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Solubilization Behavior of Mixed Micelles of Anionic and Nonionic Surfactants in Relation to Their Micellar Structures

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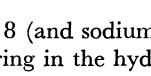
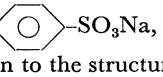
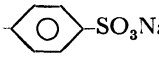
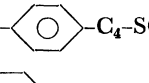
The solubilization behavior of mixed micelles of nonionic and anionic surfactants toward a water-insoluble dye, Yellow OB, has been studied. The surfactants examined were a nonionic surfactant, dodecyl polyoxyethylene ether (C_{12}POE), and anionic surfactants with the chemical structure of C_m-  -C_n-SO_3Na, where $m+n=8$ and where m or n is 0, 4, or 8 (and sodium decyl sulfonate for reference). The solubilization greatly depends on the position of the benzene ring in the hydrocarbon chain of the anionic surfactant mixed; in the mixture of C_{12}-POE and C_8-  -SO_3Na, the synergistic effect in solubilization is remarkable. The results have been discussed in relation to the structure or compactness of the polyoxyethylene shell of the mixed micelle, and in relation to the interaction of anionic and nonionic surfactants in their mixed micelle, which had previously been observed by NMR measurements.

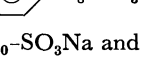
In general, the solubilizing capacity of a nonionic surfactant of the polyoxyethylene type for water-insoluble matetials is much greater than that of an ionic surfactant with the same hydrocarbon chain length as that of the nonionic surfactant. For example, the solubilizing capacity of dodecyl polyoxyethylene ether (C_{12}POE) for a water-insoluble dye, Yellow OB, is approximately ten times greater than that of sodium dodecyl sulfate.[1] This fact suggests that the polyoxyethylene part in the molecule plays an important role in solubilization, and also that the solubilizing capacity depends greatly on the structure of the polyoxyethylene shell of the micelle.

In previous papers[2,3] studying mixed micelles of C_{12}POE and an anionic surfactant with a benzene ring in the molecule by nuclear magnetic resonance (NMR), it has been shown that, in the mixed micelle, an interaction occurs between the polyoxyethylene part of C_{12}POE and the benzene ring of the anionic surfactant. The extent of the interaction depends also on the position of the benzene ring in the hydrocarbon chain. Such an interaction might be related to the solubilization behavior of the mixed micelles of nonionic and anionic surfactants of these types.

In the present work, the solubilization behavior toward Yellow OB of the following mixed surfactant systems has been studied in order better to understand the interaction of two different surfactants in their mixed micelle and the effect of the structure of the polyoxyethylene shell of the mixed micelle on its solubilization behavior:

System I: C_8-  -SO_3Na and C_{12}POE

System II: C_4-  -C_4-SO_3Na and C_{12}POE

System III:  -C_8-SO_3Na and C_{12}POE

System IV: C_{10}-SO_3Na and C_{12}POE

The three anionic surfactants in Systems I, II, and III are different only in the position of the benzene ring in the hydrocarbon chain, and the C_{10}-SO_3Na surfactant in System IV has no benzene ring in the molecule.

1) F. Tokiwa, *J. Phys. Chem.*, **72**, 1214 (1968).
2) F. Tokiwa and K. Tsujii, *J. Phys. Chem.*, **75**, 3560 (1971).
3) F. Tokiwa and K. Tsujii, *J. Colloid Interface Sci.*, **41**, 343 (1972).

Experimental

Materials. The sodium *p*-octylbenzene sulfonate (abbreviated to $C_8\phi S$), sodium δ-(4-butyl phenyl) butyl sulfonate (abbreviated to $C_4\phi C_4S$), and sodium ω-phenyloctyl sulfonate (abbreviated to ϕC_8S) were the same samples as those used in the previous experiments.[2,3] The sodium decyl sulfonate (abbreviated to $C_{10}S$) was prepared by the reaction: $C_8H_{17}CH{=}CH_2+NaHSO_3\rightarrow C_{10}H_{21}SO_3Na$, using *t*-butylperbenzoate as the catalyst. The product obtained, $C_{10}S$, was recrystallized three times from an ethanol-water mixture (95:5). The dodecyl polyoxyethylene ether with 9 oxyethylene units purified by the countercurrent solvent extraction method,[4] was the sample used in a previous work.[2] The polyethylene glycol (abbreviated to PEG), the average molecular weight of which was approximately 400, was of a reagent grade and was purified by ion exchange with Amberlite IR-120 and IRA-410. The Yellow OB (1-*o*-tolyl-azo-2-naphthylamine) was of a reagent grade; it was purified by a procedure previously described.[1]

