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ASSOCIATION OF THE TRIS(1,10-PHENANTHROLINE)IRON(II) CATION WITH A CATIONIC ALKYLTRIMETHYLAMMONIUM MICELLE

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The rate of dissociation of $[Fe(phen)_3]^{2+}$ increased in cationic micellar solutions of alkyltrimethylammonium bromide, $C_nH_{2n+1}N(CH_3)_3Br$ (n=8 − 16). The complex ion is very probably incorporated into the micelle together with the counter ion.

Micellar effects on inorganic reactions aroused increasing attention in recent years.[1)] For the association of ionic reactants with ionic micelles, electrostatic interaction plays a major role. Thus, a reactant with a charge of the same sign as that of a micelle is usually repelled electrostatically from the micelle. Catalytic effects of micelles have rarely been observed for first order reactions of such a reactant. On the other hand, we have previously found that the dissociation rate of a cationic metal complex, $[Fe(phen)_3]^{2+}$, increased slightly in cationic micellar solutions of octyl- and decyltrimethylammonium bromides.[2)] The cause of the increase in the rate, however, is not clear so far. The present communication describes a further investigation of the increase in the rate in micellar solutions of alkyltrimethylammonium bromides, $C_nH_{2n+1}N(CH_3)_3Br$ (n=8-16).

The dissociation rate of the complex was obtained at 32 °C from the decrease in absorbance (510 nm) with time of the solution containing 5×10^{-5} mol dm^{-3} $[Fe(phen)_3]Br_2$, a proper concentration of alkyltrimethylammonium bromide, and nickel(II) chloride (5×10^{-4} mol dm^{-3}) as a scavenger of liberated phenanthroline. Experimental details were similar to those described in our previous paper.[2)]

Figure 1 shows the rate constants for the dissociation of the complex in alkyltrimethylammonium bromide solutions; the marks on dashed lines are the results previously reported.[2)] In the region below the critical micelle concentrations (cmc) of each alkylammonium bromide, the decrease in the rate has been related to the formation of aggregates such as $[Fe(phen)_3]^{2+}\cdot C_nH_{2n+1}\overset{+}{N}(CH_3)_3$ and $[Fe(phen)_3]^{2+}\cdot Br^-\cdot C_nH_{2n+1}\overset{+}{N}(CH_3)_3$ through hydrophobic interaction.[2)] In solutions above the cmc's of decyl-, dodecyl-, and tetradecyltrimethylammonium bromides studied here, the rate increased considerably with increasing concentrations of surfactants. This assures that the complex cation interacts with the cationic micelle. Figure 2 shows the effects of potassium bromide on the reaction rates in the presence and in the absence of dodecyltrimethylammonium bromide (0.4 mol dm^{-3}, > cmc). Without the surfactant micelles, the dissociation rate decreased

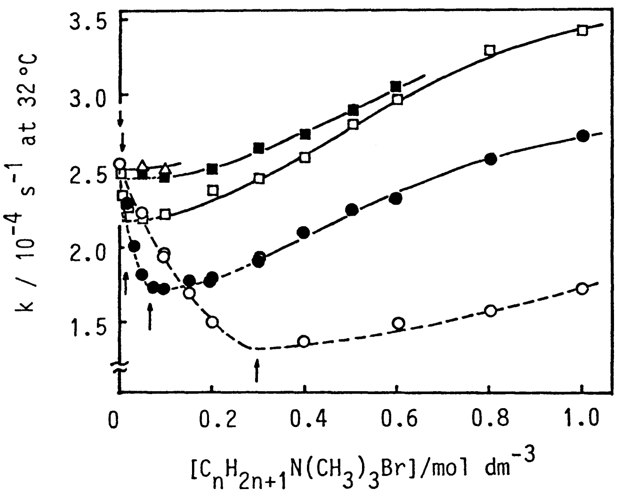

Fig. 1. Rate constants in $C_nH_{2n+1}N(CH_3)_3Br$ solutions: n=8, ○; n=10, ●; n=12, □; n=14, ■; n=16, △. Arrows indicate cmc values.

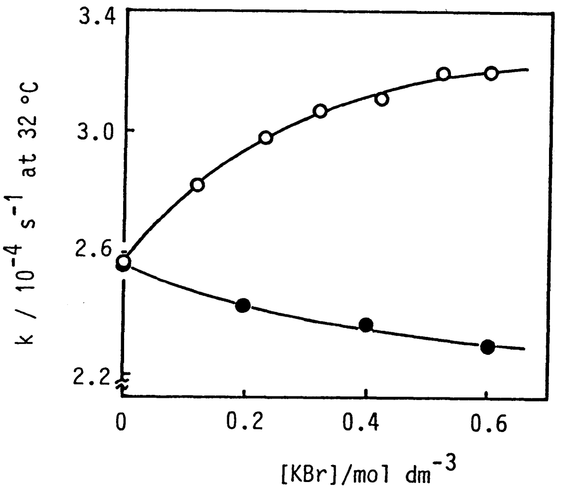

Fig. 2. Rate constants in KBr solutions with (0.4 mol dm^{-3}, ○) and without (●) $C_{12}H_{25}N(CH_3)_3Br$.

with the increase in the KBr concentration, while with the micelles, the rate increased. This suggests that the acceleration of the dissociation by the micelles was brought about by a concerted effect of bromide ions and the surfactant micelles, even in the absence of added KBr (Fig. 1).

Studies were also made on the effects of counter ions of alkyltrimethylammonium micelles on the dissociation rate. In 0.5 mol dm^{-3} tetradecyltrimethylammonium chloride, the rate was 4.9×10^{-4} s^{-1} at 32 °C; this is considerably larger than the rate in the corresponding bromide solution (2.74×10^{-4} s^{-1}) and than the rate in pure water (2.54×10^{-4} s^{-1}). The larger rate in the chloride solution can be related to a stronger nucleophilic interaction of a chloride ion, than that of a bromide ion,3) with the complex ion in an ion-pair; such a mechanism (the ion-pair interchange mechanism) of dissociation has been proposed previously to account for the different rate of the dissociation of the complex ion in aqueous3) and aqueous methanol4) solutions containing different kinds of anions. The larger rate in the micellar solutions than in aqueous solution containing 0.5 mol dm^{-3} potassium chloride (2.54×10^{-4} s^{-1}) or bromide (2.31×10^{-4} s^{-1}) may be related to a lower dielectric constant of the medium surrounding the complex ion in the micellar solutions; the activation energy to form a less polar transition state from the ion-pair is lower in a medium of a lower dielectric constant.4) The visible absorption band (510 nm) of the complex ion broadens slightly toward the longer wavelength in the micellar solution. A similar spectral change was observed for the [$Fe(phen)_2(CN)_2$]-sodium dodecylsulfate system, where the complex ion was suggested to be incorporated into the micelle.5) All the experimental results described above suggest that the $[Fe(phen)_3]^{2+}$ ion is incorporated into the cationic micelle of alkyltrimethyammonium ions together with its counter ion (Br^-).

References

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