March, 1984] © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 57, 831—835 (1984)* 831

Interactions between Anionic Surfactants and Oil Dyes in the Aqueous Solutions. III. Thermochromism in the Presence of Surfactant Micelle and Dye–Surfactant Complexes

Masahiko Abe,*,†,†† Mitsuo Ohsato,† Nobuyuki Suzuki,† and Keizo Ogino†,††
†*Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278*
††*Institute of Colloid and Interface Science, Science University of Tokyo, 1-3, Kagurazaka, Shinjuku-ku, Tokyo*

(Received July 1, 1983)

The interactions between 4 anionic surfactants and 3 azo oil dyes have been studied by a spectrophotometer. The spectrographic behavior of these solutions was dependent on the kinds of hydrophilic groups in each surfactant and the kind of auxochrome in the azo oil dyes. In particular, a sulfate and two sulfonates including strongly hydrophilic groups interacted strongly with the oil dyes (4-NH_2) which have an amino group at 4-position of naphthalene. At lower concentrations, an isosbestic point was recognized; this occurred because of the formation of the hydrophobic dye–surfactant complex (1:1). In the neighborhood of the cmc region, the spectrum with a peak at 520 nm changed with temperature into another one with a 440 nm band; this is the so-called thermochromism. This may be attributed to the fact that, in the presence of surfactant micelles, the 4-NH_2 exhibits an azo form at higher temperature, but a resonance stabilized azonium form is found at lower temperature.

A number of investigations have been made on the interactions between surfactants and dyes in order to clarify the formation of dye–surfactant complexes.[1–3] In recent years, Nemoto[4] and Kuroiwa[5] have published reviews on interactions between surfactants and dyes. For example, Kuroiwa[6] studied a complex of dispersing dye and anionic surfactant; Nemoto[7] studied that of acid–nonionic surfactant. But few studies have been made on the interactions between oil dyes and surfactants.

The changes of complementary color of the dye solutions include solvatochromism,[8] halochromism,[9] and thermochromism.[10] However, these have not been measured in the presence of surfactant micelles.

We have reported the solubilization of some oil dyes by sodium dodecyl sulfate.[11] We found that the surfactant anion interacted strongly with the oil dye including amino group at 4-position of naphthalene; moreover, the spectrum with a peak at 520 nm changed with temperature into another one with a 440 nm band.

In this paper, we report the interaction between 4 anionic surfactants, which have different hydrophilic groups, and 3 azo oil dyes, which have different functional groups in aqueous solutions by the spectrographic method. We discuss the effect of surfactant micelle structure on the protonation equilibrium of azo oil dyes.

Experimental

Materials. *Anionic Surfactants*: Sodium dodecyl sulfate (SDS) was supplied by Nihon Surfactant Industries, Co., Ltd, Tokyo, Japan; sodium 1-dodecanesulfonate (DSS), sodium dodecylbenzenesulfonate (SDBS), and sodium laurate (SL) were purchased from Tokyo Kasei Kogyo Co., Ltd, Tokyo. They are more than 99.5% pure. All surfactants were extracted with ether and crystallized from ethanol; their purities were ascertained by surface tension measurements and differential thermal analysis. Oil dyes: The details of 4-phenylazo-1-naphthylamine (4-NH_2), 4-phenylazo-1-naphthol (4-OH), and Naphthalene-1-azobenzene (NA) were described in our previous paper.[11]

Methods. *Preparation of Surfactant Solution Including Oil Dye*: Into several 100 ml glass-stoppered Erlenmeyer flasks, 50 ml portions of a given concentration of a surfactant solution were placed; a measured amount of oil dye was added to each. The mixtures were stirred with ultrasonic waves for 5 min, then they were stirred by a shaker (model SS-82 D type of Tokyo Rikakikai Co., Ltd, Tokyo) for 24 h and allowed to stand for 24 h in a thermostat at 30 °C in order to establish a solubilization equilibrium.

