THE INTERACTION BETWEEN ACID DYES AND NONIONIC SURFACTANT

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INTRODUCTION

For the purpose of clarifying the action of nonionic surfactants as an auxiliary in a dye bath, several investigations on the interaction between a nonionic surfactant and an acid dye have been reported by various authors (1 − 4). Most of them, however, have been carried out without any electrolytes, at lower temperature (10 − 45°C), but it should be noted that the research of the interaction systems in the presence of electrolyte at higher temperature would be rather necessary for practical dyeing. For this purpose, spectrophotometry which is one of typical methods for the studies of interaction would not be available. However, measurement of cloud point for a nonionic surfactant solution containing dye is thought to be quite useful ; the cloud point of the nonionic surfactant solution increases by the addition of acid dye corresponding to the extent of interaction.

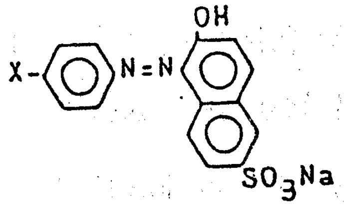
Therefore, in the present report, we will discuss the interaction mechanism at higher temperature (70 − 100° C), on the basis of the results obtained by the measurement of cloud point of the nonionic surfactant solution containing both acid dye and electrolyte.

EXPERIMENTAL

Materials. 10 oxyethylene nonylphenyl ether (NP10), used as a nonionic surfactant, was the same product as that in the previous paper (4), and its purity was ascertained by the absence of a minimum in the surface tension curve.

The following acid dyes, derivatives of sodium 1 − phenylazo − 2 − naphthol − 6 − sulfonate, were used.

Each synthesized dye was purified with ethyl alcohol−diisopropyl ether mixed solvent.



X; $-CH_3$, $-NO_2$, $-OH$
(D-1) (D-2) (D-3)

Sodium dodecyl sulfate (SDS) was purified by repeated recrystallization of the commercial product from ethyl alcohol.

Method. The procedure for the measurement of cloud point was similar to that of Schott (5).

RESULTS AND DISCUSSION

The dyes adopted in the present experiments have a characteristic that they interact with micelles but do not with only a single molecule of NP10; the values of Y, which are proportional to the amount of complex formed in the solution (4), increased only above the cmc of NP10 and were negligible below the cmc. From these facts, it is believed that the formation of mixed micelles composed of NP10 and acid dye takes place.

In Fig. 1, the solid line shows the effect of electrolytes on the cloud point at the constant concentration of D−1 (3×10^{-4} M) and NP10 (5×10^{-3} M), where the cloud point is 95° C. For comparative purpose, the cloud points in the absence of dye are also illustrated by the dashed line. Several experimental results have shown that the electrolytes depress the cloud point of nonionics in proportion to their concentrations(6, 7). This was confirmed by experiments carried out for the concentrations above 0.1 M of electrolyte, as shown by the dashed line, while any of changes can scarcely be observed for the concentrations below 0.1 M of electrolyte. However, when electrolyte was added to the NP10 solution with D−1, the cloud point curve showed significant changes even below 0.1 M of electrolyte, and a clear transition point(Z) could be observed in the curve, as shown by the solid line.

In order to clarify the reason for the existence of Z in the cloud point curve, an attempt was made; when the solutions were allowed to stand at various temperatures above the cloud points for about 8 hr, some interesting phenomena were observed in their solution states, as shown in Fig. 2. In region I, below the cloud point, the solution remains clear. Above the cloud point, first the solution clouds due to the separated particles in the solution and then the

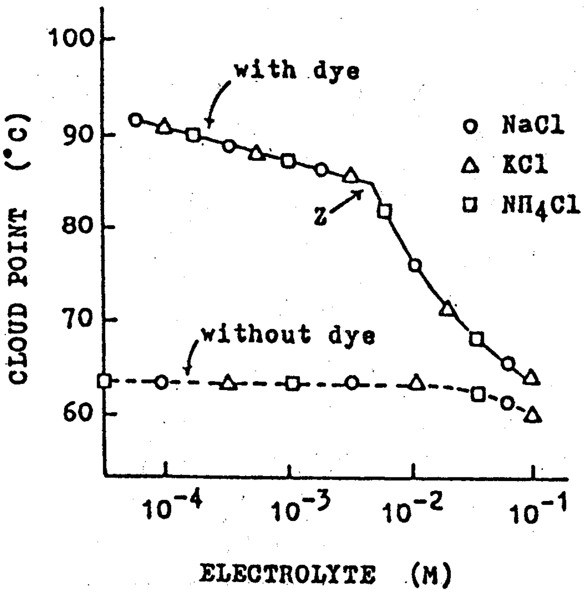


Fig. 1. Effect of electrolyte on the cloud point for the solution containing both NP10 and D−1, and on the cloud point for the NP10 solution without dye.