Solubilization Measurements. The sample solutions were prepared by adding the desired amounts of the anionic surfactant to an aqueous solution of the nonionic surfactant, $C_{12}POE$, of 5×10^{-3} M. Solubilization runs were made in a water bath at 30 ± 0.1 °C for 65 hr to attain equilibrium, the procedure described elsewhere[1] being employed. The Yellow OB described above was used as a solubilizate. The amounts of the solubilized dye were determined by optical-density measurements at a wavelength of 445 mμ by means of a Shimadzu Model AQV-50 spectrophotometer.

The critical micelle concentration (CMC) and the solubilizing capacity of each surfactant were determined from the inflection and slope respectively of the solubilization *vs.* concentration curve.

A similar method was used to determine the solubility of Yellow OB in the mixed solvent of PEG and water at various mixing ratios.

Results and Discussion

Figure 1 shows the solubilization *vs.* concentration curves for Systems I, II, III, and IV, where the amount of Yellow OB, *S*, solubilized by mixed micelles is plotted against the molar concentration of each anionic surfactant, *C*, the concentration of the nonionic surfactant, $C_{12}POE$, being kept constant at 5×10^{-3} M. (On the ordinate, the value of *S* for $C_{12}POE$ alone is displaced to zero.) In System I, a remarkable, synergistic effect in the solubilization of the mixture of $C_8\phi S$ and $C_{12}POE$ is observed. In the other systems, however, their solubilizing capacities in the region of relatively low concentrations are smaller than that of $C_{12}POE$ alone; they depend on the type of anionic surfactant.

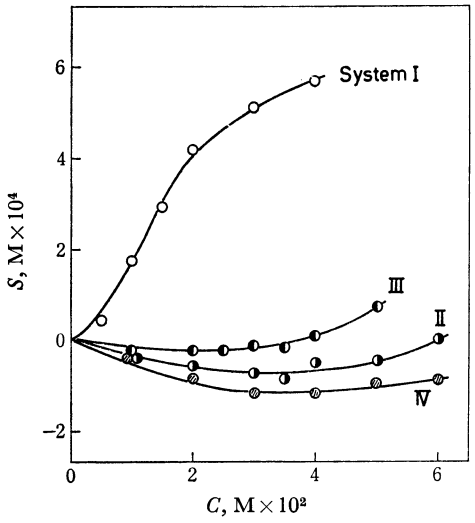


Fig. 1. The curves of the solubilization of Yellow OB *vs.* the concentration of anionic surfactant for Systems I, II, III, and IV at 30 °C, the concentration of $C_{12}POE$ being kept constant at 5×10^{-3} M.

It is known that when two different surfactants are mixed in an aqueous solution, mixed micelles are formed rather than the respective micelles of each surfactant. If we assume that the additivity rule can be applied to the solubilizing capacity, *s*, of these mixed micelles, then the value of *S* can be expressed as:

$$S = (C^t - C^\circ_{1,2})(s_1x_1 + s_2x_2) \quad (1)$$

where the subscripts 1 and 2 refer to anionic and nonionic surfactants respectively; *s*, the solubilizing capacity; *x*, the mole fraction in the micelle phase; $C^\circ_{1,2}$, the CMC of the mixture of the two surfactants, and C^t, the total concentration, *i.e.*, the sum of the concentrations of Surfactants 1 and 2. The $(C^t - C^\circ_{1,2})$ term in Eq. (1) expresses the concentration of surfactants forming mixed micelles. The values of s_1, s_2, and C^t are known, and the values of x_1, x_2, and $C^\circ_{1,2}$ may be estimated as will be shown below.

If we consider a two-component system consisting of both monomer and micelle phases, and assume the system to be ideal, we know that for each component the chemical potentials in the two phases are identical at equilibrium. Under such conditions, the equilibrium between monomers and micelles in a mixed solution of anionic and nonionic surfactants may be expressed[5,6] as:

$$y_1C^\circ_{1,2} = x_1C^\circ_1 \quad (2)$$

and:

$$y_2C^\circ_{1,2} = x_2C^\circ_2 \quad (3)$$

where *x* and *y* are the mole fractions of the surfactants in the micelle and monomer phases respectively, and where C° is the CMC. From Eqs. (2) and (3), the CMC of the mixed surfactants, $C^\circ_{1,2}$, may be written in the form:

$$C^\circ_{1,2} = (C^\circ_1 - C^\circ_2)x_1 + C^\circ_2 \quad (4)$$

as $x_1+x_2=1$ and $y_1+y_2=1$. By definition, on the other hand, the value of x_1 is expressed by:

$$x_1 = \frac{C_1^{\,M}}{C_1^{\,M}+C_2^{\,M}} = \frac{C_1^{\,t}-C_1^{\,m}}{C^t-C^\circ_{1,2}} = \frac{\alpha_1C^t-y_1C^\circ_{1,2}}{C^t-C^\circ_{1,2}} \quad (5)$$

where the superscripts m and M refer to the monomer and the micelle respectively, and where α_1 is the mole fraction of Surfactant 1 in the bulk solution. By combining Eq. (5) with Eqs. (2) and (4), we obtain:

4) K. Nagase and K. Sakaguchi, *Kogyo Kagaku Zasshi*, **64**, 635 (1961).

5) F. Daniels and R. A. Alberty, "Physical Chemistry," John Wiley, New York, N. Y. (1966), p. 145.

6) F. Tokiwa, K. Ohki, and I. Kokubo, This Bulletin, **41**, 2845 (1968).

$$x_1 = \frac{1}{2}\{(1+r)-[(1+r)^2-4r\alpha_1]^{1/2}\}$$

$$r = \frac{C^t}{C_1^\circ - C_2^\circ} \tag{6}$$

The value of $C_{1,2}^\circ$ can also be evaluated by substituting x_1 into Eq. (4). The values of C_1° and C_2° used for these calculations are given in Table 1, together with the values of s_1 and s_2 calculated from the slope of the S *vs.* C curve for each surfactant.

Table 1. Values of C_1° and C_2° (mol/l), and s_1 and s_2 (mol, yellow OB/mol, surfactant) for each system

	$C_1^\circ \times 10^2$	$C_2^\circ \times 10^4$	$s_1 \times 10^3$	$s_2 \times 10$
System I	1.17	1.30	13.0	1.13
System II	2.90	1.30	4.67	1.13
System III	3.45	1.30	8.20	1.13
System IV	4.50	1.30	5.50	1.13

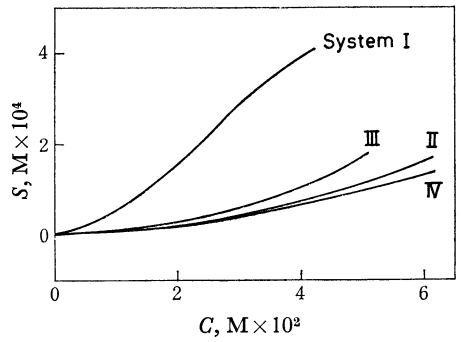


Fig. 2. The solubilization *vs.* concentration curves, calculated by Eq. (1), for Systems I, II, III, and IV.

Using the values of x_1 and x_2 (by definition, $x_2 = 1-x_1$) for Eq. (1), we can draw the S *vs.* C curves of Systems I, II, III, and IV shown in Fig. 1. When these calculated S *vs.* C curves are compared with the observed S *vs.* C curves shown in Fig. 1, we can see that Eq. (1) does not well explain the solubilization behavior of each system; that is, in System I the observed curve is higher than the calculated curve throughout the concentration region examined, and in Systems II, III, and IV the observed curves are lower than the calculated ones. As will be described later, the remarkable, synergistic effect in solubilization observed in System I can be explained in terms of a strong interaction between the benzene ring of $C_8\phi S$ and the polyoxyethylene chain of C_{12}POE in the mixed micelle.[2,3]

The solubilizing capacity of the C_{12}POE micelle toward Yellow OB is probably closely related to the compactness or structure of the polyoxyethylene shell of this micelle. According to previous works,[1,7] sodium dodecylpolyoxyethylene sulfate, which has an ionic head at the terminal of the polyoxyethylene chain, can solubilize the dye much less than C_{12}POE because of less compactness of the polyoxyethylene shell as a result of the electrical repulsion between the charged heads.

7) F. Tokiwa, *J. Phys. Chem.*, **72**, 4331 (1968).