Determinaton of Maximal Absorption (λ_{max}) and Optical Density of the Solution Owing to Temperature Change. After equilibrium had been established, these mixtures were centrifuged. Then the supernatant liquids of these solutions were collected. The temperature dependence of each maximal absorption and the optical density of each solution were measured by a double beam spectrophotometer (model UVIDEC 505 of Nihon Bunko Ltd, Tokyo) with a quartz cell (1.0, 10.0, or 20.0 mm in length).

Determinaton of cmc of Surfactant by Dye-solubilization Method. The cmc of surfactants determined by the dye-solubilization method were the same as reported previously.[11]

Determination of cmc of Surfactant Alone. The cmc of surfactants alone were determined by the surface tension method.[12] The surface tensions of the surfactant alone were measured at 30 °C with a Wilhelmy tensiometer (model CBVP-A3 of Kyowa Kagaku Co., Ltd, Tokyo) equipped with a platinum plate.

Determinaton of Binding Molar Ratio of Dye-surfactant Complex. The binding molar ratio of dye-surfactant complex was investigated with the continuous variation in optical density method by Kuroiwa and Ogasawara[13] at 30 and 70 °C.

Results

The cmc Given by Dye-solubilization Method and by Surface Tension Method. The cmc given by dye (4-NH_2) solubilization method (I), and that of the surfactant alone given by surface tension method (II) are shown in Table 1. The spectrographic measurements have been made at the following concentrations: A region (below I), B region (between I and II), and C region (above II).

Thermochromism. Oil dyes used in this study were almost insoluble in water at room temperature, but they dissolved slightly in hot water: the complementary color of the solution was yellowish. The complementary color of 4-NH_2 in SDS, DSS, and

Table 1. Cmc by dye solubilization method (I) and surface tension method (II)

Surfactant	cmc/mol dm^{-3}	
	I	II
SDS	2.1×10^{-3}	8.0×10^{-3}
DSS	2.5×10^{-3}	9.8×10^{-3}
SDBS	1.4×10^{-2}	2.0×10^{-2}
SL	1.8×10^{-2}	3.0×10^{-2}

SDBS micellar solutions changed (reddish→yellowish) with increasing temperature; thus the so-called thermochromism occurred. However, the complementary color of 4-NH_2 in SL micellar solution (yellowish) did not change with increasing temperature. Moreover, in the case of NA, and 4-OH, no thermochromism occurred in any surfactant micellar solution.

The Shift of Maximal Absorption with Increase of Temperature. (1) For SDS–4-NH_2 Systems: (a) Concentration of SDS; (i) A Region. Optical densities for the SDS solutions of 3.2×10^{-4} mol dm^{-3} including 4-NH_2 of 1.6×10^{-4} mol dm^{-3} in the temperature range 30 °C to 70 °C are plotted against the measuring wavelength in Fig. 1. As can be seen from Fig. 1, the maximal absorption was about 440 nm; this was not dependent on temperature. But the optical density at maximal absorption increased with increasing temperature: the so-called transition of chemical species. An isosbestic point was recognized at higher wavelength (about 520 nm) than that at the maximal absorption (440 nm).

(ii) B Region. Optical densities for the SDS solutions of 5.0×10^{-3} mol dm^{-3} including 4-NH_2 of 1.6×10^{-4} mol dm^{-3} in the temperature range 30 °C to 72 °C are plotted against the measuring wavelength in Fig. 2. The maximal absorption shifted from longer wavelengths (520 nm) to shorter wavelengths (440 nm) with increase in temperature: the so-called hypsochromic shift.

