# Kinetic Study of the Penetration of an Anthraquinoid Acidic Dye into Cationic Micelles

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(Received November 15, 1980)

The penetration of an anthraquinoid acidic dye into the micelle of a cationic surfactant, hexadecyltrimethylammonium bromide (HTAB), was studied kinetically by the stopped-flow method. The rate-determining step of this process was considered to be the dye reorientation from the micelle surface to its core. The apparent rate constants, $k_{app}$, of the dye penetration were determined by the first-order kinetics. The $k_{app}$ values were a function of the surfactant micellar concentration. Above a certain micellar concentration (CMC) the $k_{app}$ values become constant. The constant $k_{app}$ was about 0.37—0.38 $s^{-1}$ regardless of the total dye concentration. In the lower micellar concentration, there was a linear relationship between the $k_{app}$ value and the number of the dye molecules which penetrated into a single micelle, $n$. This $n$ was one of the factors which governed the dye penetration process.

Although the static properties of surfactant micelles, of their solubilization and of their interaction with organic compounds have been investigated extensively, only a few kinetic studies have been reported, probably due to the difficulty of measuring such rapid reactions. The development of modern techniques of analyzing fast reactions, such as the stopped-flow, the temperature-jump, the pressure-jump, and the ultrasonic relaxation methods, made it possible to discuss the kinetics of the micelle formation and dissociation.[1] Kinetic studies of the dye penetration into micelles have been reported recently.[2-4]

The micelles are in a dynamic equilibrium with themselves. The relaxation times obtained by the above techniques lead to the conclusion that there are at least two relaxation processes. The slower process is the micelle formation and dissociation, and its relaxation times are calculated to be about $10^{-2}$ s from the results of the temperature- and/or the pressure-jump experiments.[5] The faster one is the exchange of surfactant monomers between the aqueous and the micellar phases, and its relaxation times are estimated as $10^{-6}$ s by the ultrasonic relaxation method.[6] Since the micellization processes were faster than the dye penetration into micelles, these effects would be negligibly small in the kinetic study of the dye penetration.[2-4]

The kinetic studies of the dye penetration have been carried out by using ionic dyes with opposite charges to that of the surfactants, by the stopped-flow method.[2-4] In all cases, the apparent rate constants, which were calculated assuming a first-order reaction, increased with the increase in surfactant micellar concentration, and subsequently became constant. The mechanism at the lower micellar concentration was not discussed in detail, probably because of some complicated and unknown factors. In the region of constant $k_{app}$ values, the mechanism was simplified, since these factors can be neglected. Thus, the discussions have been concentrated on this region.[7]

In the present paper, the rate constants of the penetration of an anthraquinoid acidic dye into cationic micelles were determined by measuring the change of dye absorbance, using the stopped-flow method. The main purpose is to develop a reasonable mechanism. The problem in the lower micellar concentration is discussed in detail, referring to the spectroscopic data[8] on the dye-surfactant system used in this study.

## Experimental

*Materials.* Hexadecyltrimethylammonium bromide (HTAB), was obtained from Tokyo Kasei Industries Co. Ltd., and purified by recrystallizing from ethyl acetate containing 10 vol% ethanol and vacuum-drying at 80 °C. The CMC was determined to be $9.7 \times 10^{-4}$ mol $dm^{-3}$ by conductometry.

The dye, which was synthesized from the same process as used in a previous work,[4] has the structure shown in Fig. 1. The dye was paper-chromatographically pure, and the interaction among the dye molecules themselves was negligible spectrophotometrically in the concentration range used in this study.

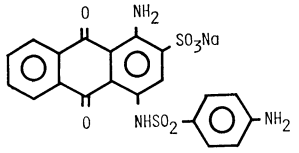


Fig. 1. Structure of an anthraquinoid acidic dye.

