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A Formulation of Chemical Kinetics in Micellar Solutions

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Reaction kinetics in the presence of micelles is formulated on the basis of a microheterogeneous reaction in accordance with a current model of micellar catalysis. The necessary molecular parameters are the radius of the hydrocarbon core of a spherical micelle, the thickness of a reaction surface layer, the surface and zeta potentials, and a distribution coefficient of a hydrophobic substrate. The derived expression was applied to the hydrolysis reaction of methylorthobenzoate in the presence of sodium dodecylsufate micelle to describe reaction properties such as a rate-surfactant concentration profile, inhibition by added electrolyte, and activation energy. The micellar effect on the reaction rate was explained by a simple concentration effect of the reactants; the stabilization of the transition state by the micellar surface potential need not be taken into consideration. Inhibition of the orthoester hydrolysis by a cationic surfactant is also predicted.

The last decade has witnessed a remarkable development in studying chemical reactions in surfactant solutions,[1–3] wherein 5- to 1000-fold acceleration of rates as well as inhibitions of various magnitudes have been reported. Most reactions are analyzed by a chemism formula akin to the Michaelis-Menten equation to obtain a rate constant at the micellar phase k_m, and one at the bulk phase k_b, separately. However, no attempt has been made to look into the physical and chemical significances of k_m, except for a few works.[4–7]

In this communication a model that has been proposed by organic chemists will be formulated and analyzed on the basis of a microheterogeneous reaction in order to give insights into the nature of micellar catalysis.

Theoretical

Now let us define $v(\boldsymbol{r})$, which may be called the "reaction density,"

$$v(\boldsymbol{r}) = k(\boldsymbol{r})C_A(\boldsymbol{r})C_B(\boldsymbol{r}) \qquad (1)$$

In this equation, which is apparently that of a second order reaction, $v(\boldsymbol{r})$ is a reaction rate in an elementary volume $\mathrm{d}\boldsymbol{u}$, $k(\boldsymbol{r})$ is a rate constant, and $C_A(\boldsymbol{r})$ and $C_B(\boldsymbol{r})$ are the concentrations of reactants A and B in the volume. It should be noted that they are all expressed as a function of the coordinate $\boldsymbol{r}$. A reaction rate in an entire reaction vessel is obtained by integrating Eq. (1) over the vessel

$$\mathrm{d}n/\mathrm{d}t = \int_V v(\boldsymbol{r})\mathrm{d}\boldsymbol{u} \qquad (2)$$

More specifically, consider that there are N micelles in the reaction vessel, each micelle being equivalent, and that the micellar concentration is too dilute for any two micelles to approach each other. Then this system is approximated by an assembly which consists of N subsystems, where in a subsystem it is supposed that a micelle is located at the center. The subsystem satisfies $(4/3)\pi\rho^3 = V/N$, ρ being the radius of the spherical subsystem. A reaction rate in the subsystem is expressed as

$$I = 4\pi\int_0^\rho x^2 k(x)C_A(x)C_B(x)\mathrm{d}x \qquad (3)$$

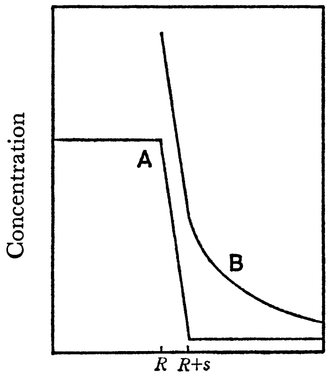

Fig. 1. Schematic representation of concentration profile around a micelle. A: a hydrophobic reactant, B: an ionic reactant.

where x is the distance from the center of a spherical micelle which is very likely at concentrations not far above a critical micelle concentration (CMC). It can be further assumed that reactant A is a hydrophobic substrate, and reactant B an ionic species, without losing generality too much. Concentration profiles of these reactants around a micelle are illustrated in Fig. 1, where R is the radius of the hydrocarbon core of a micelle, and s the thickness of a surface layer around a micelle. This surface layer is presumed to be the reaction site which contains the so-called Stern layer and extends up to a plane of shear. Reactant A is partitioned in the micellar phase because of its hydrophobicity, and $C_A(x)$ decreases across the surface layer down to the bulk concentration C_{Ab}. Reactant B is concentrated around micelles by the Coulombic force if the charge is opposite to that of the micelle. The ionic reactant scarcely penetrates into the hydrocarbon core of a micelle, and, beyond the surface layer, is distributed in a diffused double layer down to the bulk concentration C_{Bb}. Then Eq. (3) is integrated in two regions: $R \leqq x \leqq R+s$, and $R+s \leqq x \leqq \rho$, respectively.

