Adsolubilization Behavior of Dyes Caused by Mixed Surfactant Bilayers Formed on Alumina

Kunio ESUMI,* Yuichi SAKAMOTO, Tetsuya NAGAHAMA, and Kenjiro MEGURO
Department of Applied Chemistry and Institute of Colloid and Interface Science,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

(Received March 24, 1989)

The adsolubilization of dyes (yellow OB and azobenzene) was performed on mixed bilayers consisting of anionic and nonionic surfactants formed on α-alumina. The adsolubilization capacity of the two dyes increased with the increase in the concentration of the dyes solubilized in the supernatant. The mixed bilayer consisting of anionic hydrocarbon (lithium dodecyl sulfate) and nonionic hydrocarbon surfactants (polyoxyethylene nonylphenyl ether) showed a greater adsolubilization capacity than that consisting of anionic fluorocarbon (lithium perfluorooctanesulfonate) and nonionic hydrocarbon surfactants. Further, the adsolubilization capacity of the dyes was affected by the oxyethylene chain length of the nonionic hydrocarbon surfactant in the mixed bilayer.

The solubilized amounts of solubilizates depend on the kinds of surfactants. Generally, the order of solubilization capacity, i.e., the moles of hydrocarbons and polar compounds solubilized per mole of surfactant, appears to be as follows: nonionics>cationics>anionics for surfactants with the same hydrophobic chain length.[1–3] The solubilization behavior by mixed micelles of anionic and nonionic surfactants has also been investigated;[4–7] Muto et al.[8] reported, from their comparisons of ideal and observed solubilized amounts, that the ratio of observed solubilized amounts to ideal amounts of yellow OB and azobenzene decreases when two surfactants are mixed, while it decreases with an increase in the difference of the moles of solubilizates per mole of surfactant between two surfactants in the mixed systems.

On the other hand, the structure of a surfactant adsorbed layer on particles has been characterized by using a fluorescence technique, ESR, and Raman spectroscopy.[9–11] Chandar et al.[9] demonstrated that the adsorbed layer of sodium dodecyl sulfate at the alumina-water interface is similar to that in hemimicellization. Esumi et al.[12,13] reported on mixed surfactant bilayers consisting of hydrocarbon and fluorocarbon surfactants formed on ferric hydrosol and alumina. The microenvironmental properties of these mixed bilayers were studied on the alumina by means of the fluorescence-probing method. However, this fluorescence-probing method could not be used for ferric hydrosol because of the large scattering by the sol alone. Such adsorbed surfactants of micelle-like surfactant aggregates are called admicelles.[14] When micelles incorporate other molecules into their structure, it is called solubilization: here, incorporation by admicelles will be referred to as adsolubilization.[15]

Recently, we found[16] that some alcohols are adsolubilized more efficiently into anionic surfactant bilayers formed on alumina than they are solubilized into the micelles. Thus, it is interesting to compare the solubilization behavior into a micelle system to the adsolubilization into the surfactant bilayer on particles, since they seem to have similar properties.

In this work, the adsolubilization of yellow OB and azobenzene into single and mixed surfactant bilayers formed on α-alumina is investigated by measuring the amounts of the dyes adsolubilized.

Experimental

Materials. Lithium perfluorooctanesulfonate (LiFOS) and lithium dodecyl sulfate (LiDS) were synthesized.[17] LiFOS was purified by repeated crystallizations from dioxane after extraction with ethanol, and LiDS with ethanol together, and with a mixture of hexane and 2-propanol. The purity of these samples was confirmed by elemental analyses and by the lack of a minimum in the surface tension. The polyoxyethylene nonylphenyl ethers (NP7.5 and NP20) were supplied by the Nikko Chemicals Co., Ltd.; each number of the NP indicates the average oxyethylene chain length in the molecule. These NPs were used without further purification. The yellow OB and azobenzene were obtained from the Tokyo Kasei Co. and were used as received.

The alumina used was α-alumina of a 99.995% purity, supplied by Showa Denko K. K. The specific surface area, determined from the nitrogen-gas adsorption at −196 °C, was 10.1 $m^2 g^{-1}$ The average particle diameter was 500 nm, as determined by means of a particle analyzer based on photon correlation spectroscopy (Autosizer Model 700, Malvern Co., Ltd.).