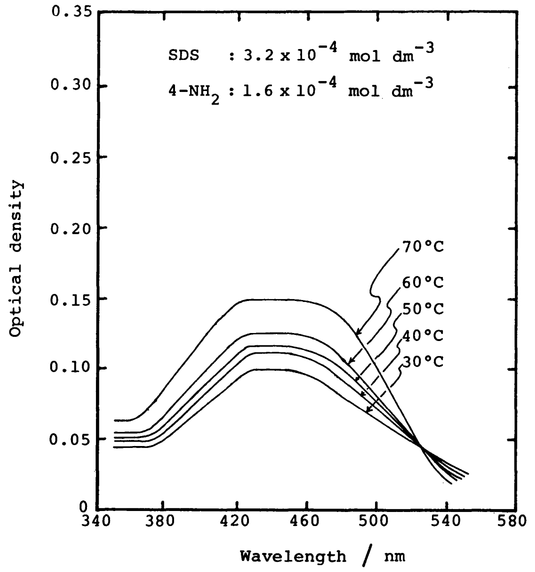

Fig. 1. Effect of temperature on absorption spectra for SDS solution which have dissolved 4-NH_2. (below I: A region)

(iii) C Region. Optical densities for the SDS solutions of 1.6×10^{-2} mol dm^{-3} including 4-NH_2 of 1.6×10^{-4} mol dm^{-3} in the temperature range 30 °C to 70 °C are plotted against the measuring wavelength in Fig. 3. The maximal absorption was not dependent on temperature; its wavelength was about 520 nm, which was about 80 nm higher than that below the cmc. The optical density at maximal absorption increased with increase in temperature. The maximal absorption caused by the increase of temperature changed considerably in the SDS concentration range 2.2×10^{-3} mol dm^{-3} to 1.0×10^{-2} mol dm^{-3}. The shifting temperature, at which the maximal absorption moved from 520 nm to 440 nm, increased with increasing concentration of SDS at the above-mentioned cmc region (58 °C to 70 °C).

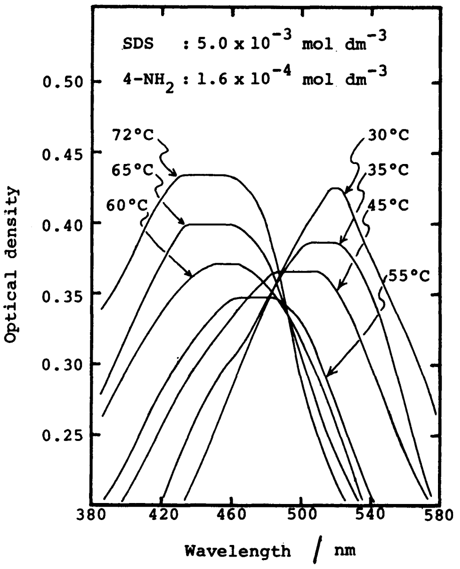

Fig. 2. Effect of temperature on absorption spectra for SDS solution which have dissolved 4-NH_2. (between I and II: B region)

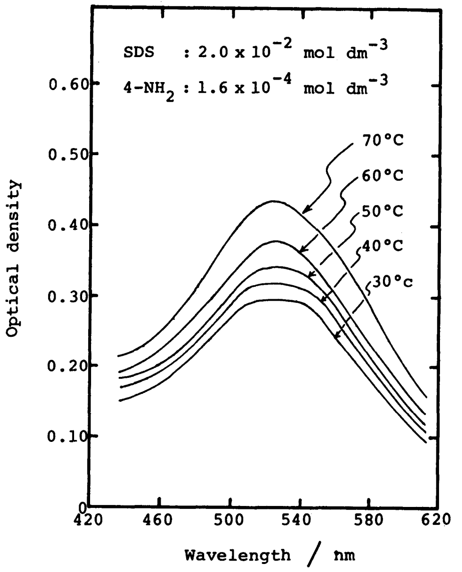

Fig. 3. Effect of temperature on absorption spectra for SDS solution which have dissolved 4-NH_2. (above II: C region)

(b) Concentration of 4-NH_2: As the amounts of 4-NH_2 in each concentration of SDS were considerably higher than the limits of solubilization, thermochromism was not observed. The optimum amount of 4-NH_2 for the observation of thermochromism was just lower than the limit of solubilization.

