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# Analysis of the Effect of Added Electrolyte on the Micellar Catalysis

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The effect of added electrolyte on micelle-catalyzed reaction was analyzed. The log [L.S] *vs.* log (total counter ion concentration) plot gives a straight line, where [L.S] is a limiting slope on a rate-surfactant concentration plot at an infinitely dilute micellar concentration. The slope is related to the number and the magnitude of the Coulombic term that may be included in the concentration effect of reactants, and in the intrinsic micellar effect, or the relative stabilization of a transition state in the presence of micelles. The above treatment was applied to (1) the hydrolysis of trimethyl orthobenzoate in sodium dodecyl sulfate solution, (2) the fading reaction of Crystal Violet in hexadecyltrimethylammonium bromide (CTABr) solution, and (3) the nucleophilic substitution reaction of 2,4-dinitrofluorobenzene in CTABr solution. It was found that the concentration effect is predominant in (1), while the relative stabilization of the transition state occurs in (2) and (3) in addition to the concentration effect.

A marked inhibition takes place in many systems on addition of an electrolyte to a micelle-catalyzed reaction. The interpretation of experimental results seems to be qualitative since most experiments were performed at a constant surfactant concentration with varying concentration of added electrolyte.[1-6] The constant surfactant concentration with various amounts of the added electrolyte is not considered to be at a corresponding state. As an example, cmc decreases with an increase in the added electrolyte concentration leading to the increase in micellar concentration.

In a previous paper,[7] a formula was derived for a micelle-catalyzed reaction based upon a microheterogeneous reaction. This was found to be useful for describing the mode of such as rate-surfactant concentration profile, inhibition of a micellar catalysis by an added electrolyte, and an activation energy, taking the hydrolysis of trimethyl orthobenzoate (MOB) in sodium dodecyl sulfate (SDS) solution as a model system.

This communication shows the obtained data to be in line with the derived equations, analysis of the effect of the added electrolyte on the micellar catalysis being made. The selected systems are: (1) MOB–SDS–NaCl system which has been examined by using the published data,[4] (2) Crystal Violet (CV)–Hexadecylammonium bromide (CTABr)–NaBr system,[8,9] and (3) 2,4-dinitrofluorobenzene (DNFB)–CTABr–NaBr system.[5]

## Theoretical

The following equation was derived for a chemical reaction of the type, A+B→P, in a micellar solution.[7]

$$k_2 = (\phi_{es}K_AK_Bf+1)k_b/(\phi_mK_A+1) \tag{1}$$

where $k_2$ is the second-order reaction rate constant in a micellar solution, and $k_b$ that in the bulk, $K_A$ and $K_B$ are the distribution coefficients of reactants A and B between the micellar and bulk phases, respectively, $\phi_m$ and $\phi_{es}$ are the volume fractions of the micelles and the effective surface reaction-layer around a micelle, respectively, and $f=\exp(-\Delta G^*/RT)$ represents an intrinsic micellar effect, where $\Delta G^*=G_m^*-G_b^*$, $G_m^*$, and $G_b^*$, being the activation free energies in the presence and absence of micelles, respectively. At a very low concentration with respect to micelles, under which assumption Eq. 1 was derived, the volume fractions are represented by $\phi_m=\alpha_m[M]$ and $\phi_{es}=\alpha_{es}[M]$, where $\alpha_i$ is the molar volume of region i, and [M] the micellar concentration, both quantities being on the monomer concentration basis. We get the following equation from Eq. 1.

$$\begin{aligned}[\mathrm{L.S}] &= \lim_{[\mathrm{M}]\to 0} \mathrm{d}(k_2/k_b)\mathrm{d}[\mathrm{M}] \\ &= \alpha_{es}K_AK_Bf-\alpha_mK_A \fallingdotseq \alpha_{es}K_AK_Bf\end{aligned} \tag{2}$$

where [L.S.] denotes the limiting slope of a rate-surfactant concentration profile. The last approximation in Eq. 2 is fairly good for most cases of efficient micellar catalysis. The electrical surface potential of a micelle, $\psi_0$ is written as a function of the total counter ion concentration, $C_t$:[10]