Methods and Measurements. An aqueous surfactant solution required to form a bilayer was placed in contact with 0.3 g of alumina. A series of solutions was prepared, containing various concentrations of yellow OB or azobenzene solubilized in surfactant solutions. Then, these solutions containing solubilizates were added to the suspensions. After attaining the equilibrium of adsolubilization, the suspension was centrifuged. The concentration of dyes solubilized in the supernatant was determined using a UV spectrophotometer (200 A, Hitachi Co.).

The amount of solubilizates adsolubilized was determined from the difference between the concentrations before and after the adsolubilization. Similarly, the amounts of solubilizates solubilized in micelles in the absence of alumina were determined. The amounts of anionic surfactants adsorbed were determined by means of an isotachophoretic analyzer (IP-3A, Shimadzu Ltd.), while those of nonionic surfactants, which have an absorption band at 275 nm, were determined by means of a UV spectrophotometer.

All the experiments were performed at 25 °C and at pH 3.5, which was adjusted by the use of nitric acid. In order to keep the ionic strength constant, 10 mmol dm^{-3} of lithium nitrate was used.

Calorimetric measurements were made with a Multi micro calorimeter MMC-5111 (Tokyo Rico Co., Ltd.), in which the reaction vessel was immersed in a thermostatted bath maintained at 25±0.05 °C. The enthalpies of the formation of surfactant bilayers on the alumina were determined by breaking glass ampoules containing flocculated alumina in an LiDS or LiFOS aqueous solution into NP aqueous solutions. Correction was made for the heat change associated with the breaking of the ampoules and with mixing of the surfactant aqueous solutions.

Results and Discussion

When LiFOS or LiDS is adsorbed on positively charged alumina, the alumina flocculates. In this study, it is found that the optimum flocculation concentration for alumina is 1 mmol dm^{-3} for both LiFOS and LiDS. On the addition more than 0.6 mmol dm^{-3} of NPs to the optimum flocculated alumina, the alumina becomes redispersed. This redispersion process has been interpreted as being caused by the formation of a mixed bilayer[12,18,19] on the alumina in such a manner that the NP molecule is adsorbed on the LiFOS or LiDS-covered alumina, with its hydrophilic groups oriented towards the liquid phase. Thus, the mixed bilayer of LiFOS and NP is formed by the interaction between the hydrocarbon chains of NP and the fluorocarbon chains of LiFOS, while that of LiDS and NP is formed by the interaction between the hydrocarbon chains of NP and of LiDS. The redispersion state was confirmed by measuring the particle size of alumina; it was found to be about 500 nm. The interior environment in the mixed bilayer thus formed appears to have properties similar to those in mixed micelles.

Figure 1 shows the adsolubilization capacity for yellow OB in the mixed bilayers on the alumina. Here, the additive concentration of NPs was 1 mmol dm^{-3}. The adsolubilization capacity for yellow OB is expressed by dividing the amount of the yellow OB adsolubilized per unit of weight of the alumina by the total amounts of surfactants adsorbed per unit of weight of the alumina. Table 1 tabulates the amounts of surfactants adsorbed in the mixed bilayers. It can be seen that the amount of NP decreases with an increase in the oxyethylene chain lengths of NP for both LiDS-NP and LiFOS-NP

Table 1. Amounts of Surfactants Adsorbed in Mixed Bilayers

System	Amount adsorbed ($\times10^{-5}$ mol g^{-1}) LiFOS	LiDS	NP	Total
LiFOS-NP7.5	1.62	—	2.30	3.92
LiDS-NP7.5	—	1.98	3.20	5.18
LiFOS-NP20	1.62	—	1.80	3.42
LiDS-NP20	—	1.98	2.20	4.18