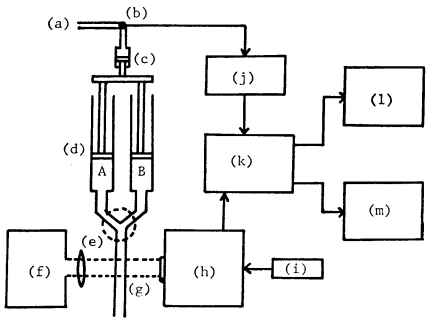


Fig. 2. Block diagram of RA-1100 and RA-108S systems.
(a): $N_2$ gas, (b): electromotive valve, (c): pushing syringe, (d): sample syringes, (e): mixing cell, (f): monochromator, (g): optical cell, (h): photomultiplier, (i): DC source, (j): trigger circuit, (k): digital memory RA-108S, (l): oscilloscope, (m): X-Y recorder.

*Apparatus.* The stopped-flow apparatus was a Fast Reaction Analyzer RA-1100 of Union Scientific Eng. Co. Ltd.. Its block diagram is shown in Fig. 2. The reagents were forced by a pressure of *ca.* 0.3 MPa into the optical cell, whose path was 10 mm, through a four-jet mixing cell. The mixing was established within 1 ms. The dye absorbance change at 547 nm against time was stored in the digital memory apparatus (RA-108S), and subsequently displayed on an oscilloscope or recorded on an X-Y recorder. During the experiment, the cell temperature was controlled by circulating water at 30±0.5 °C.

*Methods.* The sample syringes A and B were filled with a given concentration of dye solution and a certain concentration of the surfactant solution above CMC, respectively. The results were analyzed by first-order kinetics.

## Results and Discussion

Some typical spectra of the dye in HTAB solution are shown in Fig. 3. The two characteristic bands at 510 and 547 nm are called α- and β-bands, respectively. The α-band appeared in absence of HTAB. In the presence of a sufficient amount of HTAB, the α-band changed to the β-band, indicating that dyes interacted with surfactants and/or micelles. The fact that the absorbance of both α- and β-bands increased in proportion to the dye concentration proved that there was no dye-dye interaction. The spectrum of the dye which had interacted with surfactants and/or micelles was similar to that the dye dissolved in methanol or acetone. These results lead to the inference that dyes are located in a methanol- or acetone-like atmosphere of the micelle core near the micellar surface. This is in agreement with the result of Sepulveda.[9]

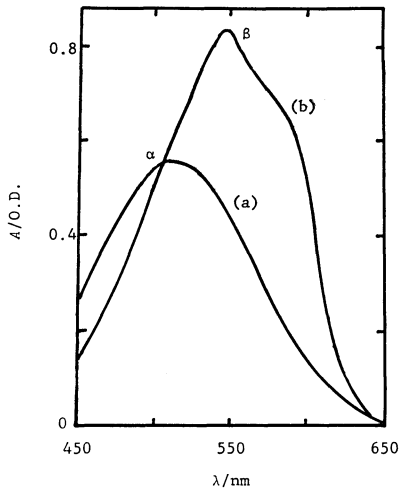


Fig. 3. Typical dye spectra.
(a) In absence of HTAB, (b) in presence of 10 mmol dm$^{-3}$ of HTAB. The dye concentration is 0.1 mmol dm$^{-3}$.

Table 1. Mixing conditions and results

| Run | A solution / mmol dm$^{-3}$ | B solution / mmol dm$^{-3}$ | Mixed solution / mmol dm$^{-3}$ | Dynamic abs. change |
|---|---|---|---|---|
| 1 | Dye 0.2 | Water | Dye 0.1 | None |
| 2 | HTAB 20 | Water | HTAB 10 | None |
| 3 | Dye 0.2 | HTAB 2 | Dye 0.1<br>HTAB 1 | Increase slightly |
| 4 | Dye 0.1<br>HTAB 1 | HTAB 20 | Dye 0.05<br>HTAB 10.5 | Increase greatly |
| 5 | Dye 0.2 | HTAB 20 | Dye 0.1<br>HTAB 10 | Increase greatly |

After mixing solutions of dye and surfactant, the system was followed by the absorbance at 547 nm; the results are listed in Table 1. Then, the time scale for observation of absorbance change against time changed from 10 ms to 50 s in all the Runs. It was difficult to determine the rate constant in Run 3, since the absorbance change was very slight. On the contrary, appreciable changes were observed in Runs 4 and 5, and both the absorbance changes were nearly the same.