$$\psi_0 = -(kT/z_ie)\ln C_t + \text{constant} \tag{3}$$

where $k$ is the Boltzmann constant, $T$ absolute temperature, and $z_ie$ the electric charge of reactant i. If the electrostatic term is included, *e.g.*, in $K_B$, it should be of the form, $K_B=K_0\exp(-z_Be\psi_0/kT)$, where $K_0$ is a nonelectrostatic part of the distribution coefficient. The $f$-factor also may contain a $z_ie\psi_0$ term if the relative stabilization of the transition state is electrostatically caused by the surface potential. In this case, $z_i$ is the number of charge of the transition state taken relative to that of the reactant state, in the rate-determining step. Taking logarithm of Eqs. 2 and 3, and rearranging, we have

$$\ln[\mathrm{L.S}] = -\nu\ln C_t + \text{constant} \tag{4}$$

where $\nu=\sum_i[-z_ie\psi_0/|e\psi_0|]$ is the algebraic sum of the number of surface potential terms possibly contained in $K_A$, $K_B$ and/or in $f$-terms. If $z_ie\psi_0<0$, $K_A$ and $K_B$ concentrate ionic reactant A and B, respectively, around micelles, and $f$-term accelerates the reaction, and *vice versa*. The dependence of $\alpha_{es}$ on $c_t$ is neglibigly small. Although Eq. 1 was derived for a reaction system consisting of a buffered reaction partner ($H^+$ or $OH^-$ for most cases), it is easily extended to a system in which no buffered reactant is included:

$$k_2 = (\phi_{es}K_AK_Bf+1)k_b/(\phi_mK_A+1)(\phi_{es}K_B+1) \tag{5}$$

which is similar to an equation derived by Yatsimirski *et al.*,[6] and leads to the following formula.

$$\begin{aligned}[\mathrm{L.S}] &= \lim_{[\mathrm{M}]\to 0} \mathrm{d}(k_2/k_b)/\mathrm{d}[\mathrm{M}] \\ &= \alpha_{es}K_AK_Bf-\alpha_mK_A-\alpha_{es}K_B \fallingdotseq \alpha_{es}K_AK_Bf\end{aligned} \tag{6}$$

The last approximation again holds for efficient micelle-catalyzed reactions. Thus the present treatment does not depend on whether a reaction partner is buffered or not.

## Experimental

Most of the experimental techniques were taken from previous works;[4,5,8,9] only the modifications and specifications will be mentioned.

*Materials.* The synthesis and purification of MOB was the same as in literatures,[4,11] its purity being checked by NMR and UV spectroscopies. DNFB (Tokyo Chemical Ind. Co., Ltd.) was distilled under reduced pressure. CV (C.I. Basic Violet 3) of reagent grade (Wako Pure Chemical Ind. Ltd.) was used. The SDS was the same sample as used previously.[12] CTABr (Tokyo Chemical Ind. Ltd.) was recrystallized once from carbon tetrachloride, and three times from acetone-ethanol mixture (15 : 2 in volume). The cmc's at 25 °C are 8.2 mM for the SDS, and 0.95 mM for the CTABr, which are in good agreement with the authentic values.[13]

*Procedures.* The reaction was followed with a spectrophotometer (Hitachi model 139) equipped with a pen recorder. The temperature of the cell chamber was kept constant by circulating water from a thermostat. Into 1 ml of a solution containing the surfactant and electrolyte which had been equilibrated in a cuvette, was added 1 ml of a substrate solution with a pipette, and the reaction mixture was quickly stirred with a tiny plastic rod. The substrate solution and the pipette were equilibrated in a thermostat.

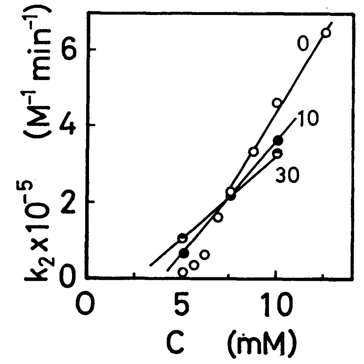

Fig. 1. The second-order rate constant of MOB-SDS system (25 °C, pH 5.40). The numbers in the figure represent the amount of added NaCl in mmol/l. The rate constant at SDS concentration = 4 mmol/l in 10 mmol/l NaCl solution coincides with that in 30 m mol/l NaCl solution.

