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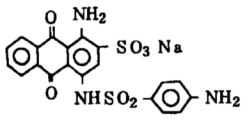
INTERACTION OF ANTHRAQUINOID ACID DYES WITH NONIONIC SURFACTANTS

Tran Dinh TUONG* and Shigeo HAYANO
Institute of Industrial Science, The University of Tokyo
7-22-1 Roppongi, Minato-ku, Tokyo 106

The interaction of an anthraquinoid acid dye with a nonionic surfactant of the nonylphenol ethylene oxide type has been investigated by spectroscopic measurements and gel permeation chromatography . The results are interpreted by assuming that the dye is adsorbed on the surfactant micelles and the Freundlich isotherm has been found to correlate well the data.

Since the thirties, the interaction of dyes with nonionic surfactants has been noted, and applied in dyeing processes.[1] The action of surfactants on the behavior of dyes in solutions has attracted much interest from colorists, dyers and workers in the field of colloid chemistry. A number of papers have been published on this topic, and some features of the interaction have been established. At present, however, there has not been a unanimous solution to this important problem. Although there is a possibility that the mechanism of interacting may change with the special system to be considered, an investigation of the data accumulated shows that it is highly probable that regardless of differences in structures of the dye and/or of the surfactant, there is much in common in the way of interacting. This work has been undertaken to contribute to the understanding of the main features of the mechanism of the interaction of acid dyes with nonionic surfactants.

The system selected to study is an aqueous solution of dye D containing a nonionic surfactant of the nonylphenol-ethylene oxide type. The structures of the dye and of the surfactant, denoted as NP-10, are shown below. It was found that the absorbances of aqueous solutions of D strictly obeyed Lambert-Beer's law in the concentration range (1.0 to 10.0 X 10^{-5} mol/dm^3) used throughout this work. Aggregation of the dye thus can be neglected.[2] NP-10 was chosen because the properties of its solution are well documented.



Dye D

$C_9H_{19}\cdot C_6H_5(OC_2H_4)_{10}OH$

Surfactant NP-10

The spectrum of D in aqueous solution was not affected upon addition of NP-10 up to *ca.* 5 X 10^{-5} mol/dm^3 of the latter. When the surfactant was further added, the position of maximal absorption was shifted to longer wavelengths until it finally became 550 nm as compared with the initial value of 515 nm. The molecular extinction coefficient at the maximum also increased. As shown in Figure 1, an isosbestic point was clearly observed at 510 nm. These findings suggest that the dye exists in the system under two, and only two forms: free (or more exactly, hydrated) dye, and dye associated with surfactant micelles. Changes in absorption spectra of acid dyes caused by nonionic surfactants have been observed by previous workers.[3-5] In some instances, it has been found that the surfactant, even at concentrations lower than the cmc, affects the spectrum of the dye

and this observation forms the basis of arguments that in the range above the cmc, the interaction between dyes and nonionic surfactants is also of an intermolecular nature.[5] In our work, however, we found that even if molecular interaction does not occur, at least as observed by spectroscopic methods, a nonionic surfactant can also affect the spectrum of an acid dye, and thus, the interaction must be interpreted as to be caused by the surfactant micelles.

From the spectral data, the concentrations of free dye, and of surfactant associated dye could be estimated. Quantitative analyses were then attempted, based on the following models:

(a) simple complex model:[4]

$$aS + bD \rightleftharpoons S_aD_b$$

(b) mixed-micelle model :[3]

$$S_n + D \rightleftharpoons S_nD$$

(here, S stands for the surfactant, D the dye, and S_n the surfactant micelle)

The results were that all these models could not be fitted by the data of our work. It can be concluded that models requiring the constancy of the molar ratio of dye versus surfactant are not satisfactorily substantiated.