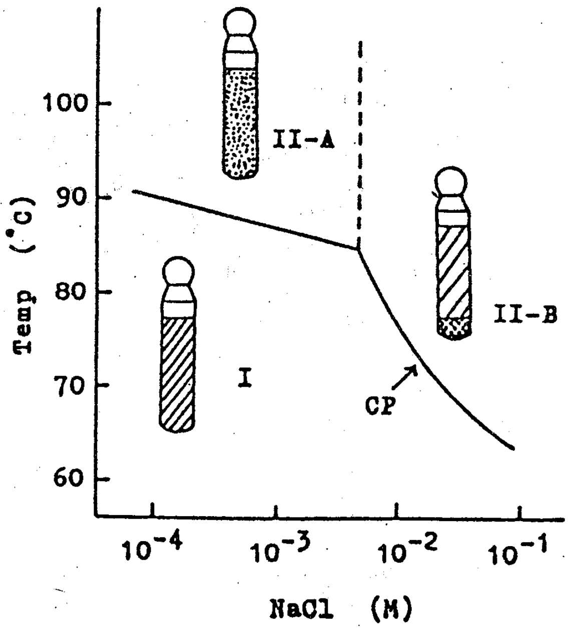


Fig. 2. A phase diagram obtained by maintaining the solution used in Fig. 1, at temperature below and above the cloud point (CP).

appearence of the clouded solution undergoes a change, depending upon the concentrations of NaCl after standing for about 30 min. Namely, in region II − A, the solution still remains turbid and the fine particles in the solution are quite stable even after standing for a long time. This might be due to the electronic repulsion which results from the negative charges of acid dye in mixed micelles. In region II − B, where the concentrations of NaCl are considerably high, the charges of the mixed micelles would be decreased and the particles in the solution become unstable. As a result, the particles coagulated ; a separated layer is obtained and the remaining part, equilibrium solution, becomes transparent in about 30 min.. The dashed line, which represents a boundary for region II − A and II − B, joins at the point of Z. Therefore, Z is considered to be a triple point at which three types of mixed micelles coexist.

Then it might be required to evaluate the molar fraction of each component, acid dye, nonionic surfactant or electrolyte, on which three types of mixed micelles are formed respectively. For this subject, the cloud point must be measured over a wide range of concentrations of each component. It is, however, difficult to measure the cloud point at higher concentrations of dye owing to its deep colour. The molar fraction was therefore evaluated with SDS as a model of acid dye, which also interacts with micelle but do not with a

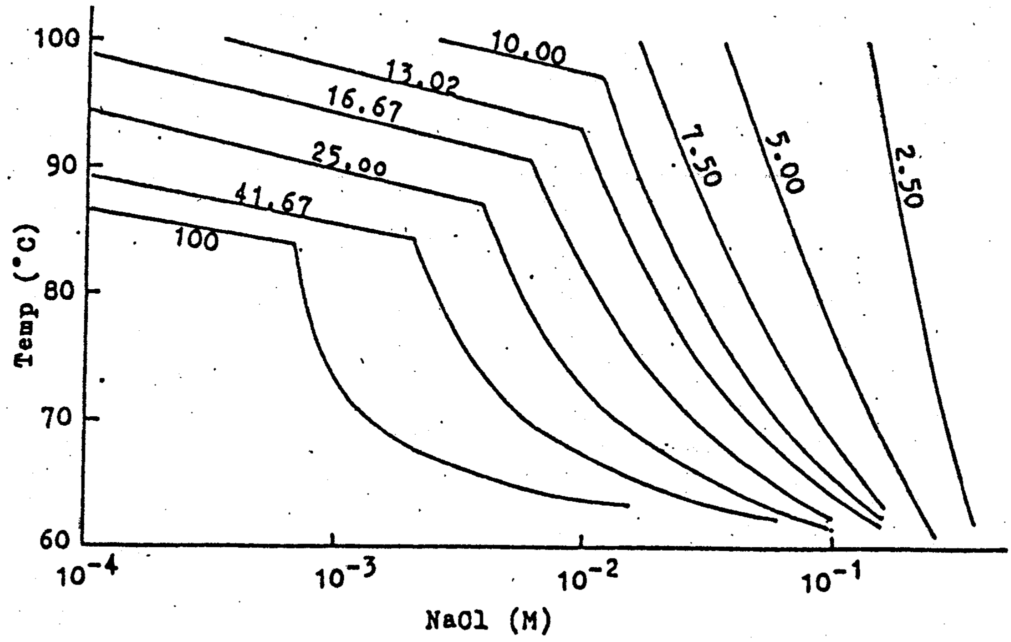


Fig. 3. Cloud points of the NP10 solution with SDS as a function of the concentration of NaCl at various constant molar ratios of NP10 to SDS

single molecule of NP10. Fig. 3 shows the cloud points of the NP10 solution with SDS as a function of the concentration of NaCl at various constant molar ratios of NP10 to SDS. The curves in Fig. 3 are similar to the solid line in Fig. 2, but the shape of the curve undergoes a change shifting to the right- and up-side in Fig. 3 with a decreasing value of NP10/SDS. When the value of NP10/SDS is 7.50 or below (NP10/SDS≦7.50), T^{z}, the temperature at Z, seems to be above 100°C; actually the value can not be measured under the condition of atomospheric pressure, where only micelle I and II-B can be observed.