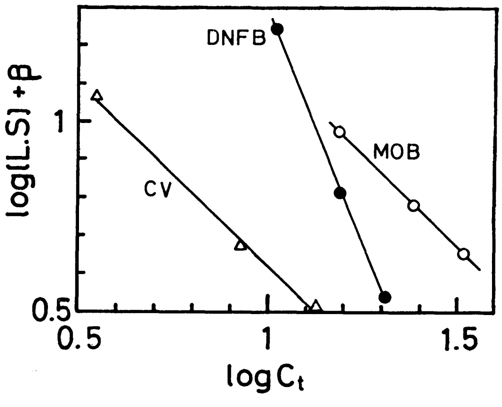

Fig. 2. log[L.S] *vs.* log $C_t$, $C_t$ in mmol/l.

## Results and Discussion

*MOB–SDS System.* The second-order rate constants of the MOB hydrolysis at 25 °C with pH 5.40 (0.01 M sodium acetate buffer) are shown in Fig. 1 as a function of SDS concentration, where the multiphasic feature of the profile is partly seen. The initial gradual rise followed by a linear portion would be due to a large substrate-micelle concentration ratio, not assumed explicitly in Eq. 1. Thus the linear portion was taken as a [L.S], since a constant amount of substrate per micelle (probably one substrate molecule per micelle) may be partitioned there. The slope of the linear portion becomes smaller on addition of NaCl. In Fig. 2, log[L.S] is plotted against log $C_t$ in accordance with Eq. 4, where the relation, $C_t$=cmc+ the buffer concentration + the added electrolyte concentration, is assumed. A slope of $\nu=0.98\fallingdotseq1$ was obtained. This is identical with the one[7] evaluated by analyzing the data of Dunlap and Cordes.[4] It should be noted that a slope at relatively concentrated region of NaCl (>0.1 M) was used in the previous analysis,[7] because the micellar concentration remains nearly constant at 0.01 M SDS with an increase in NaCl concentration. On the other hand, a slope at relatively low region of the added salt concentration (0—0.03 M) was employed in the present work. The conclusion is naturally the same: $\nu\fallingdotseq1$ is caused by the concentration effect of proton around micelles, or $K_B=K_0\exp(-z_Be\psi_0/kT)$ with $z_B=1$. The electrostatic stabilization of the transition state is not so important, since the oxonium, a reactant of the rate-determing step, is stabilized to the same degree as the carbonium ion at the transition state, resulting in no relative stabilization, which is contrary to the conclusion of Dunlap and Cordes.[4]

*CV–CTABr System.* The fading reaction of Crystal Violet was carried out in 3 mM NaOH solution at 30 °C. The pseudo-first-order rate constants are shown in Fig. 3 as a function of CTABr concentration with various amount of added NaBr. The added electrolyte suppresses the reaction rates at all CTABr concentrations studied. The linear portion was too small to determine the [L.S] directly, because of a strong saturating tendency as compared with those of MOB–SDS and DNFB–CTABr systems. The [L.S] was determined by graphical differentiation. The log[L.S] *vs.* log $C_t$ plot in Fig. 2 gives $\nu=0.94\fallingdotseq1$, which may be brought about by a little complicated mechanism: the carbonium dye is charged similarly to CTABr micelles, and the same charge yields $\exp(-|e\psi_0|/kT)$ term in $K_A$, which is, however, cancelled out by $\exp(+|e\psi_0|/kT)$ term contained in $K_B$, or the $OH^-$ concentration effect. The resultant effect would be zero unless there is a relative stabilization by the micellar charge. It seems that the relative stabilization of the transition state is affected by the fact that the reactant dye is similarly charged to micelles and therefore destabilized, while the transition state is

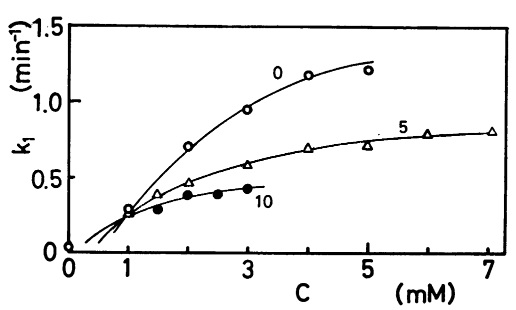

Fig. 3. The pseudo-first-order rate constant of CV–CTABr system (30 °C, 3 mmol/l NaOH). The numbers in the figure refers to the amount of added NaBr in mmol/l.