We have some data on the interaction between HTAB and the dye.[8] At first, the dye forms with HTAB an insoluble 1:1 salt (DS). The salt is resolved by further addition of HTAB below CMC, and the concentration of resolved salt is a linear function of that of HTAB. Thus, the authors assume that the dye forms a small complex with HTAB. The slope of the straight line shows that the complex consists of a single dye and three HTAB molecule. Moreover, the complex ($DS_3$) has similar spectroscopic characteristics, *i.e.* similar shape of the absorption curve and wavelength of maximum absorption (547 nm), to those of the dye which penetrated into micelles. Above CMC, the absorbance at 547 nm increases more intensively with the increase in the concentration of HTAB, and finally becomes constant. This absorbance is regarded to be caused by the dye penetration into the micelles. The magnitudes of the absorbances at 547 nm of both the complex below CMC and the dye which penetrated into micelles are proportional to the concentration of the dye, but the molar extinction coefficients are different, as shown in Table 2. The authors assume that the dye forms a complex with HTAB in the bulk of solution prior to the penetration in the mixing experiment. Consequently, the following sequence was proposed;

$$D + S \longrightarrow DS \longrightarrow DS_3 \longrightarrow D_m,$$

where $D_m$ refers to the dye which penetrated into the micelles. Here, the process to forms $DS_3$ from DS would be very fast, because there exists a larger amount of $DS_3$ in Run 3 a short time after mixing. Accordingly, the process to form $D_m$ from $DS_3$ will be the rate-determining step in the above sequence. If the dye penetration was established by the accu-

Table 2. Molar extinction coefficients of the dye

| State of dye | ε at 547 nm[a] / dm$^3$ mol$^{-1}$ cm$^{-1}$ |
|---|---|
| Hydrated (D) | 4470 |
| Complex ($DS_3$) | 7870 |
| In micelle ($D_m$) | 9620 |

a) Ref. 8.

mulation of HTAB molecules around $DS_3$ (refers to the induced micellization),[2] the rate would be comparable to the micellization from the HTAB monomers. But, the relaxation in this study is much slower (about 10 s) than the micellization. A more reasonable model is though to be the adhesion of $DS_3$ to the micelle surface. At first, $DS_3$ diffuses onto the micelle surface, then the dye reorients into the inner hydrophobic portion of the micelle. The diffusion coefficient of $DS_3$ would be larger than that of HTAB micelle; it was estimated to be about $10^{-6}$ $cm^2$ $s^{-1}$ by the polarographic measurements.[10] Thus, as the diffusion process of $DS_3$ onto the micelle surface is also expected to be fast, it is not the rate-determining step. On the micelle surface, HTAB molecules in $DS_3$ may be replaced by that in the micelle and in the bulk in a short time.[11] Therefore, the dye would be in the state of $DS_3$ or a naked state in a dynamic equilibrium. As a result, the reorientation mentioned above is the most probable rate-determining step. The previous work[4] showed that the salt addition accelerated the reaction, probably due to the reduction of the surface potential of the micelle, and it supports the above assumption. During the dye penetration, the momentary fluctuation in the physical properties of the micelle, such as the aggregation number, can be neglected, because the micelle equilibrates much faster than the dye penetration.[11]