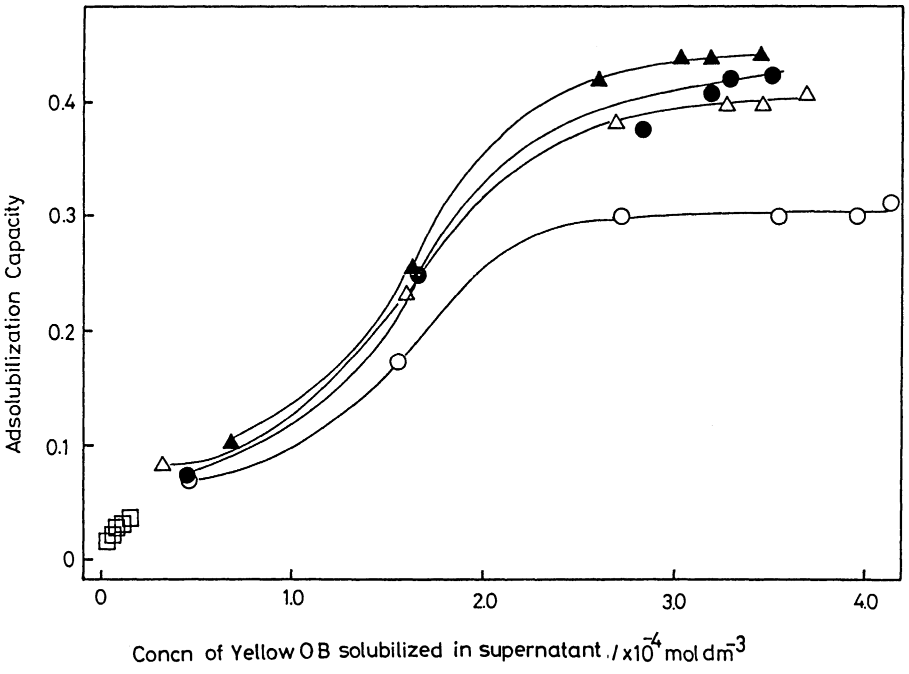

Fig. 1. Adsolubilization capacity for yellow OB in bilayers on alumina as a concentration of yellow OB solubilized in supernatant: (△) LiDS-NP7.5; (○) LiFOS-NP7.5; (▲) LiDS-NP20; (●) LiFOS-NP20; (□) LiDS-LiDS.

systems, and that the total amount of surfactant is greater for the LiDS-NP system than for the LiFOS-NP system with the same oxyethylene chain length of NP. The adsolubilization capacities for yellow OB in the mixed bilayers increase with an increase in the concentration of yellow OB solubilized in the supernatant; they appear to approach 0.5 except for the LiFOS-NP7.5 system. This indicates that the incorporation of yellow OB occurs systematically with the mixed bilayer (ratio of yellow OB : NP : LiDS or LiFOS=1 : 1 :1). These results also show that the systems containing NP20 have a higher adsolubilization capacity than those containing NP7.5, and that the LiDS-NP systems also have a higher adsolubilization than do the LiFOS-NP systems with the same ethylene oxide chain length of NP.

These differences may be attributed to the location of the adsolubilization site of yellow OB and to the magnitude of the hydrocarbon chain-hydrocarbon chain interaction and the hydrocarbon chain-fluorocarbon chain interaction of the surfactants. That is, generally it may be said that yellow OB is soluble in the poly(oxyethylene) shell of nonionic surfactant micelles and in the hydrocarbon core of anionic surfactant micelles.[20] In the mixed bilayers, since yellow OB is considered to be adsolubilized mainly in the poly(oxyethylene) chains of NP, the adsolubilization capacity of a system containing NP20 is greater than that of a system containing NP7.5. The difference in the adsolubilization capacity between the LiFOS-NP20 and LiDS-NP20 systems is small, however, probaly because of the less significant contributions from the hydrocarbon chain-hydrocarbon chain and hydrocarbon chain-fluorocarbon chain interactions. On the other hand, in the systems containing NP7.5, the adsolubilization capacity for yellow OB in the LiDS-NP7.5 system is greater than that in the LiFOS-NP7.5 system. This is presumably caused by the difference in the magnitudes of the hydrocarbon chain-hydrocarbon chain interaction and the hydrocarbon chain-fluorocarbon chain interaction of the surfactants.

