NOTES

Solubilization of Azo Dye by Nonionic Poly(2-oxazoline) Surfactant in Aqueous Solution

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Solubilization of organic compounds by surfactants in an aqueous solution is very important for various industrial applications such as emulsion polymerization and leveling of dyestuffs. Usually nonionic surfactants having a polyoxyethylene chain as a hydrophilic segment are used for the leveling, because the solubility ability of the nonionic surfactants is much larger than that of anionic ones.[1]

Electrophilic (cationic) ring-opening polymerization of 2-oxazolines conveniently produces poly(N-acylethlenimine),[2] where the hydrophilic/hydrophobic property can be easily controlled by choosing the acryl group. Recently we have synthesized novel nonionic surfactants possessing a hydrophilic poly(2-oxazoline) chain,[3–6] e.g., the introduction of hydrophobic group is achieved by the quantitative termination of living ends of the hydrophilic polymer with hydrophobic nucleophiles such as a higher alkylamine. Furthermore, the surfactants showed good surfactant properties.

This paper describes solubilization behaviors of an oil-soluble azo dye by a nonionic poly(2-oxazoline) surfactant 1 in aqueous solution. The azo dye used is Oil Yellow OB (1-o-tolylazo-2-naphthylamine). The surfactant 1 possesses an ester group of higher fatty acid as a hydrophobic group and a hydrophilic poly(N-acetylethylenimine) chain.[6]

$$\text{Me-(NCH}_2\text{CH}_2)_n\text{-O}_2\text{CR}$$
$$\text{Me-}\overset{|}{\text{C}}\text{=O}$$

1
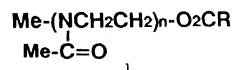
EXPERIMENTAL

Materials

Nonionic polymer surfactant 1 was prepared according to our method.[6] Other reagents and solvents were purified in a usual manner.

Solubilization

Solubilization test was carried out as follows. A large excess of Oil Yellow OB was added to the surfactant solution and the mixture was incubated with shaking at a rate of 140 times per min in a thermostat. The incubation was kept at 30°C for 48 h to attain the equilibrium. The excess of the dye was removed by filtration using a 5C filter. The amount of the solubilized dye in the filtrate was determined on the basis of the UV absorption at 445 nm.

Measurements

The surface tension (γ) of the aqueous surfactant solution was measured by a Shimadzu Du Noüy tensiometer at 25°C. UV spectra were recorded on a Shimadzu UV-200

spectrometer. ^{1}H NMR spectra were recorded on a 250 MHz Bruker AC-250T spectrometer.

RESULTS AND DISCUSSION

Typical results for solubilization in an aqueous solution of **1** are shown in Figure 1. The critical micelle concentration (cmc) of **1** has been determined as 4.5×10^{-5}—4.1×10^{-4} mol l^{-1} by measuring the surface tension (γ) of the aqueous surfactant solution with varying the concentration of **1**. Therefore, the solubilization tests of **1** were carried out at the concentrations higher than the cmc of **1**. In all cases examined, the amount of solubilized Oil Yellow OB increased linearly with the concentration of the surfactant. The solubility power (SP) of the surfactant was obtained from the slope of the line (Figure 2). The SP values were much larger than those of ionic surfactants.[1] These data indicate that the poly-(2-oxazoline) portion in the molecule plays an important role in solubilization.
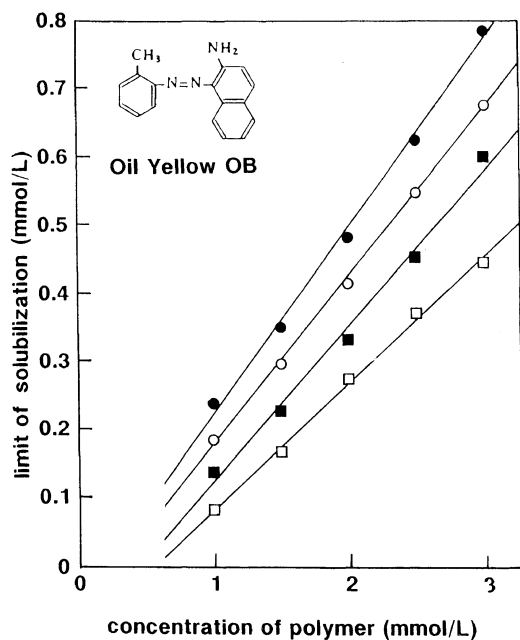
In comparison with the solubility ability of typical nonionic surfactants having a poly-oxyethylene chain, the solubility ability of polyoxyethylene laurylate (the number of polyoxyethylene unit = 10) was examined in a similar condition. The SP value obtained was 0.13, which is smaller than that of poly(2-oxazoline) surfactant having a laurylate group.

