CHEMISTRY LETTERS, pp. 1319-1322, 1977. Published by the Chemical Society of Japan

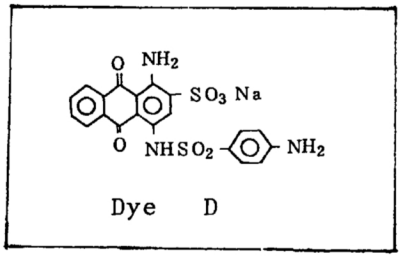
BEHAVIOR OF ANTHRAQUINOID ACID DYES IN AQUEOUS SOLUTION OF SODIUM DODECYL SULFATE

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

The behavior of an anthraquinoid acid dye in an aqueous solution of an anionic surfactant, sodium dodecyl sulfate, was investigated by electronic spectroscopy and gel permeation chromatography. The experimental findings suggest that above the cmc, one dye molecule is associated with one surfactant micelle.

Effects of surfactants on the dyeing behavior of acid dyes have been known since the thirties. In application, many surfactants have been used as levelling agents in dyeing processes.[1] It is generally established that while non-ionic surfactants exert marked influence on the behavior of acid dyes in water baths, the interaction of anionic surfactants with dyes is considered to be relatively small, and hence, little attention has been paid to this problem. In recent years, we have been interested in the mechanistic studies of the interaction of surface active agents with organic compounds, especially with dyes, and we realize that a complete and systematic view cannot be advanced without studying the effect of anionics. There are very few works on this topic, and except some qualitative observations,[1,2] no detailed mechanistic studies have been known. The present investigation was undertaken to fill this serious gap, and we have tried, whenever possible, to analyze the problem in quantitative terms. The preliminary results of this study are reported in this paper.

As the anionic surfactant, sodium dodecyl sulfate was selected because its properties are well documented in the literature. The acid dye chosen in our study has the structure shown on the right. The absorbances of the aqueous solutions of the dye, denoted as D, strictly obeyed Lambert - Beer's law in the concentration range (1.0 to 10 X 10^{-5} mole/dm^3) used throughout this investigation. It can be safely considered that in our system, aggregation, if any, of the dye only occurred to a negligible extent.[3] In calculations, we thus can assume that the total concentration of D is equal to that of monomeric dye. Another advantage in employing D is that, as stated later, it showed relatively large changes, both in the position of maximal absorption and in the molecular extinction coefficient when coexisting with the surfactant. Calculations of the concentrations of various species from spectral data are expected to be highly accurate and reliable.



Dye D

Solutions containing a constant quantity of D (1 X 10^{-5} mol/dm^3) and sodium dodecyl sulfate (SDS) at concentrations covering a wide range (from 0.2 to 500 X 10^{-3} mol /dm^3) were subjected to spectroscopic measurements. At lower concentrations of SDS, the spectrum of the dye was altered in an irregular way. This is indicating of an

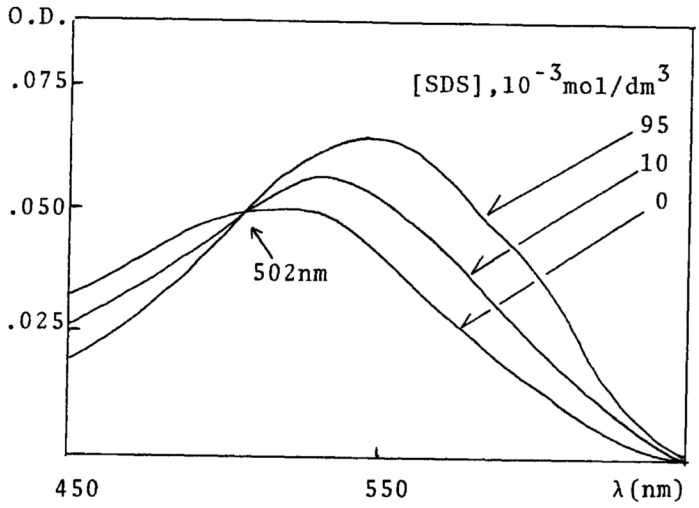


Fig.1 Spectra of aqueous solutions of dye D (1 X 10^{-5} mol/dm^3) at the presence of SDS. The concentrations of the surfactant are shown in the figure.

intermolecular interaction between the dye and the surfactant,resulting in the formation of more than one kind of simple complexes, as proved by the absence of an isosbestic point. It has been reported in the literature that SDS forms complexes with C.I.Acid Blue 120 at concentrations below the cmc.[2] At concentrations above the cmc, the surfactant affected the spectrum of D in a systematic way.As is shown in Figure 1, the position of maximal absorption was shifted to longer wavelengths, and the molecular extinction at λ_{max} increased with an increase in [SDS]. An isosbestic point was clearly recognized at 502 nm. These findings suggest that the dye exists in the system under two,and only two, essentially different molecular environments. In one, the dye is free (or more exactly,hydrated), and in the other, it is associated with SDS. The concentrations of the free dye, and of the surfactant-associated dye can be estimated by the following procedure.

