*The Interaction between Dyes and Surfactants. I**

By Tamotsu KONDO and Kenjiro MEGURO

(Received July 7, 1958)

In previous works[1,2], we found the fact that the dye in aqueous solution is flocculated by adding a small amount of ionic surfactant, when the charge of surfactant is opposite to that of the dye.

We also found this flocculate** is dispersed again with further addition of surfactant. We call these phenomena "flocculation and deflocculation of dye by surfactant". To clarify the mechanism of these phenomena, we studied the interaction between anionic surfactants with

* Presented before the 11th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1958.

** This flocculate is considered to be a stoichiometric complex salt formed between dye and surfactant. Details of its properties will be described in a later paper.

1) K. Meguro *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagakn Zasshi*), 77, 72 (1956).
2) T. Kondo et al., ibid., 77, 1240 (1956).

alkyl chains of different lengths and a cationic dye, and also between cationic surfactants having gegenions of different degrees of hydration and an anionic dye.

Experimental

Materials.—Rhodamine 6G and Eosine were used as cationic and anionic dyes respectively. Both were commercial samples and were purified by the method described previously[3].

The anionic surfactants employed were sodium decyl (Na. De. S.), dodecyl (Na. D. S.) and tetradecyl sulfates (Na. T. S.). These alkyl sulfates were prepared from the corresponding alcohols by sulfation. The details of the preparation and the purification of these compounds were described already[4].

Dodecylpyridonium chloride (D. Py. Cl.), bromide (D. Py. Br.) and iodide (D. Py. I.) were used as cationic surfactants. These dodecylpyridonium halides were prepared by refluxing the dodecyl halides with pyridine for several hours. The salts were purified by recrystallization from acetone and by extraction with petroleum ether.

Procedure.—As described above, when the surfactant ion has a charge opposite to that of the dye ion, the ionic dye in solution is flocculated by adding surfactant solutions of low concentration. It was also mentioned that the flocculate disperses again in a more concentrated solution of surfactant. In order to treat these phenomena quantitatively, the flocculation value and the deflocculation value were defined as the minimum concentration of surfactants required to cause the complete flocculation and deflocculation of dye in 24 hours at constant temperature after mixing dye and surfactant.

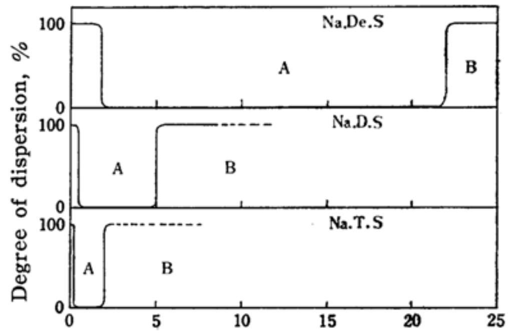
In practice, 2 ml. of dye solution of a constant concentration and equal volume of surfactant solutions of various concentrations were mixed in small test tubes, and these test tubes were permitted to stand at 30°C for 24 hours. At the end of 24 hours, the degree of flocculation was observed visually or spectrophotometrically, if necessary, after centrifuging. The flocculation and deflocculation values correspond to the minimum number of millimoles of surfactant per liter of mixed solution required to cause the complete flocculation and deflocculation. By repeating the same procedure for the dye solutions of various concentrations, the dependence of flocculation and deflocculation values upon the dye concentration was also investigated.

In order to study the properties of the complex formed between dye and surfactant, the transfer of flocculate to nonpolar solvent, such as benzene, was observed by the same procedure described already[5]. That is, 2 ml. of dye-surfactant mixture were shaken with equal volume of benzene in test tubes. After a few hours the degree of coloring of benzene phase was measured photometrically.

Results

The flocculation and deflocculation values varied with the difference in alkyl chain length and gegenion of surfactant, and furthermore with the addition of salt or organic solvent.

Effect of alkyl chain length of surfactant.—Results obtained with the alkyl sulfate—Rhodamine 6G systems in which the dye concentration was kept to be 0.5 mM/l. are shown in Fig. 1.



A: flocculation zone, B: deflocculation zone

Fig. 1. Flocculation pattern of Rhodamine 6G by sodium alkyl sulfates.