With fixing the degree of polymerization (n)—11, the SP values were obtained as a function of carbon number of the alkyl group R. The longer the alkyl chain, the higher the solubility ability. Furthermore, the effect of the n value on the solubility ability was examined by using the surfactant having a laurylate group. The SP value slightly increased as the n value increased from 3.1 to 11.5. When the n value was more than 11.5, the solubility ability was almost constant. These results imply that the solubility ability for Oil Yellow OB mainly depends on the alkyl chain length, but not on the number of poly(2-oxazoline) unit. This may be explained as follows. The situation of the solubilized dye would be near the alkyl group in the micelle. Therefore the volume of the alkyl group in the micelle increased with
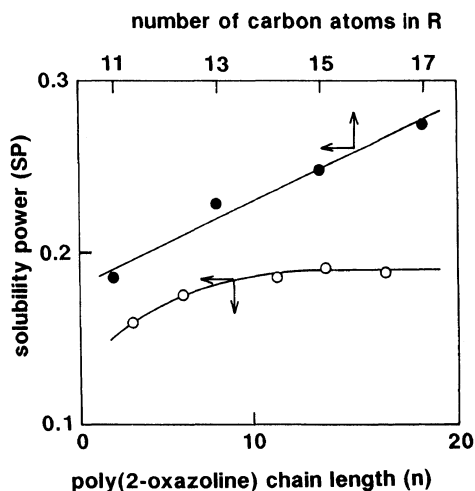
Figure 1. Relationships between the concentration of the surfactant **1** (n—11) and the limit of the solubilization of Oil Yellow OB by **1**; (–□–) R = n-$C_{11}H_{23}$, (–■–) R = n-$C_{13}H_{27}$, (–○–) R = n-$C_{15}H_{31}$, (–●–) R = n-$C_{17}H_{35}$.

Figure 2. The solubility power (SP) against the alkyl chain length and the poly(2-oxazoline) chain length in **1**; (–○–) R = n-$C_{11}H_{23}$, (–●–) n—11.

A B C D E F G H

A   C   D   E   F   G   H
↓   ↗ ↘   ↓   ↓   ↓   ↓   ↓
CH₃(NCH₂CH₂)ₙ₋₁₋NCH₂CH₂O₂CCH₂CH₂(CH₂)₈CH₃
    | |
  CH₃C=O   CH₃C=O
      ↘   ↗
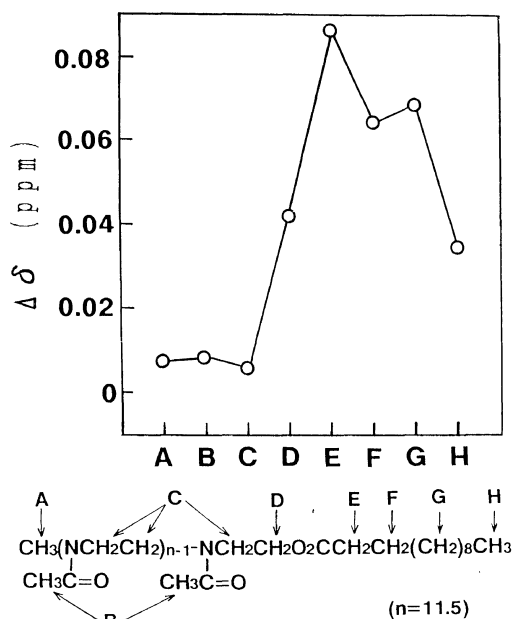   B   (n=11.5)