Zeroth Approximation. It is assumed that $k(x) = k_s$, $C_A(x) = C_{As}$, and $C_B(x) = C_{Bs}$ in the surface layer, and $k(x) = k_b$, $C_A(x) = C_{Ab}$, and $C_B(x) = C_{Bb}$ in the outer layer. Then one obtains

$$\begin{aligned} I &= 4\pi k_s C_{As} C_{Bs}\int_R^{R+s} x^2\mathrm{d}x + 4\pi k_b C_{Ab} C_{Bb}\int_{R+s}^{\rho} x^2\mathrm{d}x \\ &= V_s k_s C_{As} C_{Bs} + V_b k_b C_{Ab} C_{Bb} \qquad (4) \end{aligned}$$

In Eq. (4), V_s and V_b are volumes of the surface and bulk phases in a subsystem, respectively. Converting Eq. (4) into a conventional rate equation in a concentration scale, one has

$$\mathrm{d}C/\mathrm{d}t = (1/V)(\mathrm{d}n/\mathrm{d}t) = I/V_{\mathrm{sub}} = IN/V$$
$$= \phi_{\mathrm{s}}k_{\mathrm{s}}C_{\mathrm{As}}C_{\mathrm{Bs}} + \phi_{\mathrm{b}}k_{\mathrm{b}}C_{\mathrm{Ab}}C_{\mathrm{Bb}} \tag{5}$$

where $V_{\mathrm{sub}}=(4/3)\pi\rho^3$, and $\phi_{\mathrm{i}}=NV_{\mathrm{i}}/V$ is the volume fraction indicated by the respective subscript. Equation (5) is somewhat similar to equations previously reported,[4,5] but is not identical. The surface layer concentrations appearing in Eq. (5) are expressed in terms of the corresponding bulk concentrations by using the distribution coefficients K_{A} and K_{B},

$$K_{\mathrm{A}} = C_{\mathrm{Am}}/C_{\mathrm{Ab}} = C_{\mathrm{As}}/C_{\mathrm{Ab}} \tag{6}$$

where C_{Am} is a concentration of A in the micellar phase. The second identity, *i.e.*, $C_{\mathrm{Am}}=C_{\mathrm{As}}$ is a result of the zeroth approximation, and

$$K_{\mathrm{B}} = C_{\mathrm{Bs}}/C_{\mathrm{Bb}} = \exp(-e\psi_0/kT) \tag{7}$$

where ψ_0 is a surface potential of a micelle. Equation (5) becomes

$$\mathrm{d}C/\mathrm{d}t = (\phi_{\mathrm{s}}k_{\mathrm{s}}K_{\mathrm{A}}K_{\mathrm{B}} + \phi_{\mathrm{b}}k_{\mathrm{b}})C_{\mathrm{Ab}}C_{\mathrm{Bb}} \tag{8}$$

This equation can be expressed by the analytical concentrations of the reactants, C_{A} and C_{B}.

$$\mathrm{d}C/\mathrm{d}t = (\phi_{\mathrm{s}}k_{\mathrm{s}}K_{\mathrm{A}}K_{\mathrm{B}}+\phi_{\mathrm{b}}k_{\mathrm{b}})C_{\mathrm{A}}C_{\mathrm{C}}/(\phi_{\mathrm{m}}K_{\mathrm{A}}+\phi_{\mathrm{b}}) \tag{9}$$

where the following relations were used:

$$VC_{\mathrm{A}} = (V_{\mathrm{m}}C_{\mathrm{Am}}+V_{\mathrm{b}}C_{\mathrm{Ab}})N \tag{10}$$

and

$$C_{\mathrm{B}} = C_{\mathrm{Bb}} \tag{11}$$

In Eq. (10), V_{m} is a volume of the micellar region and C_{Am} a concentration of substrate A there. Equation (11) holds for a buffered species, although there is an argument suggesting the difficulty in estimating the concentration at the micellar surface.[8] Comparing Eq. (9) with the experimental expression, $v=k_2C_{\mathrm{A}}C_{\mathrm{B}}$, one obtains

$$k_2 = [(\phi_{\mathrm{s}}fK_{\mathrm{A}}K_{\mathrm{B}}+\phi_{\mathrm{b}})/(\phi_{\mathrm{m}}K_{\mathrm{A}}+\phi_{\mathrm{b}})]k_{\mathrm{b}} \tag{12}$$

where $k_{\mathrm{s}}=fk_{\mathrm{b}}$ is introduced, and f implies an intrinsic micellar effect taken relative to k_{b}.

