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Successive and Simultaneous Solubilizations of Two Different Water-insoluble Dyes by Detergents

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Although the solubilization of water-insoluble materials by detergents is a familiar phenomenon,[1] this subject is not neccessarily well understood. During the course of other work,[2,3] the present author observed an interesting aspect of behavior,

1) M. E. L. McBain and E. Hutchinson "Solubilization and Related Phenomena," Academic Press, New York (1955).

2) F. Tokiwa, *J. Phys. Chem.*, **72**, 1214 (1968).
3) F. Tokiwa, *J. Colloid Interfac. Sci.*, **28**, 145 (1968).

as will be described below, with respect to the solubilization of two different water-insoluble dyes.

This note will describe two types of solubilization for two different dyes. The first type is a successive solubilization in which two dyes are solubilized step-by-step in a detergent solution after the saturation of either of the two. The second type is a simultaneous solubilization in which two dyes are solubilized at the same time. From among the many water-insoluble dyes, two sets of dye combinations, Yellow OB and Sudan Blue GN, and Yellow OB and Aniline Blue, have been chosen by taking into account the possibility of an easy, separate determination by their optical densities. As solubilizing agents, anionic, cationic, and nonionic detergents were used to ascertain the effect of their electrical character on the solubilization.

Experimental

Materials. The sodium dodecyl sulfate ($NaC_{12}S$) and dodecyl nonaoxyethylene ether ($C_{12}(EO)_9$) were samples similar to those used in previous works.[2,3] Dodecyltrimethylammonium chloride ($C_{12}NCl$) was a laboratory-prepared sample purified by repeated recrystallization from acetone. The yellow OB (YW), 1-*o*-tolyl-azo-2-naphthylamine, was described in a previous paper.[2] The Sudan Blue GN (SB), 1-*m*-toluidine-4-methylaminoanthraquinone, and Aniline Blue (AB), *N*-phenylated rosaniline, which were both of a reagent grade, were obtained from Chroma-Gesellschaft, Germany. They were purified by recrystallization from a methanol-water solvent and an acetone-water solvent respectively. Mixed solubilizates were prepared by dissolving two different dyes in an acetone-benzene solvent and by then evaporating the solvent at 50°C.

Solubilization and Absorption Spectra. Solubilization runs were carried out in a water bath at 25°C for 50 hr, a method described elsewhere[2] being employed. The determination of the amount of solubilized dye was made by optical-density measurements at the wavelength of the absorption maximum. The absorption spectra of the dyes were measured by using a Shimadzu Model MPS-50 spectrophotometer at about 25°C.

Results and Discussion

Before discussing the successive and simultaneous solubilizations, the common solubilization of single dyes will be described briefly. Table 1 gives the saturation values of YW, SA, and AB in the aqueous solutions of $NaC_{12}S$, $C_{12}NCl$, and $C_{12}(EO)_9$. These values were obtained from the slope of the linear portion of the solubilization curve, in which the amount of the solubilized dye is plotted against the concentration of the detergent, as has been described in a previous paper.[2] The saturation value of YW in a $C_{12}NCl$ or $C_{12}(EO)_9$ solution is quite high as compared with the other values. It has been shown from spectral study[2] that, in the $NaC_{12}S$ solution, the solubilization of YW

Table 1. Saturation values of oil-soluble dyes in detergent solutions

Detergents	Saturation Values (g of dye/g of detergent × 10^3)		
	YW	SB	AB
$NaCl_{12}S$	10.7	4.45	18.0
$C_{12}NCl$	67.8	5.00	10.7
$C_{12}(EO)_9$	52.9	4.34	5.90

occurs mainly in the hydrocarbon interior of the micelle, while in the $C_{12}(EO)_9$ solution it occurs in both the hydrocarbon core and the polyoxyethylene shell of the micelle. This explains the large value for YW in the $C_{12}(EO)_9$ solution. With YW in the $C_{12}NCl$ solution, the probable locus of solubilization is the surface of the micelle (otherwise, we can not explain such a large value).

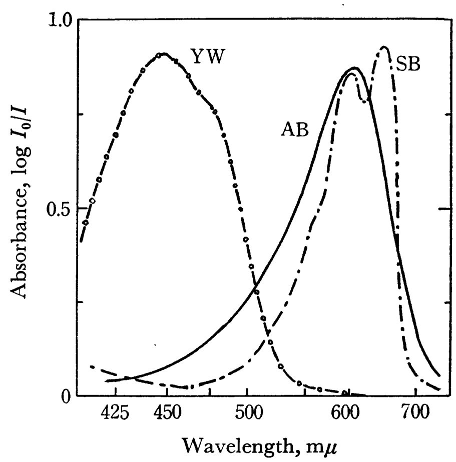

Fig. 1. The absorption spectra of YW, SB and AB in ethanol: concentration, approximately 1.7×10^{-3}%.