Fig. 4, which is drawn from the results in Fig. 3, shows the values of NP10/SDS as a function of the concentration of NaCl, at 86°C. From the curves in Fig. 4, the molar fraction in each boundary can be evaluated.

Fig. 5 illustrates the equilibrium phase diagram of three types of mixed micelles for the system, NP10-SDS-NaCl, at 86°C. Each top of triangle represents a component alone. It can be seen in Fig. 5 that the formation of micelle II-A and II-B takes place within a limited range; particularly micelle II-A is formed only on higher molar ratios of NP10 to other components.

Although the results in Fig. 3, 4 and 5 were obtained with SDS, it is likely that similar results will also be obtained even with usual acid dyes.

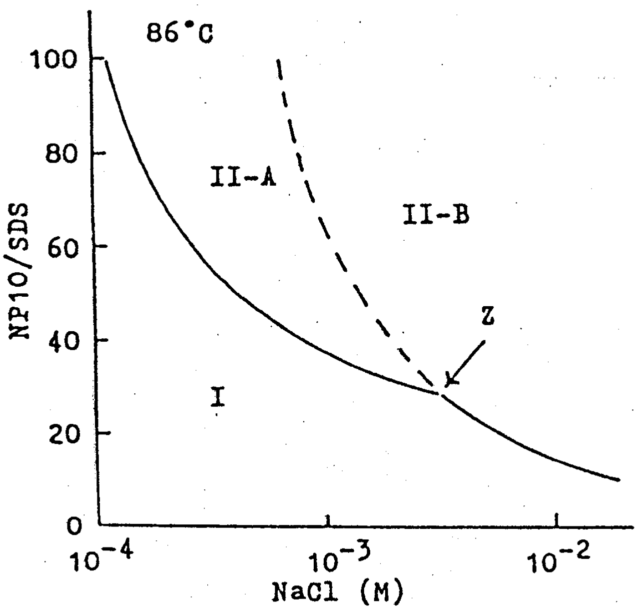


Fig. 4. Plots of NP10/SDS vs. the concentration of NaCl, at 86°C.

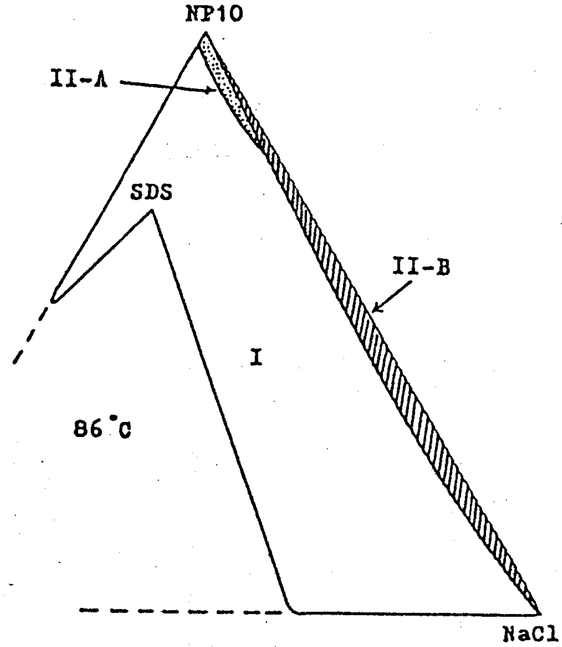


Fig. 5. An equilibrium phase diagram of three types of mixed micelles for the system, NP10 − SDS − NaCl, at 86°C.

The analysis of the separated layer in region II − B (Fig. 2) by means of a polarizing microscope showed this product to be a liquid crystal. This liquid crystal, which might be formed in a dye bath, is thought to be very important in dyeing; wool would be covered with it and dyeing might proceed through the liquid crystal layer.(8).

CONCLUSIONS

Three types of mixed micelles, micelle I, micelle II − A and micelle II − B, were found in the interaction system composed of nonionic surfactant, acid dye and electrolyte by the measurement of cloud point for the solution. The hydrophobicity of these mixed micelles is likely in order of micelle II − B > micelle II − A > micelle I.

The equilibrium phase diagram for the formation of these mixed micelles was determined for the NP10 − SDS − NaCl system, evaluating the molar fraction among three components, where SDS was adopted as a model of acid dye. Consequently it was found that micelle II − A and II − B were formed within a limited range of the molar fraction.

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