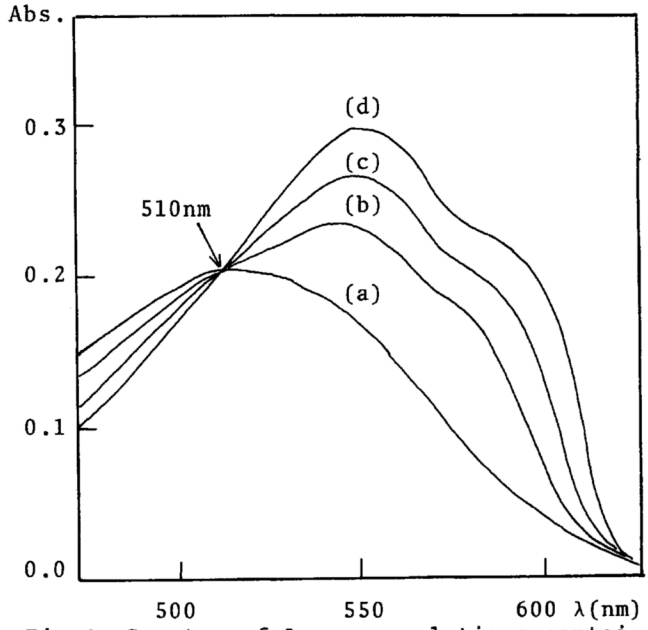


Fig.1 Spectra of Aqueous solutions containing Dye D (4×10^{-5} mol/dm^3) and NP-10 (a, 0; b, 2×10^{-4}; c, 4×10^{-4}; d, 12×10^{-4} mol/dm^3). Temperature: 25°C.

Several properties of surfactant solutions are known to be well explained if the micelles are assumed to form a microscopically separate phase.[6] From this point of view, we attempted calculations based on the assumption that the dye molecules are adsorbed on the micellar phase, and as is shown in Figure 2, we found that the experimental data could be well correlated by the Freundlich isotherm. The fact that the results corresponding to systems containing different total concentrations of the dye are correlated by the same isotherm strongly supports the present idea. The distribution of organics between micellar and aqueous phases has been noted by several workers to be explicable in terms of adsorption processes.[6,7] From our analysis, we feel that our system provides another example of the applicability of this concept. The interaction of dye D and NP-10 can thus be portrayed simply by the following model:

$$nS \rightleftharpoons S_n \xrightleftharpoons{D\ \text{adsorbed}} S_nD_x$$

where x may vary with the concentrations of S and/or of D.

In an extensive study of the interaction of anthraquinoid acid dyes with nonionic surfactants, Datyner and his co-workers have explained their results by postulating the following processes:[5]

surfactant molecules $\rightleftharpoons$ surfactant micelles

surfactant molecules and dye $\rightleftharpoons$ surfactant-dye complex

The central idea of this model is that the interaction, as described by the lower process, is that between molecules of the dye and of the surfactant .This model is different from ours in that it rejects the interaction between dye molecules and surfactant *micelles*. Although this model can explain qualitatively several experimental facts, i.e. the raising of the clouding points of the surfactants in the presence of dyes,the relative efficiency of surfactants having different number of ethylene oxide units, etc.,no quantitative analyses were performed. In addition to this, the model itself could not explain results obtained from measurements of the size of dye-containing particles and the workers had to add to their model the assumption that the dye-surfactant complex may aggregate to form larger particles.

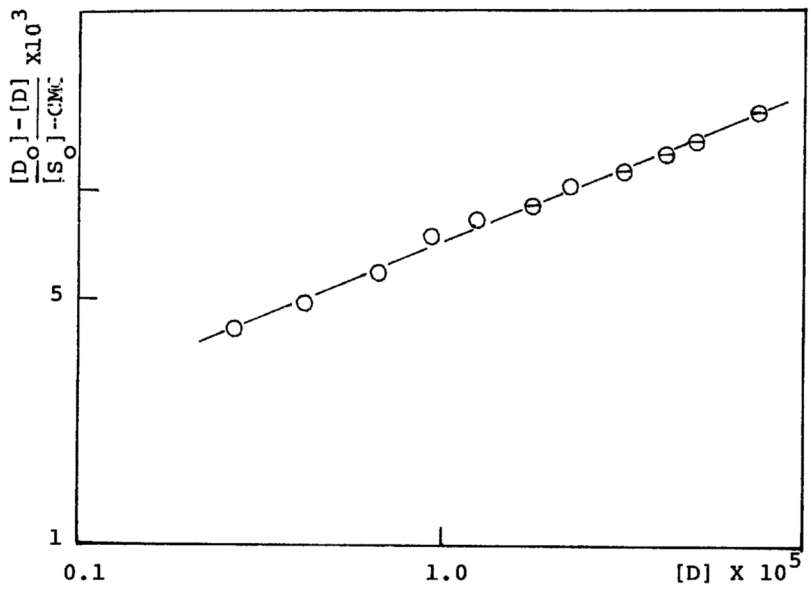


Fig.2 Freundlich Plots.[D_o]:total concentration of dye D; [D]: molar concentration of free (hydrated)dye; [S_o] :total molar concentration of surfactant NP-10; CMC : critical micelle concentration of NP-10 (=7.5 X 10^{-5}mol/dm^3).
[D_o] = 5 X 10^{-5} mol/dm^3 (○), 10 X 10^{-5} mol/dm^3.(⊖)
[S_o] = 1 ∿ 30 X 10^{-4} mol/dm^3 . Temperature : 25°C.