This figure shows that the minimum amounts of sulfate required to cause the complete flocculation and deflocculation markedly decrease with the increase in alkyl chain length of sulfate. In other words, the width of flocculation zone, i.e., the value obtained by subtracting the flocculation value from the deflocculation value, which is the net amount of surfactant necessary for the complete deflocculation of flocculate, decreases with increasing alkyl chain length.

As the dye concentration decreased, the flocculation and deflocculation values became smaller. Results for Rhodamine-dodecyl sulfate system are shown in Fig. 2. Similar results were obtained with decyl and tetradecyl sulfates.

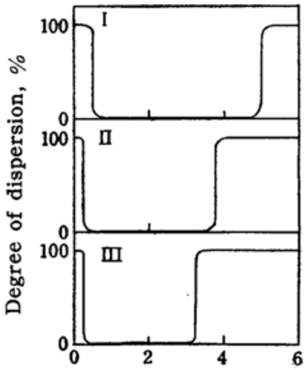
The plots of the width of flocculation zone against the dye concentration gave a straight line. Results are shown in Fig. 3. It can be seen that the slope of the straight line rises with decreasing alkyl chain length of sulfate.

Effect of gegenion of surfactant.—Fig. 4 shows the flocculation and deflocculation

3) T. Kondo, ibid., 77, 1281 (1956).

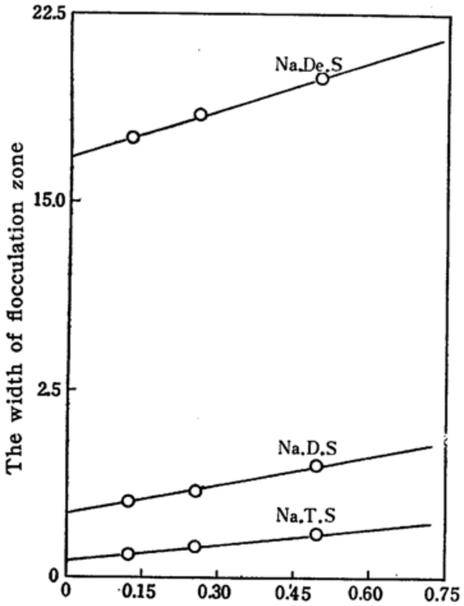
4) O. Yoda, K. Meguro, T. Kondo and T. Ino, ibid., 75, 1272 (1954).

5) K. Meguro, *Memoirs of the Musashi University, Supplement*, 5, 33 (1957).



Concn. of Na. D. S., mM/l.
Rhodamine 6G concn.: I 0.50 mM/l., II 0.25 mM/l., III 0.125 mM/l.

Fig. 2. Effect of Rhodamine 6G concentration on its flocculation by Na. D. S.



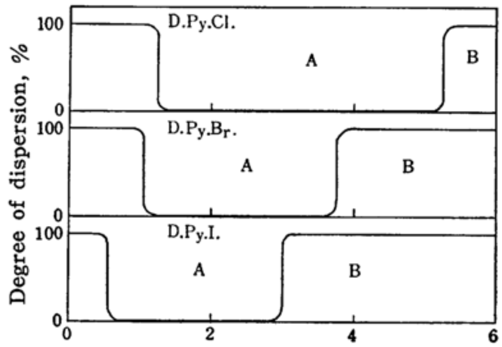
Dye concn. mM/l.

Fig. 3. The value of width of flocculation plotted against the dye concentration Rhodamine 6G. Sodium Alkyl Sulfate systems.

of Eosine, the concentration of which is 0.5 mM/l., by dodecylpyridonium halides.

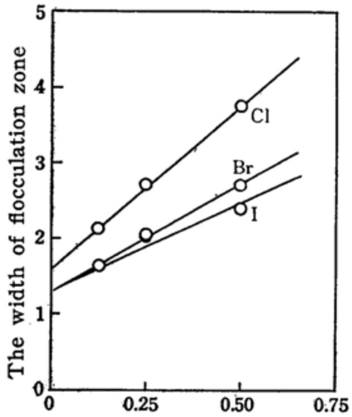
In this figure, the chloride gives the largest flocculation and deflocculation values while the iodide gives the smallest ones. That is, the larger the hydration of gegenion of surfactant, the greater the width of flocculation zone.

The linear relation between the width of flocculation zone and the dye concentration for Eosine-dodecyl pyridonium halide systems is as shown in Fig. 5.