First Approximation. At this stage, it is assumed, based on a more realistic model, that the concentrations of the reactants decrease linearly in the surface layer, *i.e.*,

$$C_{\mathrm{A}}(x) = C_{\mathrm{Am}}[1-(K_{\mathrm{A}}-1)(x-R)/K_{\mathrm{A}}s] \tag{13}$$

and

$$C_{\mathrm{B}}(x) = C_{\mathrm{Bm}}[1-[1-\exp(-(\zeta-\psi_0)/\mathrm{k}T)](x-R)/s] \tag{14}$$

In Eq. (14), the zeta potential ζ was used to denote the concentration of reactant B at $x=R+s$, or the plane of shear. Substituting Eqs. (13) and (14) into Eq. (3) for the surface layer part I_{s}, one has

$$I_{\mathrm{s}} = 4\pi fk_{\mathrm{b}}C_{\mathrm{Am}}C_{\mathrm{Bm}}$$
$$\times \int_R^{R+s} x^2[1-(K_{\mathrm{A}}-1)(x-R)/K_{\mathrm{A}}s]$$
$$\times [1-[1-\exp(-e(\zeta-\psi_0)/kT)(x-R)/s]\mathrm{d}x \tag{15}$$

Comparing Eq. (15) with Eq. (4), one can understand that the integral in Eq. (15) corresponds to the volume of the surface layer, and it may be called the effective volume of the surface layer V_{es}. Replacing ϕ_{s} in Eq. (12) with $\phi_{\mathrm{es}}=NV_{\mathrm{es}}/V$, an effective volume fraction of the surface layer, one has

$$k_2 = k_{\mathrm{b}}(\phi_{\mathrm{es}}fK_{\mathrm{A}}K_{\mathrm{B}}+1)/(\phi_{\mathrm{m}}K_{\mathrm{A}}+1) \tag{16}$$

where $\phi_{\mathrm{b}}=1$ was used in accordance with an assumption of very dilute micellar concentration. Equation (16) has many more detailed physicochemical contents than does the formally similar equation.[2]

Application to MOB–SDS System. Now our discussion will be confined to the hydrolysis kinetics of methylorthobenzoate (MOB) in sodium dodecylsulfate (SDS) solution, for the kinetic studies on MOB in aqueous and in SDS solutions have been fully described,[1,3,10] and since SDS is one of the most explored surfactants, the necessary molecular parameters are available.[1–3,11] First, the rate enhancement k_2/k_{b} at 0.01 M SDS in micellar form will be estimated according to Eq. (16). The necessary parameters are listed in Table 1. Prior to the numerical calculation, the parameters are briefly examined. Dougherty and Berg have recently reported the distribution coefficient of MOB between the micelle and the bulk phases by the ultrafiltration method.[12] The value they obtained varies with the substrate concentration, but at the concentration in the kinetic experiment (about 5×10^{-5} M), $K=1.4\times10^4$ (MOB mol fraction in micelle/MOB mol fraction in the bulk), which is converted to $K_{\mathrm{A}}=C_{\mathrm{Am}}/C_{\mathrm{Ab}}$ [(mol of solubilized MOB/micellar volume)/(mol of MOB in the bulk/l of water)] by using the molar volume of SDS micelle=0.3 l/mol, which is between the partial molar volume of SDS micelle, 0.25 l/mol,[13] and a calculated micellar volume with a radius=$R+s$ and aggregation number of a micelle=70, 0.33 l/mol. The value of K_{B}, or exp $(-e\psi_0/kT)$ is taken from that calculated by Stigter and Mysels using a modified Gouy-Chapman potential, which differs by only a few milivolts from the spherical potential.[9,14] There may be various factors affecting f. The factor f should have a form $f=\exp(-\Delta G^{\ne}/RT)$, where $\Delta G^{\ne}$ is an activation free energy representing the relative stabilizations of the transition state by the hydrophobic interaction, the orientation effect, and electrostatic effects including the Coulombic as well as dipole-field interactions. For the moment $f=1$ is assumed, although there is an opinion stressing the electrostatic stabilization of the transition state,[3,15] *i.e.*, $f>1$; this is an overestimation, as will be shown later. Equation (16) gives $k_2/k_{\mathrm{b}}=103$, which is com-