In order to test the validity of our model, we investigated our system by the technique of gel permeation chromatography. Our idea in using this method is very simple : if the adsorption model is correct, the dye-containing micelles must be larger than the pure micelles. GPC was expected to give direct information on the relative sizes of these two kinds of particles.

Sephadex G-200 was selected as the gel, because it can be used in aqueous media , and ,considering the size of the micelles,[8] it has an appropriate sieving range. Another reason is that the gel is known to exhibit less serious retarding effects as compared with other gels of the same series.

The elution patterns of related systems are shown in Figure 3. From the developing conditions, peak (II) corresponds to the pure micelles of NP-10.[8] Peak (III),observed under conditions where free dye was almost absent due to the use of a large quantity of NP-10 in the eluant, can be assigned to the dye-containing particles.Judging from the elution volumes, GPC provided another evidence for the adsorption model : the dye - containing micelles are definitely larger than the pure NP-10 micelles.

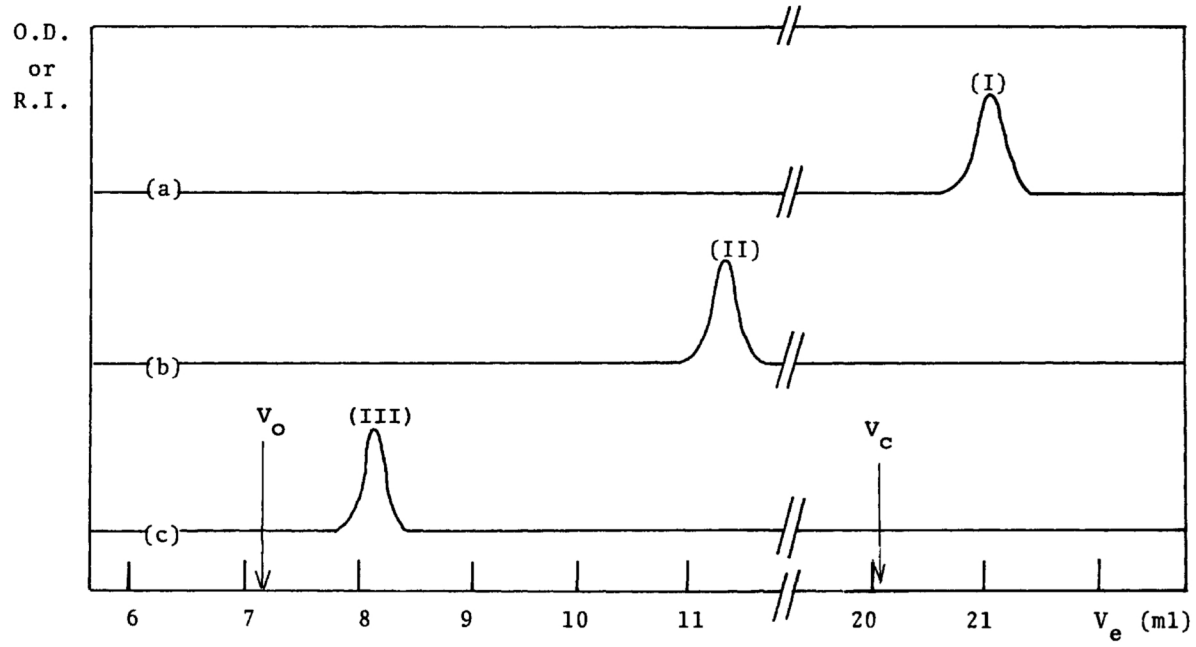


Fig.3 GPC Elution Patterns.Column:9 X 300mm; Gel: Sephadex G-200; Temperature:25°C
Chromatogram (a) : injected sample :20μl of aq.sol. of D(1 X 10^{-4} mol/dm^3);eluant: water;detected by visible absorption (500nm).
Chromatogram (b) : injected sample :50μl of aq.sol. of NP-10(0.01 mol/dm^3);eluant: aq.sol of NP-10 (1 X 10^{-4} mol/dm^3);detected by differential refractory index.
Chromatogram (c) : injected sample :50μl of aq.sol.containing D (5 X 10^{-5} mol/dm^3) and NP-10 (0.01 mol/dm^3); eluant : aq. sol. of NP-10 (0.01 mol/dm^3); detected by visible absorption (500nm).
Notations : V_o: void volume, determined by eluting Blue Dextran (mol.weight 2X10^6)
V_c : column volume ; V_e: elution volume.

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NOTES AND REFERENCES

* To whom all inquiries about the paper should be addressed.

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