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KINETIC STUDY OF PENETRATION OF AN ANIONIC DYE INTO SURFACTANT MICELLES

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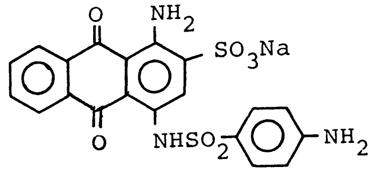
The rate of penetration of an anionic dye into micelles, of hexadecyl trimethyl ammonium bromide(HTAB), was measured by the stopped-flow method using the specific absorption band. The rate constants, *k*'s , were determined to be 0.34-0.37 sec^{-1} at 30°C. The kinetic effect of the halide ions on the penetration was discussed.

Although the equilibrium properties of surfactant micelles, of solubilization, and of their interaction with organic compounds have been investigated extensively 1)2)3), only few kinetic studies have been reported, probably because of the difficulty of measuring the such rapid reactions. The development of several techniques of analyzing fast reactions, such as stopped-flow, temperature-jump, pressure-jump, and ultrasonic relaxation methods4), made it possible to discuss the kinetics of the micelle formation and dissociation. Recently, the rate constants of penetration of cationic dyes into anionic micelles have been measured by the stopped-flow method5)6). The investigation suggested the possible mechanisms of interaction between dyes and micelles. The purposes of the present work are to interpret the obtained results in terms of a suitable mechanism and to discuss the effect of the halide ions on the penetration rates.

HTAB used in this study was obtained from WAKO Pure Chemical Industries Co.Ltd., and purified by recrystallizing from ethyl acetate containing 10 vol% ethanol. The CMC was determined to be 9.7×10^{-4} mol/dm^3 by measuring electrical conductivities. The anionic dye, which was synthesized by the Ullmann condensation and purified by recrystallizing with hot water, has the structure shown on the right. The spectral properties of this dye have been previously described2)3). The potassium halides were G.R. reagents obtained from WAKO Pure Chemical Industries Co.Ltd., and used without further purification.



The stopped-flow apparatus was UNION Giken Fast Reaction Analyzer RA-1100. The reagents were forced by a pressure of *ca.* 2-4 kg/cm^2 into the optical cell, whose path was 2 mm, through a four-jet mixing cell. The change of the absorbance of the dye at 547 nm against time was displayed on an oscilloscope and subsequently recorded on an X-Y recorder. During the measurements, the cell temperature was controlled within 30 ± 0.5 °C by circurating water.

Some typical observed spectra of the dye in HTAB solutions are shown in Fig.1. Two characteristic absorption bands were observed at 514 nm and 547 nm. Figure 2 shows the change of the absorbance at 547 nm with surfactant concentration. When the concentration of HTAB was below 6×10^{-4} mol/dm^3, the absorbance of the dye could not be determined accurately due to the formation of a precipitate. As the surfactant was further added, the absorbance at 547 nm increased sharply during a relatively small range of concentration, and then became constant.

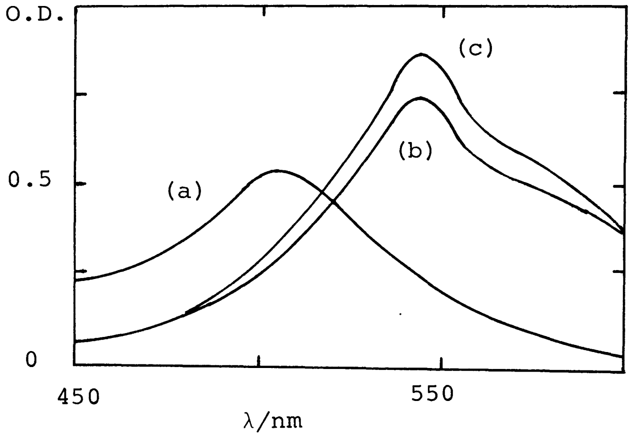


Fig. 1 Spectra of HTAB solutions (a, 0; b, 1×10^{-3}; c, 1×10^{-2} mol/dm^3) of dye (1×10^{-4} mol/dm^3).

In the mixing experiments, an appreciable change at 547 nm was observed, and the results are analyzed using rate equation of the first-order reaction. The rate constants, k's, were evaluated from the slope using the least-squares method. As well as the change of absorbance, k increased sharply with the surfactant concentration above the CMC and subsequently became constant, as shown in Fig. 3.

The addition of potassium halides accelerated the rate of the penetration (Table 1), and the extent of acceleration increased in the order of $I^- > Br^- > Cl^-$.

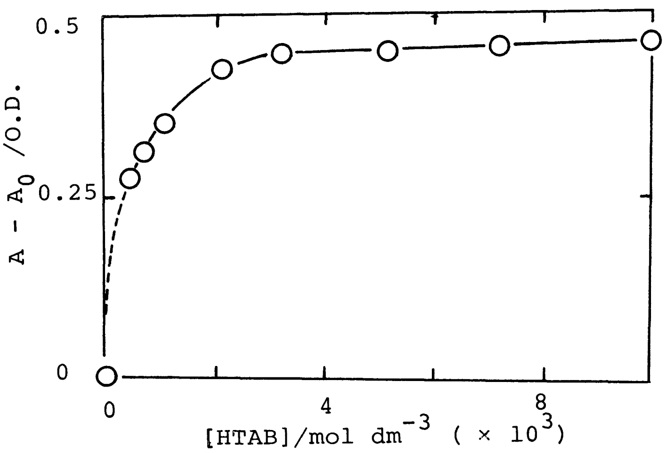


Fig. 2 Absorbance change of HTAB solutions of dye (1×10^{-4} mol/dm^3) at 547 nm. A and A_0 are absorbances in the presence and absence of HTAB, respectively.