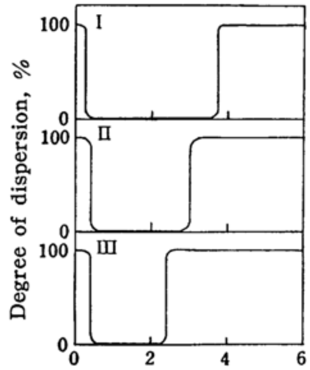
Concn. of dodecyl pyridonium halide, mM/l.
A: flocculation zone, B: deflocculation zone

Fig. 4. Flocculation pattern of Eosine by dodecyl pyridonium halides.



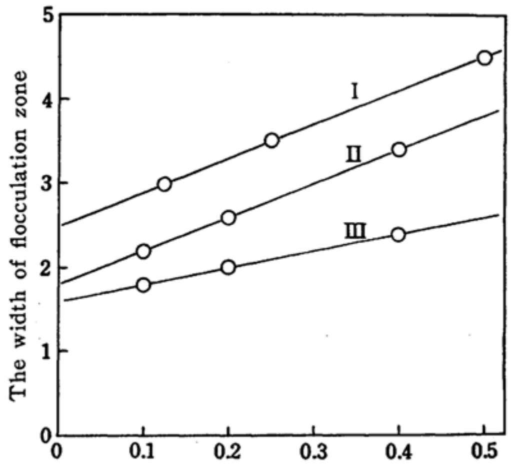
Dye concn., mM/l.

Fig. 5. The value of the width of flocculation zone plotted against the dye concentration for Eosine-D. Py. Halide systems.



Concn. of Na. D. S., mM/l.
I: no salt, Rhodamine 6G 0.25 mM/l.
II: NaCl 8 mM/l., Rhodamine 6G 0.20 mM/l.
III: NaCl 16 mM/l., Rhodamine 6G 0.20 mM/l.

Fig. 6. Effect of NaCl on the flocculation of Rhodamine 6G by Na. D. S.

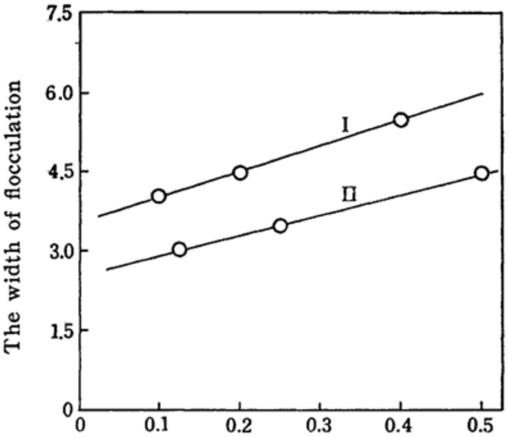


Dye concn., mM/l.
I: no salt, II: NaCl 8 mM/l.
III: NaCl 16 mM/l.

Fig. 7. Effect of NaCl on the relation between the width of flocculation zone and the dye concentration in Rhodamine 6G—Na. D. S. system.

Effect of added salt.—Added salt depressed the flocculation to a certain extent but promoted the dispersion of flocculates. A typical result obtained with Rhodamine 6G—Na. D. S.—sodium chloride system is shown in Fig. 6. and 7.

Effect of added alcohol.—The addition of ethanol to Rhodamine 6G—Na. D. S. system did not alter the flocculation value of dodecyl sulfate but exerted a slight influence on its deflocculation value. The width of flocculation zone, therefore, varies slightly as shown in Fig. 8.



Dye concn. mM/l.
I: ethanol 8.1 wt. %, II: no alcohol.

Fig. 8. Relation between the width of flocculation zone and dye concentration for Rhodamine 6G—Na. D. S. system in water-ethanol mixture.

Transfer of dye-surfactant complex into organic solvent.—Results for the transfer of Rhodamine 6G—D. S. complex into benzene are shown in the following table.

TABLE I
TRANSFER OF RHODAMINE 6G—D. S. COMPLEX INTO BENZENE

Dye concn. mM/l.	Na. D. S. concn. mM/l.						
	0.10	0.25	0.50	1.00	2.50	3.75	5.00
0.125	++	+++	++	+	+	−	−
0.25	++	+++	++	++	+	−	−
0.50	+	++	+++	++	++	+	−

In this table, the number of + signs denotes the degree of coloring of benzene phase, and the − sign shows the non-coloring.