In the present cases, by considerations similar to those indicated above, the polyoxyethylene shell of the C_{12}POE micelle will be made less compact or diluted by mixed micelle formation with an anionic surfactant. This will then result in less solubilization. The compactness of the polyoxyethylene shell consisting of n_2 molecules of C_{12}POE may be written in the form:

$$p = \frac{(M_{POE}/N)n_2}{v_{POE}} \tag{7}$$

where p is the compactness expressed by weight/volume; v_{POE}, the volume of the polyoxyethylene shell of the micelle; M_{POE}, the molecular weight of the polyoxyethylene chain of the C_{12}POE molecule, and N, the Avogadro number. When n_1 molecules of an anionic surfactant are incorporated into this micelle, the volume of the shell will be increased proportionally to n_1. Then, the value of p becomes:

$$p = \frac{(M_{POE}/N)n_2}{v_{POE}+\beta n_1} \tag{8}$$

where β is a constant, *i.e.*, the volume factor of the anionic surfactant molecule added.

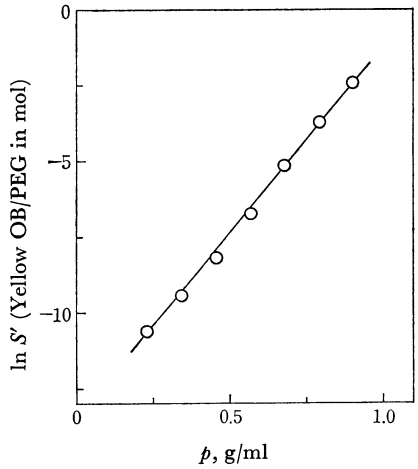


Fig. 3. The solubility of Yellow OB in aqueous PEG solution as a function of the concentration of PEG at 30 °C.

Let us now turn our attention to the solubility of Yellow OB in mixed solvents of PEG and water at different mixing ratios in order to relate p to the solubilizing capacity of mixed micelles. In Fig. 3, the logarithm of the solubility of Yellow OB, S', is plotted against the concentration of PEG, p, in aqueous solution [the value of p corresponds to p in Eq. (8)]. There is a linear relation between ln S' and p; it is given by the equation:

$$\ln S' = Ap + B \tag{9}$$

where A and B are constants. From the slope and intercept of the straight line, the A and B constants may be determined to be 12.2 ml/g and −13.5 respectively.

Here, we regard the polyoxyethylene shell of a mixed micelle as a "small" mixed solvent system consisting of PEG and water. The solubility, S', in Eq. (9), may then be put equal to the solubilizing capacity, S_{dil}^M, of a "diluted" polyoxyethylene shell of the mixed micelle, since the dilution of the polyoxyethylene shell

by an anionic surfactant and the dilution by water are considered to have a similar effect on the solubility of Yellow OB. Then, the compactness, p, of the shell given by Eq. (8) may be related to p in Eq. (9). By combining Eq. (8) with Eq. (9), we obtain:

$$\ln S^{M}_{dil} = A\frac{(M_{POE}/N)n_2}{v_{POE}+\beta n_1} + B$$

$$= A\frac{(M_{POE}/N)}{(v_{POE}/n_2)+\beta(n_1/n_2)} + B \qquad (10)$$

where (n_1/n_2) is the molar ratio of the anionic/nonionic surfactants in the micelle phase and has the relation:

$$n_1/n_2 = x_1/x_2 = x_1/(1-x_1) \qquad (11)$$

The value of (v_{POE}/n_2) is evaluated by inserting the value of S^{M}_{dil} at $x_1/x_2=0$, which may be estimated from the difference between the solubilizing capacities of $C_{12}POE$ and sodium dodecyl sulfonate, into Eq. (10). By using Eq. (10), the S^{M}_{dil} *vs.* (x_1/x_2) curve, for example, at $\beta=15$ Å^3 is drawn in Fig. 4, where β is estimated as will be described later.

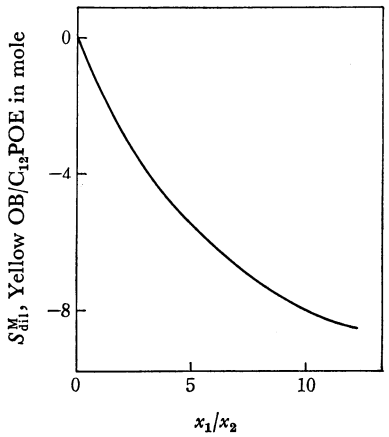


Fig. 4. The solubilizing capacity S^{M}_{dil} of a "diluted" polyoxythylene shell of mixed micelles as a function of x_1/x_2, according to Eq. (10).