According to the preceding workers[5)6)], it has been noticed that the cationic dyes interact electrostatically with the anionic surfactants prior to the penetration into the inner hydrophobic portion of micelles, and that the rate of the electrostatic interaction is very fast and lies beyond the time range of the stopped-flow experiments. In our experiments, we also assume that the dye is adsorbed onto the micelle surface and subsequently transferred into the inner hydrophobic portion of the micelles, and adopt the following sequence;

$$D_s \xrightarrow{\text{fast}} D_s \underset{k_b}{\overset{k_f}{\rightleftharpoons}} D_m$$

(free dye) (on surface) (in micelle)

where k_f and k_b are the rate constants of the forward and backward reactions, respectively. Assuming that the rate-detrmining step is the transition of dyes into the micelle, the rate equation is expressed as,

$$-\frac{d[D_s]}{dt} = k_f[D_s] - k_b[D_m]. \qquad [1]$$

Since

$[D_m] = [D]_0 - [D_s]$, and

$k_f[D_s]_e = k_b[D_m]_e$ at equilibrium,

an integration of Eq.[1] with respect to time yields

$$\ln\frac{[D_s] - [D_s]_e}{[D]_0 - [D_s]_e} = -\frac{[D]_0}{[D]_0 - [D_s]_e}k_f t, \qquad [2]$$

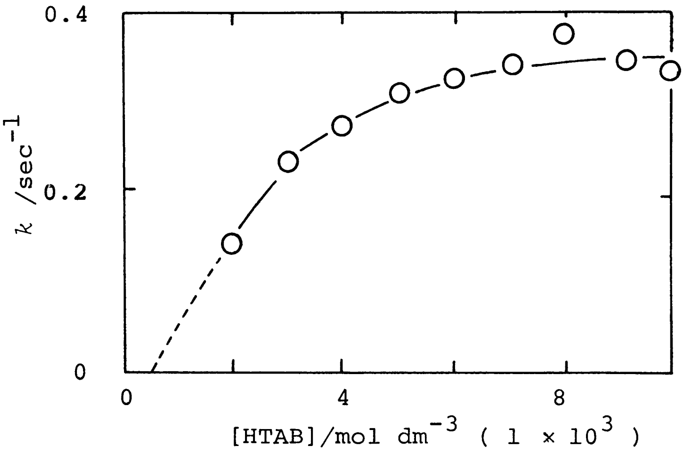


Fig. 3 Plots of k against the concentrations of HTAB. The conc. of dye is 1×10^{-4} mol/dm^3.

where $[D_s]$ and $[D_m]$ are the concentrations of the adsorbed dye on the micelle surface and of the penetrating dye into the micelles, and $[D]_0$ stands for the total concentration of the dye, and the subscript e refers to the equilibrium. At lower concentrations of micellar surfactants, the mechanism will become more complex than the above scheme, because a simple salt formation of the dye with the surfactant dispersed as monomer takes part in the scheme. Moreover, $[D_s]_e$'s are the unknown variables, being not able to measure the spectra of the dye on the micelle surface. When $[D_s]_e$ can be approximated to zero at high concentrations of the surfactant, the following equation is obtained from Eq.[2];

$$\ln\frac{[D_s]}{[D]_0} = - k_f\ t . \qquad [3]$$

The plots shown in Fig. 3 prove that Eq.[3] holds above 6×10^{-3} mol/dm^3 of HTAB. This is in agreement with our discussion on the kinetics of the penetration. Thus, kinetic argument related to the penetration of the cationics/anionics into the anionic/cationic micelles, to which the above scheme could be applied, is desirable at the high concentration of micellar surfactants.

As the factors which govern the rate of penetration, the surface potential of the micelle and the structure of the surfactant will play important role. It is well known that the increase of counter-ion of the micelle increases the extent of the counter-ion binding, thus reduces the surface potential and lowers the CMC$^{7)}$. In our case, however, the experimental condition is selected at which the penetrating rates are independent on the concentration of micellar surfactants as shown in Fig. 3. Thus the rate is dependent only on the surface potential in this case. Thus, the rate is supported by facts that the k's increased with the concentration of halide ions, and that the accelerating effect was in the order of $I^- > Br^- > Cl^-$ which was the same as that of reducing the surface potential[7]. The effect of anionic additives on the rates of penetration in this case is greater than observed for a cationic additive to anionic surfactant micelle[6], probably due to the stronger adsorptivity of anionic counter-ion onto the surface of the micelles.

Further studies on both the relation between *k* and the surface potential and the effect of various additives are in progress to gain more insight to the detailed mechanism.

Table 1 Effect of halide ions on the penetrating rates

	$\frac{Ca}{mol/dm^3}$ (× 10^3)	k/k_0
KCl	10	2.13
	20	3.74
	30	4.84
KBr	5	1.73
	10	3.19
	15	6.32
K I	0.25	1.08

k and k_0 are the rate constants in the presence and absence of added electrolytes, respectively. Ca is conc. of added electrolytes. The conc. of HTAB is $1 \times 10^{-2} mol/dm^3$ in all case.

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