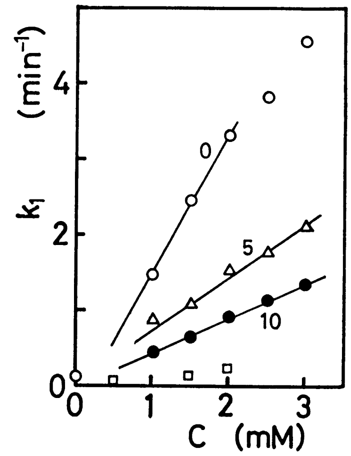

Fig. 4. The pseudo-first-order rate constant of DNFB–CTABr system (25 °C, 10 mmol/l). The numbers in the figure refers to the amount of added NaBr in mmol/l. The squares are the results of Bunton and Robinson.[5]

presumed to be an uncharged alcohol which has little sensitivity to the electrostatic potential. This conclusion is in line with that of Albrizzio *et al.* who stated "one expects less electrostatic destabilization for the zwitterion transition state than for the cation ground state by the cationic micellar surface," stressing the importance of the electrostatic contribution.[8b] The effect of the added electrolyte is offset in the concentration effects between $K_A$ and $K_B$. The experimentally observed dependence ($\nu \fallingdotseq 1$) should be ascribed to the relative stabilization of the transition state, *viz.*, the $f$-term contains $\exp(+|z_1e\phi_0|/kT)$ term.

*DNFB-CTABr System.* The pseudo-first-order rate constants of the nucleophilic substitution reaction of DNFB in the presence of 10 mM NaOH at 25 °C are shown in Fig. 4, as a function of CTABr concentration, where the results under the same conditions as those reported by Bunton and Robinson are also added.[5] The rate they observed remains low even above the cmc (*ca.* 0.6 mM in 10 mM NaOH at 25 °C), while ours increases steeply near the cmc. A similar difference was also reported by Blandamer and Reid.[15] The [L.S] was easily taken owing to the marked efficiency in the micellar catalysis. The slope (Fig. 2) gives $\nu=2.4$, which is unexpectedly large, but can be interpreted as follows. In addition to a term included in $K_B$, or the $OH^-$ concentration effect, there must be a contribution from the $f$-term. The Meisenheimer complex[3,14] which is presumably at the transition state may have a negative charge giving rise to the stabilization of the activated anion by the micellar surface potential. Bunton and Robinson ascribed the strong catalysis to the incorporation of DNFB in micelles which give hydroxide ions electrostatically favorable environment to attack the organic substrate,[5] but they did not make any further analysis. It is not clear whether the residual contribution $\nu-2=0.4$ comes from the dipole-field interaction or for some other reason. The reaction between DNFB and aniline in CTABr solution is scarcely sensitive to the added electrolyte.[3] No electrostatic term is included in either $K_A$, $K_B$, or in the $f$-term, since the two reactants as well as the Meisenheimer complex are neutral in this case leading to the result $\nu=0$.

Table 1. Analysis of the electrostatic contribution to the micellar catalysis

| System | $-z_ie\phi_0/\lvert e\phi_0\rvert$ | | | $\nu_{th}$ | $\nu_{ob}$ |
|---|---|---|---|---|---|
| | $K_A$ | $K_B$ | $f$ | | |
| MOB-SDS | 0 | 1 | 0 | 1 | 0.98 |
| CV-CTABr | −1 | 1 | 1 | 1 | 0.94 |
| DNFB-CTABr | 0 | 1 | 1 | 2 | 2.4 |

*Remarks.* The present treatment is useful in clarifying the nature of micellar catalyses, especially as regards the electrostatic effect. The results are summarized in Table 1. A tacit assumption underlying Eqs. 1 and 5 is that the micellar structure does not change much on addition of electrolytes. This assumption might not hold, but the micellar structure would not change so much, since the concentration of added electrolyte is deliberately limited as little as 0.05 M in the present work.

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