of LiDS (A)/LiFOS (B) on maximum fluorescence wavelength of pyrene-1-carboxaldehyde in co-polymer aqueous solutions. Monomer ratio of VP/VAc and feed concentration: (○) 92:8, 1 g dm^{-3}; (○) 92:8, 3 g dm^{-3}; (●) 92:8, 5 g dm^{-3}; (□) 87:13, 1 g dm^{-3}; (◆) 66:34, 0.5 g dm^{-3}; (△) 20:80, 1 g dm^{-3}; (----) Surfactant alone. Abbreviations as in Figure 2.

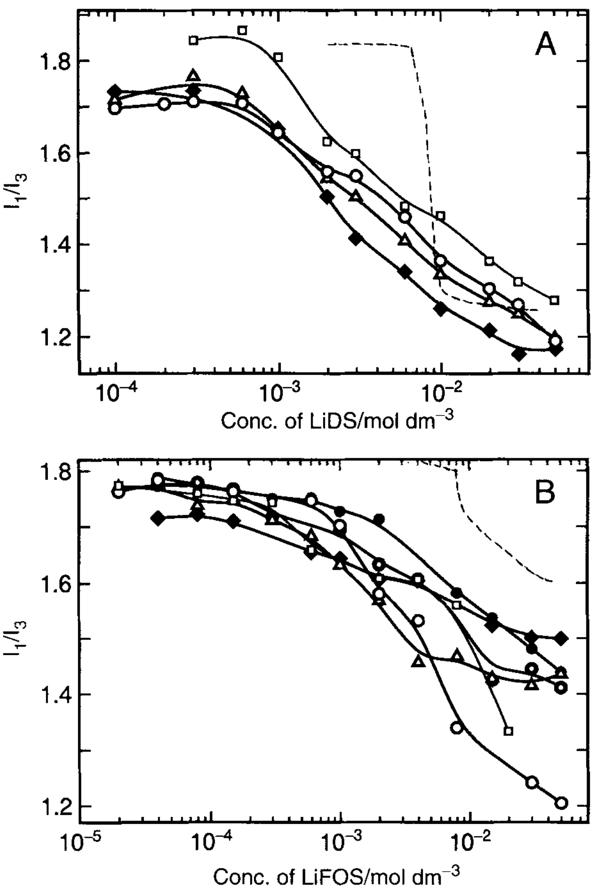

FIG. 5. Effect of LiDS(A)/LiFOS (B) on I_1/I_3 ratio of pyrene in co-polymer aqueous solutions. Monomer ratio of VP/VAc and feed concentration: (○) 92:8, 1 g dm^{-3}; (◎) 92:8, 3 g dm^{-3}; (●) 92:8, 5 g dm^{-3}; (□) 87:13, 1 g dm^{-3}; (◆) 66:34, 0.5 g dm^{-3}; (△) 20:80, 1 g dm^{-3}. (---) Surfactant alone. Abbreviations as in Figure 2.

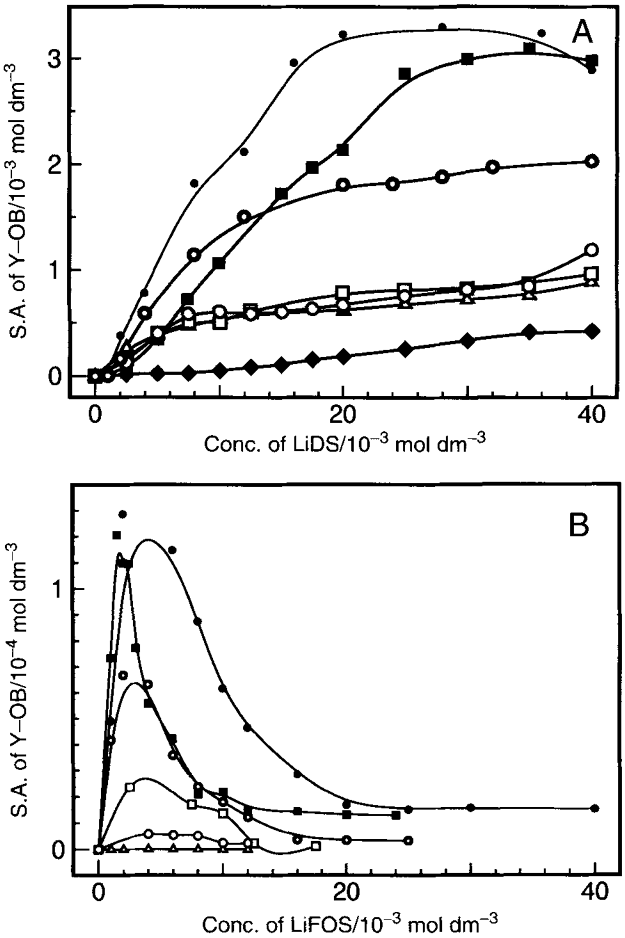

FIG. 6. Effect of LiDS (A)/LiFOS (B) on solubilized amount (S.A.) of Yellow OB in co-polymer aqueous solutions. Monomer ratio of VP/VAc and feed concentration: (○) 92:8, 1 g dm^{-3}; (◎) 92:8, 3 g dm^{-3}; (●) 92:8, 5 g dm^{-3}; (□) 87:13, 1 g dm^{-3}; (■) 87:13, 5 g dm^{-3}; (◆) 66:34, 0.5 g dm^{-3}; (△) 20:80, 1 g dm^{-3}. Abbreviations as in Figure 2.

Figure 6 shows the saturated solubilization amount of Yellow OB as a function of surfactant concentration in the co-polymer–LiDS and co-polymer–LiFOS systems. The solubilization power for the co-polymers alone is negligibly small. The co-polymer–LiDS system shows a different solubilization behavior from that in LiDS alone. The saturated solubilization amount of Yellow OB in LiDS alone, which is not given in Figure 6, is almost the same as that in the co-polymer (66:34)–LiDS system. This phenomenon has been ascribed to the formation of a water-soluble complex whose solubilization power is different from that of either co-polymer or surfactant. Solubilization in the co-polymer–LiDS mixtures occurs in two different species—complexes and regular micelles. On the other hand, in the co-polymer–LiFOS system, the solubilized amount of Yellow OB shows a maximum at a certain concentration of LiFOS at which the maximum fluorescence wavelength shows a minimum. As the co-polymer or LiFOS alone has an only slight solubilizing power, Yellow OB is regarded as soluble in the co-polymer–LiFOS complex, and the solubilized amount of Yellow OB is affected by the conformational change in the co-polymer–LiFOS complex. For both systems, a remarkable difference in the solubilizing power is not observed for the co-polymers with various composition ratios. It is noteworthy that the solubilizing power by the co-polymer–LiDS system is considerably greater than that of the co-polymer–LiFOS system. The incorporation of perfluoroalkyl chains into the co-polymer–surfactant complex has been demonstrated to result in a "desolubilization" of the aromatic hydrocarbon compound solubilized (21,22). As a result, the solubilizing power by the co-polymer–LiFOS system becomes remarkably small.

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