Actually, from the measurement of the enthalpy of formation of a mixed bilayer, the enthalpy of the LiDS-NP7.5 system (−17.3 kJ mol^{-1}) was found to be greater than that of the LiFOS-NP7.5 system (−14.1 kJ mol^{-1}). This result supports the view that the hydrocarbon chain-hydrocarbon chain interaction of the LiDS-NP7.5 system is much stronger than the hydrocarbon chain-fluorocarbon chain interaction of the LiFOS-NP7.5 system. Mukerjee[21] has also pointed out that the hydrocarbon-hydrocarbon interaction is more favorable than the hydrocarbon-fluorocarbon interaction.

Further, the adsolubilization capacities for yellow OB in the single bilayers of LiDS and of LiFOS were measured in order to compare them with those in the mixed bilayers. However, the adsolubilization capacity for yellow OB in the LiFOS bilayer was too small to detect, as was to be expected from the amount of yellow OB solubilized in the LiFOS micelle.[8] The adsolubilization capacity for yellow OB in the LiDS bilayer (Fig. 1) is considerably smaller than that in the

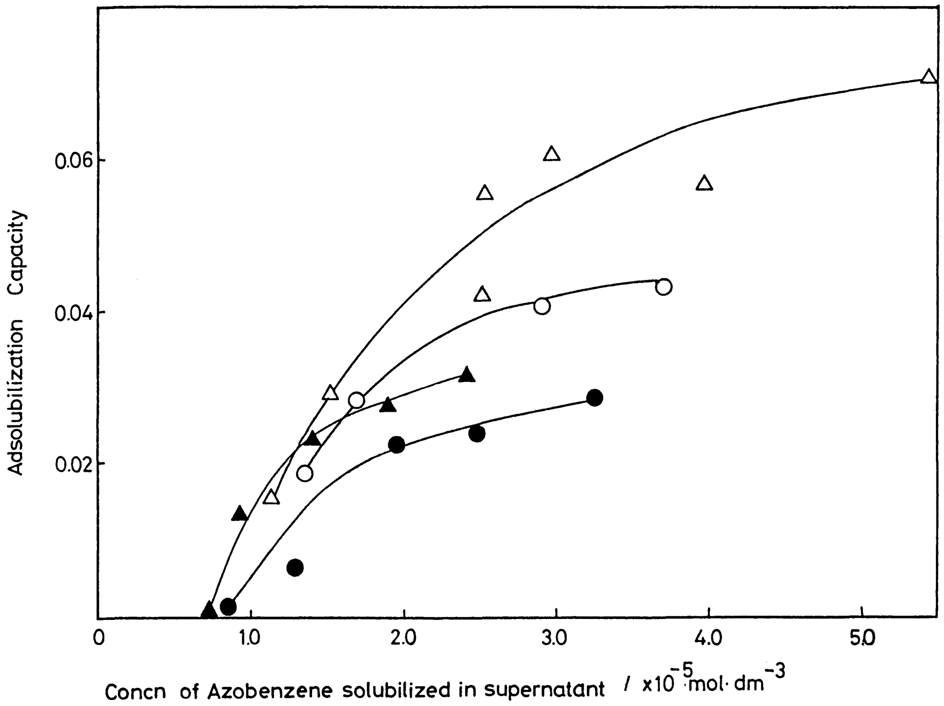

Fig. 2. Adsolubilization capacity for azobenzene in bilayers on alumina as a concentration of azobenzene solubilized in supernatant: (△) LiDS-NP7.5; (○) LiFOS-NP7.5; (▲) LiDS-NP20; (●) LiFOS-NP20.

mixed bilayers, suggesting that the hydrocarbon core in the LiDS bilayer has a very low adsolubilization capacity for yellow OB. This result corresponds with the low solubilization capacity for yellow OB in SDS micelles.[8] It is noteworthy that the adsolubilization capacities for yellow OB in the mixed bilayers are large compared to the solubilization capacity for yellow OB in the micelles; the solubilization capacities of NP7.5 and NP20 for yellow OB are 0.20 and 0.12 respectively.