Let us denote the absorbances of the dye at 550nm (where the molecular extinction coefficient of the dye was most affected) in the absence and presence of the surfactant,A_0 and A respectively. The difference ΔA (= $A - A_0$) thus represents the extent to which the dye is associated with the surfactant. If the surfactant was hypothetically added at infinite concentration, the dye might be assumed to be completely associated with the surface active agent. Let ΔA_∞ be the difference between A and A_0 under this condition. The molar concentrations of the free dye,[D] and of the surfactant -associated dye,[D_S],can be determined from spectral data, using the following relations:

$$[D_S] / [D_0] = \Delta A / \Delta A_\infty \quad \ldots\ldots (1)$$

$$[D] / [D_0] = 1 - (\Delta A / \Delta A_\infty) \quad \ldots\ldots (2)$$

$$[D_0] = [D] + [D_S] \quad \ldots\ldots (3)$$

Here,[D_0] stands for the total concentration of the dye. The value of ΔA_∞ can be easily determined from the plots of $1/[\Delta A]$ versus $1/[S_0]$ ([S_0] being the total molar concentration of SDS) , extrapolating $1/[S_0]$ to zero,namely [S_0] to infinity. We found that the value of ΔA_∞ corresponding to [D_0] = 5 X 10^{-5} mol/dm^3 was exactly 5 times that corresponding to [D_0]= 1 X 10^{-5} mol/dm^3. This result partly justifies our method to evaluate ΔA_∞.

Although intermolecular interaction between the dye and the surfactant was observed, we assume that above the cmc, the interaction is mainly caused by the surfactant micelles. The validity of this assumption will be discussed later in this paper.

In our model, x molecules of the dye are supposed to be associated with a surfactant micelle M :

$$x\,D + M \rightleftharpoons MD_x \quad \ldots\ldots(4)$$

The equilibrium of this process is defined by :

$$K_M = [MD_x] / [M]\,[D]^x \quad \ldots\ldots(5)$$

Using the mass balance equalities concerning the surfactant and the dye, we can derive the following equation:

$$K_M \frac{x}{n} \frac{[S_o] - CMC}{[D_o] - [D]} = \frac{1}{[D]^x} + K_M \quad \ldots\ldots(6)$$

where n is the aggregation number of SDS micelles. Taking into account the fact that we are dealing with a relatively weakly interacting system, we make a further assumption that the numerical value of K_M is much smaller than that of $1/[D]^x$. This allows us to rewrite Equation (6) in the following form:

$$\log \frac{[S_o] - CMC}{[D_o] - [D]} = -x.\log[D] - \log(x.K_M / n) \quad ..(7)$$

The above equation was tested by plotting the quantity on the left side against log[D]. As is shown in Figure 2, Equation (7) was proved to be well fitted by the experimental results. The figure reveals further that in our model, the value of x is equal to unity, namely, one dye molecule is associated with one micelle.

Assuming that the association of a dye molecule does not affect the aggregation number of the micelle,which has been reported in the literature to be 62,[4] the value of K_M was calculated to be 3.5 X 10^3 dm^3/mol. The earlier assumption concerning the relative magnitudes of K_M and $1/[D]^x$ (greater than 10^5 for x = 1) is thus justifiable

In analyzing spectroscopic data,as can be seen from the above arguments,we have made some apparently artificial assumptions,namely:(a)the interaction is mainly due to the surfactant micelles; (b)the association of a dye moleculedoes not alter the aggregation number,hence, the size, of the micelles . Discussions made so far are only valid if these assumptions can be verified experimentally. With this purpose in mind, we performed a series of experiments using the technique of gel permeation chromatography (GPC).