From Eq. (6), the variable (x_1/x_2) in Eq. (11) can be given by two variables, C^t and α_1, which are determined in this case only by the concentration, C, of the anionic surfactant. Thus, S^{M}_{dil} can be converted into S_{dil}, which expresses the moles of Yellow OB solubilized per liter of the surfactant solution. In Fig. 5, the S_{dil} *vs.* C relationship at $\beta=15$ Å^3 for System IV is shown.

The constant β in Eq. (10) may be estimated as follows. In System IV, where the anionic surfactant, $C_{10}S$, has no benzene ring in the molecule, we assume that no interaction occurs between $C_{10}S$ and$C_{12}POE$. On this assumption, the difference between the value observed (S_{obsd}) and the value calculated (S_{calcd}) by Eq. (1) may be ascribed to the dilution effect of $C_{10}S$ on the polyoxyethylene shell of the $C_{12}POE$ micelle, which can itself be evaluated from Eq. (10). Then, the constant β in Eq. (10) may be estimated by trial and error unitl the $(S_{obsd}-S_{calcd})$ *vs.* C curve overlaps with the S_{dil} *vs.* C curve. When the value of β is chosen as 15 Å^3, we obtain Fig. 5, where the broken line indicates the S_{dil} *vs.* C curve and where the solid line

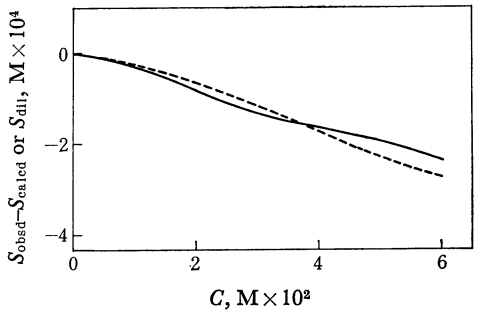


Fig. 5. The $(S_{obsd}-S_{calcd})$ *vs.* C_{calcd} curve (the solid line), and the S_{dil} *vs.* C curve (the broken line) for System IV.

indicates the $(S_{obsd}-S_{calcd})$ *vs.* C curve for System IV. These two curves are in relatively good agreement with each other, showing Eq. (10) to be reasonable although some deviation is seen at high concentrations.

The value of $\beta(=15$ Å$^3)$ seems somewhat smaller than the expected value. However, this can be explained by taking into consideration the facts that the hydrocarbon portion of the anionic surfactant molecule is located in the hydrocarbon core of the mixed micelle, and that only a part of the hydrophilic head can contribute to the dilution of the polyoxyethylene shell of the micelle. For the same reasons, it may be permissible to use the β value of $C_{10}S$ for other anionic surfactants which have different structures of the hydrocarbon part.

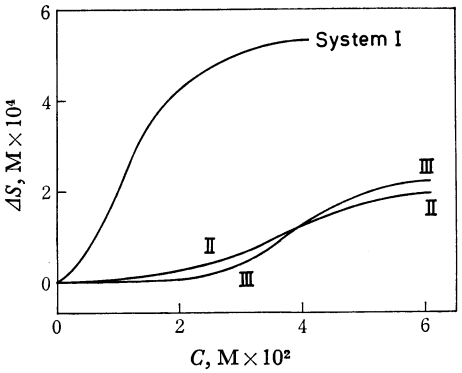


Fig. 6. The synergistic effect, ΔS, in solubilization as a function of C for Systems I, II, and III.

In System I, II, or III, where each anionic surfactant has a benzene ring in the molecule, the difference between the values of S_{obsd} and $(S_{calcd}+S_{dil})$ at a given concentration, C, of the anionic surfactant may be interpreted as a synergistic effect (ΔS) in the solubilization at this C. Figure 6 shows the ΔS *vs.* C curves for Systems I, II, and III; in the calculation of S_{dil}, β is also taken to be 15 Å^3, as has been described above. In System IV, of course, ΔS $(=S_{obsd}-(S_{calcd}+S_{dil})]$ is zero at any C, as has been assumed in the above discussion.

The NMR studies[2,3] of mixed micelles in Systems I, II, and III have shown that the polyoxyethylene chain of $C_{12}POE$ interacts with the benzene ring of the respective anionic surfactant; the extent of the interaction is in order of System I>II>III. The remarkable high values of ΔS seen in System I may

be ascribed to this interaction. On the other hand, the ΔS values in Systems II and III are smaller than the value in System I at all concentrations, and no considerable difference is seen between these two systems. This may be explained by the weaker interaction between the polyoxyethylene chains and the benzene rings in mixed micelles, although the interaction in System II, observed by NMR measurement, is slightly stronger than that in System III.[3)]

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