(2) For SDBS-4-NH_2 Systems: The maximal absorptions of the solutions below the cmc and above the cmc were the same as those of SDS. The change of maximal absorption (520 nm to 440 nm) with increase in temperature was also recognized in the SDBS solutions of 3.0×10^{-2} mol dm^{-3}. Thermochromism also occurred in the SDBS concentration of the cmc range (I, II in Table 1), and for the dye amount just lower than the limit of solubilization as in the case in SDS solutions.

(3) For DSS-4-NH_2 Systems: The maximal absorption of the solutions below the cmc and above the cmc were the same as those of SDS. The change of maximal absorption (520 nm→440 nm) with increase in temperature was also recognized in the DSS solutions of 1.0×10^{-2}mol dm^{-3}. Optical densities for the DSS solutions of 1.0×10^{-2} mol dm^{-3} (at C region) including 4-NH_2 of 1.6×10^{-4} mol dm^{-3} in the temperature range 20°C to 75°C are plotted against the measuring wavelength in Fig.4. In the case of SDS and SDBS, the optical density at about 520 nm decreased with increase in temperature, but in the case of DSS, it increased with increasing temperature until 35°C, and then it decreased for higher temperatures. 4-NH_2 in the DSS solutions was found to undergo both hyperchromic effect and transition of chemical species. Thermochromism also occurred in the SDS concentration of the cmc range (I, II in Table 1) and for the dye amount just lower than the limit of solubilization, as in the case in SDS solutions.

(4) For SL-4-NH_2 Systems: Optical densities for the SL solutions of 5.0×10^{-2} mol dm^{-3} (at B region), including 4-NH_2 of 1.6×10^{-4} mol dm^{-3} in temperature range 30°C to 70°C are plotted against the measuring wavelength in Fig. 5. Figure 5 shows that the maximal absorption of SL solutions was independent of temperature. Thus, we found that the concentration of SL is not significant.

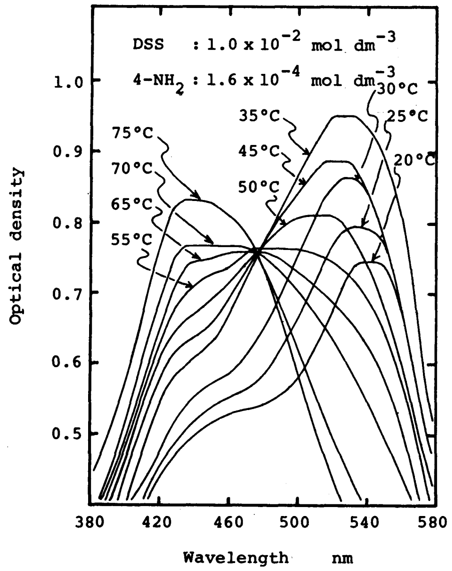

Fig. 4. Effect of temperature on absorption spectra for DSS solution which have dissolved 4-NH_2. (between I and II: B region)

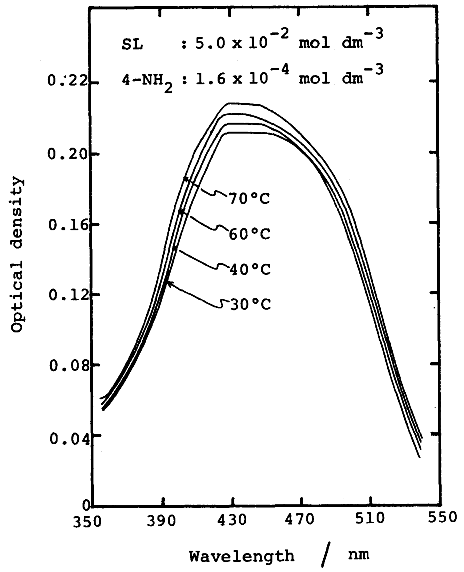

Fig. 5. Effect of temperature on absorption spectra for LS solution which have dissolved 4-NH_2. (regardless of the concentration of LS)

(5) For 4-OH and NA: All of the maximal absorptions of the solutions were unchanged with increase in temperature; the values were 480 nm (4-OH) and 380 nm (NA) for all kinds and concentrations of surfactants.