Our idea in making use of this technique is very simple. By eluting a concentrated sample of the surface active agent with an eluant containing the same surfactant at a concentration higher than or equal to the cmc , the elution volume of the sample is expec - ted to correspond to that of the sur-

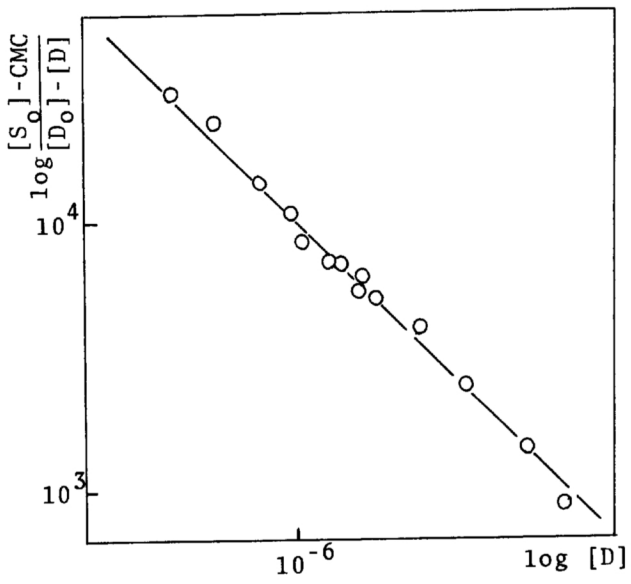


Fig.2 Plots of $\log \frac{[S_o] - CMC}{[D_o] - [D]}$ against log[D]: Test of Equation (7). For the meaning of the notations, see Text.

factant micelle.[5] If the dye is eluted by solutions of the surfactant at concentrations higher than the cmc, and if the dye is associated with the *surfactant micelles*, the elution volume of the dye will be decreased, due to the presence of large aggregates containing the dye. In extreme cases when the concentration of the surfactant in the eluant is predominantly large compared with that of the dye, we can assume that the concentration of the hydrated dye is negligible as compared with that of the surfactant-associated dye, and under these conditions, the elution volume of the dye corresponds to that of the dye - containing micelle.

Sephadex G-200 gel was selected in our investigation because it can be used in aqueous media, and because its sieving range is appropriate considering the size of the SDS micelles.[4] Another reason is that the gel is known to exhibit less serious secondary effects as compared with other gels of the same series.

The GPC results were summarized in Figure 3. It can be seen that the elution volume of the dye, as determined by its absorption in the visible region, decreased monotonously as the concentration of SDS in the eluant increased, and finally, converged to 15.2 ± 0.2 ml. The elution volume of the SDS micelles, found when a sample containing 60 X 10^{-3} mol/dm^3 was eluted with an eluant containing SDS at a concentration equal to the cmc, was 14.8 ± 0.2 ml. A differential refractometer was used as the detector in this experiment. These findings proved, within experimental errors, the validity of the assumptions stated in the preceding paragraph and provided another strong evidence to the plausibility of the model proposed in this paper.

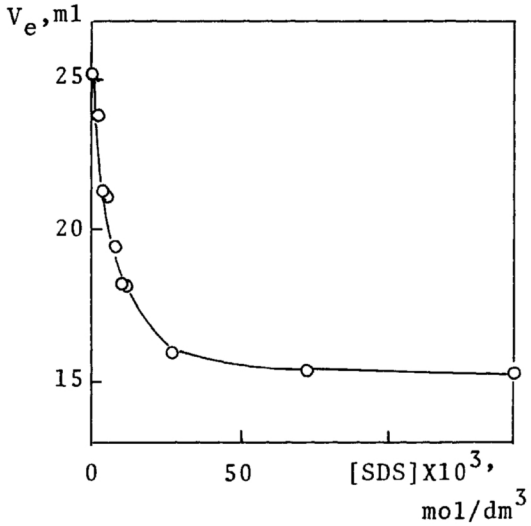


Fig.3 Dependence of the elution volumes of D on the concentration of [SDS] in the eluant. Gel: Sephadex G-200; Column: 9X300mm. Temperature: 25°C

A more detailed discussion on the mode of incorporation of the dye into the surfactant micelles, including the site and the nature of bonding, will be published in the near future.

We are grateful to Professor Mitsuhiko Hida, Tokyo Metropolitan University, for a generous gift of bromamine acid used in the synthesis of dye D. Dr. Noriko Shinozuka and Mr. Koji Hayase of this laboratory are thanked for helpful discussions.

NOTES AND REFERENCES

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

1) J.L.Moillet and B.Collie, "Surface Activity", D.Van Nostrand Co.Inc., N.Y.(1951), p.221
2) Y.Nemoto and T.Imai, Kogyo Kagaku Zasshi, 62, 1286 (1959)
3) M.Hida, A. Abe, H. Murayama and M. Hayashi, Bull. Chem. Soc. Jpn, 41, 1776 (1968)
4) A. Mysels, J. Phys. Chem., 63, 1696 (1959)
5) K.S. Birdi, Colloid & Polymer Sci., 252, 551 (1974)

(Received September 12, 1977)