Figure 3. The differences of the chemical shift in a micellar solution of **1** (surfactant concentration of $0.1\,\mathrm{mol\,l^{-1}}$) without and with the dye added (dye/surfactant ratio $1:5$).

increasing the number of carbon atom in the alkyl group, and hence, the solubility ability increased. On the other hand, the volume of the alkyl group hardly changed when the chain length of the poly(2-oxazoline) portion increased.

In order to determine the solubilized residence of the dye in the micelle, a ¹H NMR technique was used; the inherent ring current of the solubilized dye affects the chemical shift of the surfactant proton in the micelle.[7,8] The ¹H NMR measurement was carried out at the concentration higher than the cmc of **1**. Figure 3 shows the difference of the chemical shift in a micellar solution of **1** without and with the dye added. The differences of the chemical shift of alkyl protons of **1** were much larger than those of the poly(2-oxazoline) portion. Especially $\Delta\delta$ of the α-methylene protons of the alkyl group (E) is the biggest. Furthermore, $\Delta\delta$ of the protons of the poly(2-oxazoline) portion

adjacent to the ester group (D) was relatively large. These results indicate that the dye is solubilized by the interaction largely with the alkyl chain of the ester group, which agrees with the solubilization behaviors above described; the solubility ability was mainly dependent on the alkyl chain length of the ester group, but not so much on the number of the poly(2-oxazoline) unit.

In conclusion, the solubility behavior of Oil Yellow OB by the nonionic surfactant containing a hydrophilic poly(2-oxazoline) chain and a hydrophobic fatty acid ester group in an aqueous solution was examined. The surfactant possessed high solubility ability. The ability mainly depended upon the chain length of the alkyl ester group, not but much on the unit of poly(2-oxazoline). ¹H NMR analysis of the micelle also supported this view, *i.e.*, the interaction of the dye and α-methylene group of the alkyl ester moiety was the biggest.

REFERENCES

1. H. Uchiyama, M. Abe, and K. Ogino, *Yukagaku*, **35**, 1031 (1986).
2. For recent papers on 2-oxazoline polymerization, see: (a) G. Cai and M. H. Litt, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 3603 (1989). (b) N. Tsubokawa, *Polym. Bull.*, **22**, 55 (1989). (c) S. Kobayashi, H. Uyama, and Y. Narita, *Macromolecules*, **23**, 353 (1990). (d) *Idem.*, *Polym. J.*, **22**, 175 (1990). (e) M. Miyamoto, K. Naka, M. Shiozaki, Y. Chujo, and T. Saegusa, *Macromolecules*, **23**, 3201 (1990). (f) S. Kobayashi, *Prog. Polym. Sci.*, **15**, 751 (1990). (g) S. Kobayashi and H. Uyama, *Polym. News.*, **16**, 70 (1991).
3. S. Kobayashi, T. Igarashi, Y. Moriuchi, and T. Saegusa, *Macromolecules*, **19**, 535 (1986).
4. S. Kobayashi, S. Iijima, T. Igarashi, and T. Saegusa, *Macromolecules*, **20**, 1729 (1987).
5. S. Kobayashi, H. Uyama, N. Higuchi, and T. Saegusa, *Macromolecules*, **23**, 54 (1990).
6. S. Kobayashi and H. Uyama, *Polym. Prepr. Jpn.*, **39**, 291 (1990); Macromolecules, in press.
7. J. Ulmius, B. Lindman, G. Lindblom, and T. Drakenberg, *J. Colloid Interface Sci.*, **65**, 88 (1978).
8. D. Fornasiero, F. Grieser, and W. H. Sawyer, *J. Phys. Chem.*, **92**, 2301 (1988).