Successive Solubilization. The absorption spectrum of each of these three dyes in ethanol is shown in Fig. 1. The spectra indicate that each dye can be separately determined from its optical density in the presence of the other if YW-SB and YW-AB are chosen as the solubilizates.

Table 2 gives the saturation values of YW and SB in detergent solutions when they were solubilized step-by-step through the processes of YW→SB and SB→YW. In the YW→SB process, for example, YW is solubilized before SB; SB is solubilized after the saturation of YW. This table also gives the saturation values of YW and AB obtained through the YW→AB and AB→YW processes. When we compare the values shown in Table 2 with those in Table 1, we can see that the saturation value of each dye in any detergent solution is not very much influenced by the order of solubilization. For example, the YW once solubilized remains

TABLE 2. SATURATION VALUES OF OIL–SOLUBLE DYES BY SUCCESSIVE SOLUBILIZATION

Combination of Dyes	Order of Solubilization	Saturation Values (g of dye/g of detergent × 10^3)								
		In $NaC_{12}S$ Soln.			In $C_{12}NCl$ Soln.			In $C_{12}(EO)_9$ Soln.		
		YW	SB	AB	YW	SB	AB	YW	SB	AB
YW & SB	YW→SB	10.6	4.21	—	67.3	4.89	—	52.1	4.38	—
	SB→YW	10.6	4.38	—	68.4	4.76	—	52.9	4.54	—
YW & AB	YW→AB	10.9	—	17.4	69.2	—	10.7	53.6	—	5.75
	AB→YW	10.4	—	18.6	69.9	—	11.3	55.0	—	5.70

in the micelle after the solubilization of SB or AB; further, the saturation value of YW in the detergent solution containing solubilized SB or AB is roughly equal to the value in the same detergent solution containing no other dye. The following explanation seems plausible in according for this.

Let us assume that each dye, at least each of those examined here, has a specific locus of solubilization in the micelle where the dye is to be solubilized. With $NaC_{12}S$ and $C_{12}NCl$, the probable locus is the hydrocarbon interior and/or its charged surface, while with $C_{12}(EO)_9$ it is the hydrocarbon core and the polyoxyethylene shell of the micelle. If this is the case, the dye first solubilized in its own locus remains in the micelle without being influenced by the second dye, which will also be solubilized in the other locus irrespective of the presence of the first dye, as long as the solubilization is carried out step-by-step.

It is known that the addition of small amounts of long-chain alcohols or hydrocarbons to a detergent solution enhances the solubilization capacity of the detergent for oil-soluble dyes.[1,4] This has been ascribed to an increase in the space available to dye molecules by the penetration of the additive into the micelle. However, this type of solubilization is essentially different from the successive solubilization described here.

Simultaneous Solubilization. The solubilization of the mixture of two dyes, *e. g.*, YW and SB, or YW and AB, in detergent solutions was achieved by changing the mixing ratio from 0.2 to 4.0 by weight. However, reproducible saturation values could not be obtained for all of the three dyes, and the values are generally smaller, although in some cases they are larger, than those given in Table 1. As examples, typical results for the simultaneous solubilization of the mixture of YW and SB in the solutions of $NaC_{12}S$ and $C_{12}(EO)_9$ are shown in Fig. 2. In these two cases, the saturation value of YW or SB at a fixed detergent concentration is neither constant nor reproducible, and the points given in Fig. 2 are only examples of scattered, observed values. The interpretation of these results is difficult at this stage. Probably, interactions between the two dyes, and between the micelles and the dyes in the process of solubilization, are related to the above phenomenon in a complicated way.

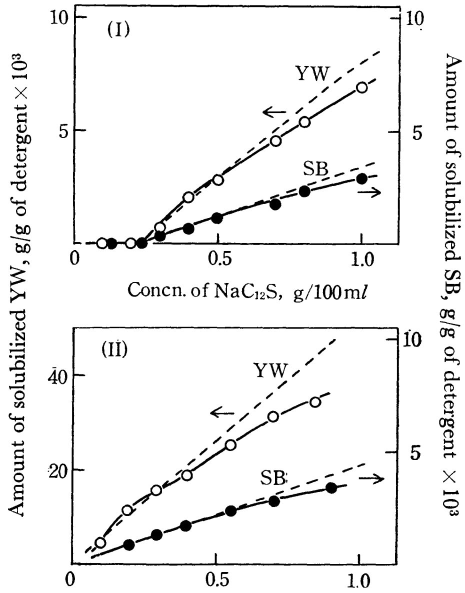

Fig. 2. The simultaneous solubilization of YW (○) and SB (●) mixed in a ratio of 1 : 1 in the solutions of $NaC_{12}S$ (I) and $C_{12}(EO)_9$ (II). The broken line indicates the solubilization curve for single YW or SB.

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4) See, *e.g.*, H. B. Klevens, *Chem. Rev.*, **47**, 1 (1950).