A reformed sequence for evaluating the apparent rate constants is proposed:

$$DS_3 \rightleftharpoons D_s \underset{k'}{\overset{k}{\rightleftharpoons}} D_m,$$

where $D_s$, $k$, and $k'$ refer to the dye which exists on the micelle surface in the state of $DS_3$ and/or a naked state, and to the rate constants of the forward and backward reactions, repectively. The authors postulate similar extinction coefficients for $DS_3$ in the bulk and $D_s$, since the atomosphere of the dye chromophore of $D_s$ is not so different from that of $DS_3$. The rate equation is expressed as

$$-\frac{d[D_s]}{dt} = k[D_s] - k'[D_m]. \quad (1)$$

In the adsorption process prior to the dye reorientation it is assumed that the dye exists predominantly on the micelle surface and that $[DS_3]$ in the bulk is negligible; thus the equilibrium constant is expected to be about $10^4$ according to the previous paper.[2] Since $[D_m]=[D]_0-[D_s]$, and $k[D_s]_e=k'\times[D_m]_e$ at equilibrium, Eq. 1 is converted to Eq. 2:

$$-\frac{d[D_s]}{dt} = \frac{[D]_0}{[D]_0-[D_s]_e}k([D_s]-[D_s]_e). \quad (2)$$

An integration of Eq. 2 with respect to time yields

$$\ln\frac{[D_s]-[D_s]_e}{[D]_0-[D_s]_e} = -\frac{[D]_0}{[D]_0-[D_s]_e}kt = -k_{app}t, \quad (3)$$

where $[D_s]$ and $[D_m]$ are the concentrations of the adsorbed dye on the micelle surface and of the dye penetrated into the micelle, respectively, and $[D]_0$ stands for the total concentration of the dye, and the subscript e refers to equilibrium.

Figure 4 shows the typical reaction curve. Absorbance increased with elapsed time, and subsequently flattened out. The total absorbance change ($\Delta A_0$) is in proportion to the amount of the dye which penetrated into the micelle at equilibrium ($[D_m]_e$), and $\Delta A$ refers to that during the relaxation process ($[D_m]$). The subtraction of $\Delta A/\Delta A_0$ from unity yields

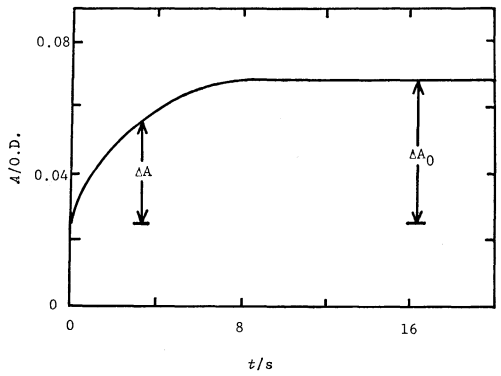


Fig. 4. Typical reaction curve.

$$1-\frac{\Delta A}{\Delta A_0} = 1-\frac{[D_m]}{[D_m]_e} = \frac{[D_s]-[D_s]_e}{[D]_0-[D_s]_e}. \quad (4)$$

Therefore, the logarithm of Eq. 4 is the same as the left-hand side of Eq. 3. The apparent rate constants, $k_{app}$, were calculated by Eqs. 3 and 4. The $k_{app}$ values increased sharply with the increase in the surfactant concentration above CMC, and subsequently became constant, as shown in Fig. 5. The $k_{app}$ had the same values regardless of the total dye concentration at high concentration of micellar surfactants.

At lower micellar concentration, some complicated factors may take part in the reaction. In papers by other workers,[2,3] there has been little explanation about the results obtained in this region. In our previous work, $[D_s]_e$ values were determined.[8] The $k_{app}$ values were recalculated in consideration of $[D_s]_e$; these are connected by the dotted lines shown in Fig. 5. This treatment lowers $k_{app}$ values to some extent, but no interesting result is obtained. Consequently, the $[D_s]_e$ values slightly affect $k_{app}$ values.