The adsolubilization of azobenzene, which is soluble in the deep region of the poly(oxyethylene) shell for nonionic surfactant micelles, in the hydrocarbon core for the anionic surfactant micelles, and in both regions for mixed micelles,[22] was undertaken. Figure 2 shows the adsolubilization capacity for azobenzene in the LiDS-NP and LiFOS-NP systems. The adsolubilization capacity for azobenzene in the respective bilayers of LiDS and LiFOS was not large enough to measure. It is apparent, however, that the adsolubilization capacity for azobenzene in the LiDS-NP system is greater than that for the LiFOS-NP system, indicating that the adsolubilization of azobenzene is less favorable in the hydrocarbon chain-fluorocarbon chain layer for the LiFOS-NP system than in the hydrocarbon chain-hydrocarbon chain layer for the LiDS-NP system. This result emphasizes the aversion of aromatic compounds for fluorocarbon chains previously noted by the present authors.[17,23,24] The adsolubilization capacity for azobenzene decreased with the increase in the oxyethylene chain length of NP, contrary to the case of yellow OB. This result is presumably associated with the hydrophobic interactions in the bilayers; these interactions will increase with a decrease in the oxyethylene chain length of NP. This difference is also supported by the fact that the solubilization capacity for azobenzene in NP7.5 is greater than that for azobenzene in NP20. As well as yellow OB, the adsolubilization capacity for azobenzene in the mixed bilayers is greater than the solubilization capacity for azobenzene in NP7.5 and NP20; their capacities are 3.79×10^{-3} in NP7.5 and 3.44×10^{-3} in NP20 respectively.

In order to describe adsolubilization behavior using two solubilizates, we employed a partition coefficient K of the solubilizate between the bilayer and the

Table 2. Partition Coefficients of Yellow OB and Azobenzene in Bilayers

	Yellow OB		Azobenzene	
	Concn. in supernatant (μmol dm^{-3})	Partition coefficient (mol^{-1})	Concn. in supernatant (μmol dm^{-3})	Partition coefficient (mol^{-1})
LiDS-LiDS	3.3	4800		
	6.1	3400		
	8.1	3300		
	11.3	2600		
	14.7	2400		
	15.5	2500		
LiDS-NP7.5	33	2600	11.5	1400
	160	1400	15.2	2000
	270	1400	25.3	2200
	327	1200	28.4	2200
	338	1200	54.4	1300
	343	1200		
LiFOS-NP7.5	49	1500	13.6	1400
	156	1100	17.6	1600
	273	1100	28.2	1500
	356	800	37.3	1400
	391	800		
	413	800		
LiDS-NP20	68	1500	9.2	1500
	163	1600	14.0	1700
	260	1600	18.8	1500
	306	1400	23.8	1300
	317	1400		
	344	1300		
LiFOS-NP20	45	1600	14.0	400
	166	1500	19.5	1200
	282	1300	24.0	1000
	318	1300	33.3	900
	327	1300		
	351	1200		

aqueous phases. The partition coefficient K is defined by Eq. 1:

$$K = \frac{S_{\mathrm{AC}}}{S_{\mathrm{W}}} \tag{1}$$

where S_{AC} is the adsolubilization capacity for dyes in the bilayer phase, and S_{W}, the concentration of dyes solubilized in the supernatant. These K values are tabulated in Table 2. The order in the magnitude of K for yellow OB is roughly as follows: LiDS-LiDS> LiDS-NP7.5, LiDS-NP20, and LiFOS-NP20> LiFOS-NP7.5. On the other hand, the K values for azobenzene are almost the same in all the systems except for the LiFOS-NP20 system. Wu et al.[15] reported that the partition coefficient of styrene into an SDS bilayer on alumina is around 300. This value is low compared with that for the dyes used here because they used ethanol to increase the solubility of styrene in an aqueous solution. For the adsolubilization of 1-hexanol and heptafluoro-1-butanol into the respective bilayers of LiDS and LiFOS,[16] the partition coefficient was obtained in the range between 100 and 500. The present data show that water-insoluble dyes, such as yellow OB and azobenzene, are adsolubilized more efficiently in the bilayers than are styrene and the two alcohols. Furthermore, it is noteworthy that, compared to the K values between micelles and bilayers, the efficiency of incorporation for water-insoluble compounds in the bilayers is significantly greater than that in micelles.[8]