Discussion

The Isosbestic Point at A Region. In the case of 4-NH_2 and anionic surfactants except SL of lower concentration, the isosbestic point was recognized at a 520 nm band, as shown in Fig. 1. Kuroiwa[14] describes how the isosbestic point like this is recognized in SDS (and/or SDBS)-1,4,5,8-tetraaminoanthraquinone system because of the formation of a dye–surfactant complex.

Nemoto *et al.*[15,16] report that the distinction between hydrophilic and hydrophobic complexes can be made by measuring the surface tension of the solution and by extracting the solution from chloroform. In the same manner, we previously confirmed the hydrophobic complex.[11] Except for SL, the formation of hydrophobic complex in the cases of SDBS and DSS was thus established. We adopted the continuous variation method[13] in order to determine the binding molar ratio of these complexes. The results are shown in Table 2. Except for SL, surfactants including strongly polar groups and 4-NH_2 seem to form a hydrophobic complex of 1 : 1.

TABLE 2. MOLAR RATIO OF COMPOUND FORMED FROM DYE (4-NH_2) AND VARIOUS SURFACTANTS BY CONTINUOUS VARIATION METHOD (λ_{max}=440 nm)

Surfactant	Ratio (S:D)
SDS	1 : 1
DSS	1 : 1
SDBS	1 : 1
SL	—

The Thermochromism at B Region. As can be seen from Figs. 1 and 3, the maximal absorption of 4-NH$_2$ at A region is at the 440 nm band, while that at C region is at the 520 nm band regardless of temperature: it seems that the maximal absorption at 440 nm band arises from the dispersing state of 4-NH$_2$ in monomer phase, while that at 520 nm band arises from that solubilized into micellar phase. The maximal absorption at B region, in other words, that at the neighborhood of the cmc, is dependent on temperature. The results can be interpreted as follows. The cmc of anionic surfactants are shifted from lower concentration to higher concentration with increasing temperature.[17] Moreover, it is well known that the amount of solubilization is dependent on the concentration of anionic surfactant.[18,19] Thus, with increasing temperature, the values of the cmc shifted from lower concentration to higher concentration and the number of surfactant micelles decreased; as a result, the 4-NH$_2$ solubilized in surfactant micelle is released into a monomer phase. Therefore, the complementary color of the solution at B region changed with temperature; the so-called thermochromism occurred.

In the C region, there are many micelles in the solution, so that the increase of the value of cmc is slight and the 4-NH$_2$ solubilized in micelle does not release into the monomer phase with increasing temperature. Therefore, thermochromism does not occur. In general, a dye including amino group in organic solvent takes the azo form.[20] The spectrum in dodecane provides an absorption band at 440 nm, which is attributed to the azo form. Accordingly, the tautomer of 4-NH$_2$ at both A region and B region under higher temperature seems to be azo form.

Secondly, we consider the structure of 4-NH$_2$ in surfactant micellar solutions other than SL. For the location of 4-NH$_2$ in surfactant micelle, we[21] found that, because the functional group of the dye is fairly strong and dissociates slightly, it thrusts the functional group out of the SDS micelles and its hydrophobic parts penetrate into the palisade layers of SDS micelles. Moreover, because the pH of the SDS solution to which 4-NH$_2$ was added is larger than that of SDS alone (6.8—7.9), 4-NH$_2$ is thought to act as a base.