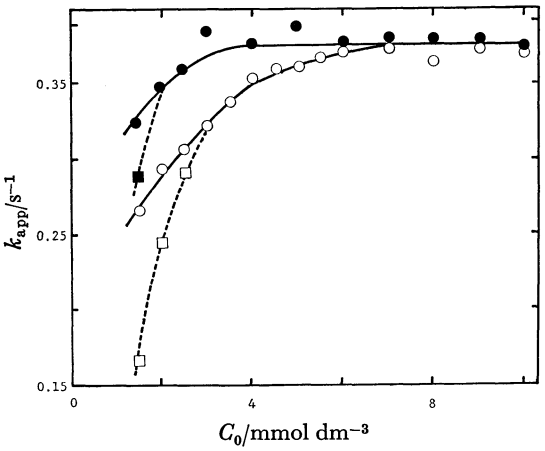


Fig. 5. Plots of $k_{app}$ against HTAB concentration, $[C]_0$. ···●···: $[D]_0=0.05$ mmol $dm^{-3}$, ···○···: 0.1 mmol $dm^{-3}$. Recalculated $k_{app}$ values in consideration of $[D_s]_e$ are connected by dotted line.

As one additional factor, the $[D_s]_e$ value induces the number of the dye molecules which penetrate into a single micelle, $n$. The $n$ value shown in Fig. 6 was obtained use of the following equation:

$$n = \frac{N([D]_0 - [D_s]_e)}{[C]_0 - CMC}, \quad (5)$$

where $N$ is the aggregation number of HTAB micelles,[1] and $[C]_0$ stands for the total HTAB concentration. The $n$ decreased with the increase in the HTAB concentration until $n$ attained unity. The $n$ value is not actually less than unity even in the higher HTAB concentration, where there are micelles containing a single dye and those without dye. The

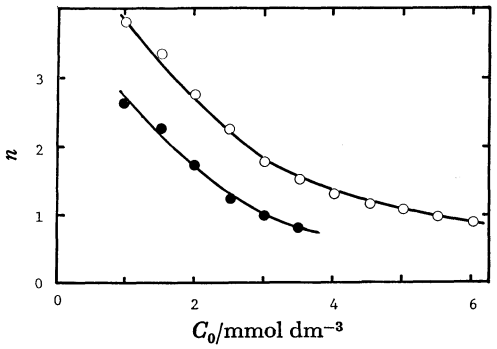


Fig. 6. Plots of the number of dye penetrated into a single micelle ($n$) *vs.* HTAB concentration, $[C]_0$. ···●···: $[D]_0$=0.05 mmol dm$^{-3}$, ···○···: 0.1 mmol dm$^{-3}$.

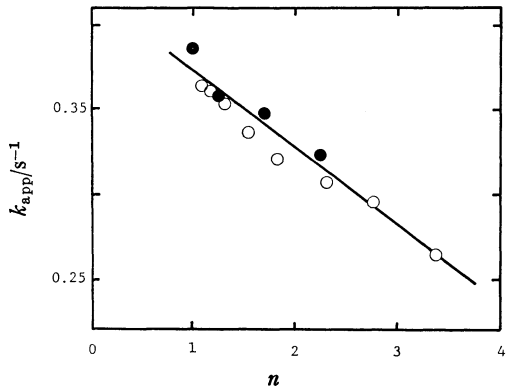


Fig. 7. Relation between $k_{app}$ and $n$. ···●···: $[D]_0$=0.05 mmol dm$^{-3}$, ···○···: 0.1 mmol dm$^{-3}$.

$k_{app}$ becomes constant at the same HTAB concentration for which $n$ is unity. Moreover, in the lower HTAB concentration, there is a linear relationship between the $k_{app}$ and the $n$ value, as shown in Fig. 7. This suggests that the $n$ value is one of the factors which govern the rate-determining step of the dye penetration. When $n$ is unity, a single dye molecule reorients into a single micelle without any interaction with the other dyes. Then, the dye mortion seems to be dominated only by the dye structure and the properties of the micelle surface. When $n$ values are more than unity, dyes on the surface of a single micelle reorient into its core slowly, since dyes are able to interact with each other directly and/or indirectly through the micellar surfactants. The increase in $n$ value strengthens this interaction, and consequently the penetrating rates are further decelerated.

The dye penetration process consists of a number of elementary reactions. The inquiry into each reaction by other techniques will make it possible to gain more insight into the detailed mechanism.

We thank Dr. Noriko Shinozuka for her helpful discussions.

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