It is noticed that the complex has a strong oilphilic property when the concentration of Na. D. S. is equivalent to that of dye. Furthermore, it is remarkable that this oilphilic property decreases again in more concentrated Na. D. S. solutions.

Discussion

The slope of straight lines shown in Figs. 3, 5, 7 and 8 will represent the minimum number of surfactant ions required to cause the complete deflocculation of a dye ion or a dye surfactant complex.

This number is termed "the deflocculation number of surfactant" and denoted by N_d in this series of papers. N_d values for surfactants employed in this work are collected in Table II.

TABLE II
VALUES OF N_d

Dye	Surfactant	N_d
	Na. De. S.	6.7
Rhodamine 6G	Na. D. S.	4.0
	Na. T. S.	2.2
	D. Py. Cl.	4.2
Eosine	D. Py. Br.	2.8
	D. Py. I.	1.9

The plots of log N_d against the number of carbon atoms of sulfate give a straight line as shown in Fig. 9, which is similar to that found between the C.M.C. and the number of carbon atoms in alkyl chain of surfactant.

On the other hand, with dodecylpyridonium halides, a linear relation between N_d value and lyotropic number of gegen-

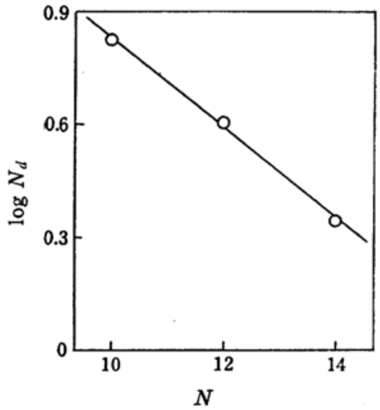


Fig. 9. Relation between log N_d and the number of carbon atoms in alkyl chain of sulfate.

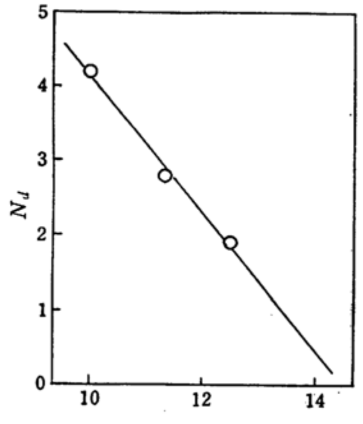


Fig. 10. Relation between N_d values and lyotropic number of gegenions of dodecylpyridonium halides.

ions is obtained as shown in Fig. 10. A similar relation is held between C.M.C. values of these cationic surfactants and lyotropic numbers of their gegenions[6).

It may be suggested that the deflocculation phenomenon of dye is closely related to the association properties of surfactant from the above-mentioned facts. As the magnitude of C.M.C. value measures the ability of micelle formation of surfactant, the N_d value seems to have a close relation with micelle forming ability of surfactant. The facts that the flocculation takes place at the equivalence between dye and surfactant, and that the deflocculation occurs in more concentrated surfactant solutions, and the facts that the flocculate has the oilphilic property, and that the deflocculate loses this oilphilic property, suggest the existence of dye surfactant aggregate composed of a dye surfactant complex, as the nucleus, and few surfactant ions. This dye-surfactant aggregate suggested by the present authors is pictured in Fig. 11.

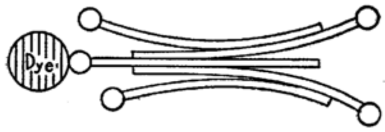


Fig. 11. Schematic representation of a dye-surfactant aggregate.

In connection with these considerations, it will be mentioned that the deflocculation of dye-surfactant complex occurs in surfactant solutions of the concentration below the C.M.C.

If we accept the above argument that a few surfactant ions can combine with a dye—surfactant complex in the deflocculation, we should expect that the surfactant ions themselves can form an aggregate owing to the interaction between their long alkyl chains below the critical concentration for micelle formation[7).

Nezu Chemical Laboratory
Musashi University
Nerima, Tokyo

6) K. Meguro, T. Kondo et al., Presented at the Symposium on Colloid and Surface Chemistry held in Tokyo, November 1956.

7) K. Meguro et al., This Bulletin 31, 472 (1958).