TABLE 1. PARAMETERS TO CALCULATE THE MICELLAR EFFECT ON REACTION KINETICS

Quantity		Unit	Ref.
Radius of hydrocarbon core, R	16.6	Å	11
Thickness of the surface layer, s	4.4	Å	11
Surface potential (0.01 M), ψ_0	−178	mV	9, 14
(0.03 M),	−161	mV	9, 14
(0.05 M),	−150	mV	9, 14
Zeta potential, $\zeta=\psi_0/2$		mV	9, 14
Distribution coefficient of MOB, K_{A}	838	(M/M)	12
Aggregation number of a micelle	70		11

parable to a 69-fold enhancement experimentally obtained for MOB–SDS system at 25 °C.[15] Many aspects of the micellar effects on the kinetics will be explained on the basis of Eq. (16)

Inhibition of Rate Enhancement by Added Electrolyte A marked dependence of the rate on the added electrolyte can be analyzed in the following manner. Under the condition, $\phi_{es}K_A f \exp(-e\psi_0/kT) \gg 1$ at a constant micelle concentration, Eq (16) becomes

$$k_2/k_b = \phi_{es}K_A f \exp(-e\psi_0/kT) \times \text{constant} \tag{17}$$

Taking the logarithm of Eq. (17), and assuming $\phi_{es}=$ constant because it varies by less than 1% even if ψ_0 is changed from 170 to 130 mV as a result of numerical calculation, one obtains

$$\ln(k_2/k_b) = -\nu\Phi_0 + \text{constant} \tag{18}$$

where ν expresses an electrostatic effect arising from terms other than K_B, possibly from $f=\exp(-\Delta G^{\neq}/RT)$, and $\Phi_0=e\psi_0/kT$ is a reduced surface potential, which can be approximated by a simplified Gouy-Chapman potential under the pertinent condition, $|\psi_0|>100$ mV,[16]

$$\Phi_0 = \ln C_t + \text{constant} \tag{19}$$

In Eq. (19), C_t is the total counterion concentration. Combining Eq. (18) with Eq. (19), one has

$$\log(k_2/k_b) = -\nu \log C_t + \text{constant} \tag{20}$$

In Fig. 2, log (k_2/k_b) is plotted against log C_t, where the kinetic data are those of Dunlap and Cordes,[15] and $C_t = cmc+$buffer concentration (0.01 M)+added salt concentration C_a. Before interpreting the features appearing in Fig. 2, it should be noted that *cmc* is remarkably diminished by the added electrolyte, and this tendency becomes approximately saturated when the added salt concentration is as much as, *e.g.*, 0.1 M.[17] Dunlap and Cordes have performed their measurement at a constant total SDS concentration of 0.01 M, and therefore the micellar concentration increases with increasing added electrolyte concentration; the fraction of micellized SDS is about 0.5 at $C_a=0$, and about 0.85 at $C_a=0.1$ M. So in accordance with the assumption of constant micellar concentration, it is the slope at the high concentration region of added electrolyte that is significant, because the micellar concentration remains nearly constant in this region of C_a. As seen in Fig. 2, the slope in the region is unity, $\nu=1$, which implies that there is no electrostatic effect other than $K_B=\exp(-\Phi_0)$ in Eq. (17). If there were any other electrostatic effect such as the stabilization of transition state,[3,15,18] a value of $\nu>1$ should be expected: in other words, $\Delta G^{\neq}$ should contain a Φ_0 term. Therefore it is considered that the carbonium ion at the transition state is stabilized by the surface potential to the same degree as the protonated MOB, a reactant of the rate-determining step, is, because of the proximity of the protonated MOB and the carbonium ion-like transition state on a reaction coordinate.[10] Thus it may be concluded that the micellar effect on MOB hydrolysis is mainly, if not solely, ascribed to the concentration effect due to the hydrophobic interaction with a micelle as well as to the electrostatic attraction of the proton.