Klotz *et al.*[22] describe the protonation process as follows: the first proton goes to the amino group and then a second proton goes to the azo group with an increase in the hydrogen ion concentration. On the contrary, Tanizaki *et al.*[9] point out that a proton addition to amino group must shift the color band to a shorter wavelength, because the electronic theory insists that the protonated amino group cannot be conjugated with the ring system because of the number of the π-type electrons is too few: the protonation to the β-azo-nitrogen atom of the dye shifts the color band to a longer wavelength than that of azo form. The halochromism of 4-NH$_2$ is shown in Fig. 6. As can be seen from Fig. 6, the spectrum with a peak at a 440 nm band in an alkaline solution changed into another one (520 nm) with an increase in the hydrogen ion concentration. According to Tanizaki *et al.*,[9] the spectrum with a peak at 520 nm seems to be the protonation to β-azo-nitrogen atom of the dye (in Fig. 7). However, this study was not made in a higher acid solution but in a neutral solution. From the study of synthesis of oil dye reported previously,[21] we found that the replacement reaction occurred not at the position of azo group, but at the position of amino group. Furthermore, Matsuoka *et al.*[23] suggest that, when the proton goes to β-azo-nitrogen atom, electric charge transfer occurs; as a result a nitrogen atom of amino group becomes positively charged. The 4-NH$_2$, described previously, was solubilized into SDS micelle as the functional group (amino group) out of the micelle,[21] and then it becomes a counterion for the surface negative charge of the micelle. And so this micelle was stable at room temperature. Therefore, the quinoidal form of 4-NH$_2$ was stabilized in the SDS micelle at room temperature.

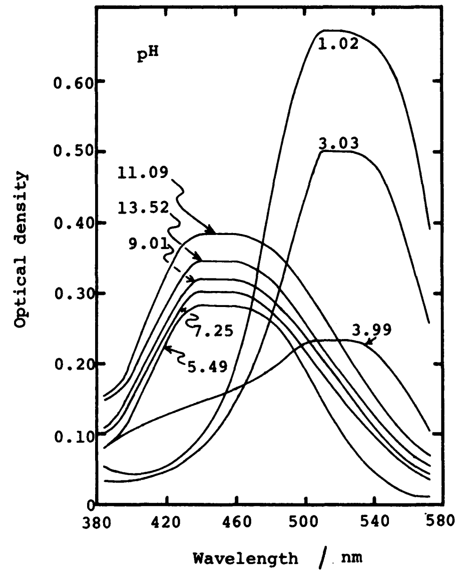

Fig. 6. Effect of pH on absorption spectra for 4-NH$_2$ aqueous solutions.

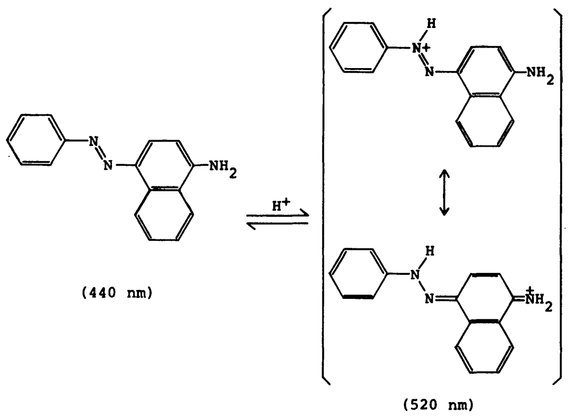

Fig. 7. Relationship between protonation process of dye and λ_{max}.

For SL Solutions. As can be seen from Fig. 5, regardless of the concentration of SL and temperature, the maximal absorption was still a peak at 440 nm. SL is mild alkaline, so that the pH value of solution is shifted to basic 8.5, to prevent protonation. In general, an aliphatic soap like SL is partly hydrolyzed in water.[24] It seems that, because the aliphatic acid produced is preferentially solubilized into SL micelles, the 4-NH_2 is adsorbed on the surface (hydrophilic parts) of the solubilized micelles, as mentioned by Kondo and Meguro.[25] Therefore, 4-NH_2 is always placed in the bulk phase, and the maximal absorption is 440 nm. However, an aliphatic soap like SL does not form a spherical micelle like SDS, but a hexagonal packing of cylindrical micelles,[26] where the insoluble hydrocarbon chains are turned inward, in a neutral particle of soap, and the heavily hydrated carboxylate group is presented to the surrounding water.[27] It seems that the 4-NH_2 exists in the surrounding water, even when the concentration of SL is somewhat above the cmc.