The above results lead to the conclusion that water-insoluble dyes are adsolubilized into surfactant bilayers formed on the alumina, where the adsolubilization capacity of the mixed bilayer is greater for the LiDS-NP system than for the LiFOS-NP system. Further, in the mixed bilayers of the LiDS-NP and LiFOS-NP systems, the adsolubilization capacity for yellow OB increases with an increase in the oxyethylene chain length of NP, whereas that for azobenzene decrease with an increase in the oxyethylene chain length of NP. These phenomena are presumably associated with the different locations of the dyes in the mixed bilayers. The adsolubilization capacity for yellow OB and azobenzene in the bilayers is considerably greater than the solubilization capacity in the corresponding micelles.

References

1) J. W. McBain and P. H. Richards, *Ind. Eng. Chem.*, **38**, 642 (1946).

2) S. Saito, *J. Colloid Interface Sci.*, **24**, 227 (1967).

3) F. Tokiwa, *J. Phys. Chem.*, **72**, 1214 (1968).

4) F. Tokiwa and K. Tsuji, *Bull. Chem. Soc. Jpn.*, **46**, 1338 (1973).

5) N. Nishikido, *J. Colloid Interface Sci.*, **60**, 242 (1977).

6) C. M. Nguyen, J. F. Scamehorn, and S. D. Christian, *Colloids Surf.*, **30**, 335 (1988).

7) M. Abe, N. Suzuki, and K. Ogino, *J. Colloid Interface Sci.*, **99** 226 (1984).

8) Y. Muto, M. Asada, A. Takasawa, K. Esumi, and K. Meguro, *J. Colloid Interface Sci.*, **124**, 632 (1988).

9) P. Chandar, P. Somasundaran, and N. J. Turro, *J. Colloid Interface Sci.*, **117**, 31 (1987).

10) P. Chandar, P. Somasundaran, K. C. Waterman, and N. J. Turro, *J. Phys. Chem.*, **91**, 148 (1987).

11) P. Somasundaran, J. T. Kunjappu, C. V. Kumar, N. J. Turro, and J. K. Barton, *Langmuir*, **5**, 215 (1989).

12) K. Esumi, Y. Sakamoto, and K. Meguro, *Colloid Polym. Sci.*, **267**, 525 (1989).

13) K. Esumi, Y. Sakamoto, K. Yoshikawa, and K. Meguro, *Colloid Surf.*, **36**, 1 (1989).

14) J. H. Harwell, Ph. D. Dissertation, The University of Texas at Austin, 1983.

15) J. Wu, J. H. Harwell, and E. A. O'Rear, *Langmuir*, **3**, 531 (1987).

16) K. Esumi and K. Meguro, unpublished work.

17) K. Meguro, M. Ueno, and T. Suzuki, *J. Jpn. Oil Chem. Soc.*, **31**, 909 (1982).

18) K. Esumi, Y. Ono, M. Ishizuka, and K. Meguro, *Colloids Surf.*, **32**, 139 (1988).

19) K. Esumi, Y. Sakamoto, K. Yoshikawa, and K. Meguro, *Bull. Chem. Soc. Jpn.*, **61**, 1475 (1988).

20) F. Tokiwa and K. Tsuji, *Bull. Chem. Soc. Jpn.*, **46**, 2684 (1973).

21) P. Mukerjee, *J. Am. Oil Chem. Soc.*, **59**, 573 (1982).

22) Y. Nemoto and H. Funahashi, *Hyomen*, **15**, 625 (1977).

23) K. Meguro, Y. Muto, F. Sakurai, and K. Esumi, "Phenomena in Mixed Surfactant Systems," ACS Symposium Series, No.311 (1986), p. 61.

24) T. Suzuki, K. Esumi, and K. Meguro, *J. Colloid Interface Sci.*, **93**, 205 (1983).