In any event, because the polar nature of SL is weaker than that of SDS, the proton in water is not in contact with the dye; so the protonation to the 4-NH_2 did not occur.

References

1) W. Luck, *Angrew. Chem.*, **72**, 57 (1960); W. Luck, *Melliand Textiller*, **41**, 315 (1960).

2) T. D. Tuong, K.Otsuka, and S. Hayano, *Chem. Lett.*, **1977**, 1319.

3) A. Datyner, *J. Colloid Interface Sci.*, **65**, 527 (1978).

4) Y. Nemoto, *Yukagaku*, **28**, 809 (1979).

5) S. Kuroiwa, *Sen'i Gakkai Shi*, **20**, 52, 183 (1964).

6) S. Kuroiwa, *Sen'i Gakkai Shi*, **36**, 27 (1980).

7) Y. Nemoto, *J. Colloid Interface Sci.*, **79**, 313 (1981).

8) M. Mitsuishi, R. Kamimura, M. Ieda, K. Shinohara, and N. Ishii, *Sen'i Gakkai Shi*, **32**, T-382 (1976).

9) Y. Tanizaki, *Bull. Chem. Soc. Jpn.*, **39**, 558 (1966).

10) S. Tokita, "Color Chemistry," Maruzen, Tokyo (1982), p. 136.

11) M. Abe, N. Suzuki, and K. Ogino, *J. Colloid Interface Sci.*, in press.

12) K. Tajima, *Nippon Kagaku Kaishi*, **1973**, 83.

13) S. Kuroiwa and S. Ogasawara, *Nippon Kagaku Kaishi*, **1976**, 790.

14) S. Kuroiwa and S. Ogasawara, *Sen'i Gakkai Shi*, **24**, 536 (1968).

15) Y. Nemoto and H. Funahashi, *J. Colloid Interface Sci.*, **62**, 95 (1977).

16) Y. Nemoto and H. Funahashi, *Shikizai Kyokai Shi*, **53**, 488 (1980).

17) B. D. Flockhart and A. R. Ubbelohde, *J. Colloid Sci.*, **8**, 428 (1953).

18) K. Ogino, M. Abe, and N. Takeshita, *Bull. Chem. Soc. Jpn.*, **49**, 3679 (1976).

19) K. Ogino, M. Abe, and N. Takeshita, *Bull. Chem. Soc. Jpn.*, **51**, 1880 (1978).

20) K. Konishi and N. Kuroki, "Gousei Senryo No Kagaku," Maki Shyoten, Tokyo (1978), p. 157.

21) M. Abe, N. Suzuki, and K. Ogino, *J. Colloid Interface Sci.*, **93**, 285 (1983).

22) M. I. Klotz, *J. Am. Chem. Soc.*, **76**, 5136 (1954).

23) M. Matsuoka, *Shikizai Kyokai Shi*, **53**, 724 (1980).

24) P. Ekwall, *Kolloid-Z.*, **92**, 144 (1940); S. Miyashita and Y. Uzu, *Yukagaku*, **29**, 350 (1980); H. W. Brouwer and W. Skoda, *Kolloid-Z.*, **234**, 1138 (1969).

25) T. Kondo and K. Meguro, *Bull. Chem. Soc. Jpn.* **32**, 267, 857 (1959).

26) K. L. Mittal and P. Mukerjee, "Micellization, Solubilizaion, and Microemulsions," ed by K. L. Mittal, Plenum Press, New York (1977), Vol. 1, p. 10.

27) J. W. McBain, "Colloid Science," D. C. Heath and Company, Boston (1950), p. 5.