Activation Energy. Another subsidiary piece of evidence that supports the absence of electrostatic stabilization of the transition state is obtained by examining the activation energy. The Arrhenius plot gives the activation energy in the presence of micelles, $E_m^{\neq}=11$ kcal/mol, which is about 4.5 kcal/mol smaller than the one in the absence of micelles, $E_b^{\neq}$.[10] Strictly speaking, $\Delta E^{\neq}=E_m^{\neq}-E_b^{\neq}$ arises from the temperature dependences of K_A, $K_B=\exp(-\Phi_0)$, and f, but the main part of it is certainly occupied by $\Phi_0 kT=-4$ kcal/mol ($\psi_0=-170$ mV), for the temperature dependence of the hydrophobic interaction is very small.[19] There would be no possibility for the f-factor to contribute another Φ_0 term originating from the electrostatic stabilization of the transition state to the activation energy, unless a fortuitous cancellation between the K_A and f terms occurs.

Rate-Surfactant Concentration Profile. It has been well known that there is a tri-phasic feature in the rate-surfactant concentration profile, which can be reproduced by Eq. (16), as shown in Fig. 3. It should be noted that a curve with a slight and broad maximum can be obtained only when a ψ_0 that decreases with increasing counterion concentration is employed: ψ_0 was varied from -172 mV at $[M]=0.005$ M to -165 mV at $[M]=0.065$ M, where [M] denotes the SDS concentration in micellar form.

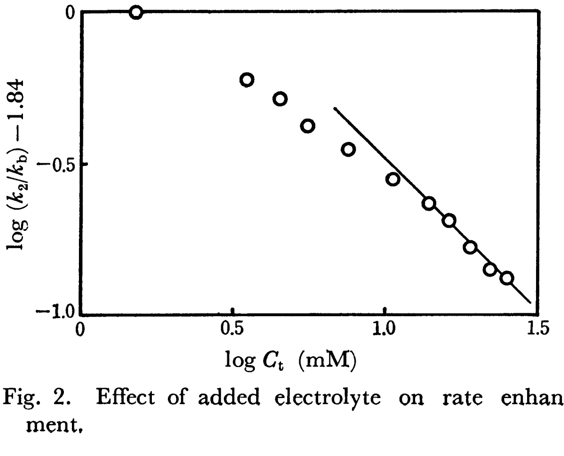

Fig. 2. Effect of added electrolyte on rate enhancement.

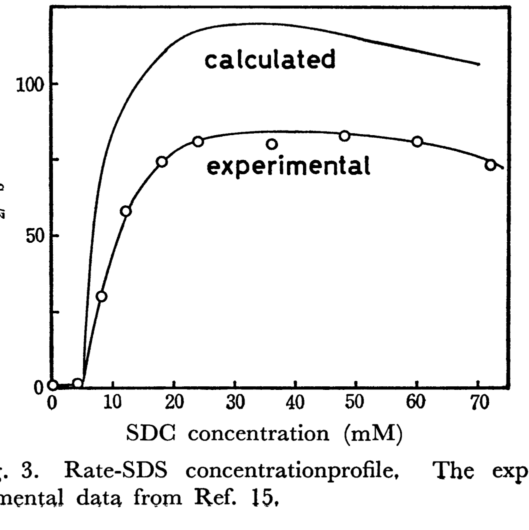

Fig. 3. Rate-SDS concentrationprofile, The experimental data from Ref. 15,

Discussion

Now let us examine the factors which are contributing to rate enhancement by means of Eq. (16). The term ϕ_{es} is numerically expressed as 0.054 [M], where [M] is a micellar concentration in SDS mol/l, and roughly evaluated by (the total SDS concentration —*cmc*), although there is some difficulty in estimating [M].[20] The numerical factor, 0.054 is an effective volume of the surface layer per one SDS molecule in l/mol. So, at $[M]=0.01$ M, for example, $\phi_{es}=0.00054$. Multiplied by K_A, $\phi_{es}K_A=0.453$, which is too small to explain the observed rate enhancement. Further multiplied by $K_B=\exp(-\Phi_0)=840$, $\phi_{es}K_AK_B=380$, which is divided by $(\phi_mK_A+1)=3.52$ to give 103-fold enhancement, an expected magnitude. There is a systematic discrepancy between the observed and the calculated rates, as seen in Fig. 3. A value of $f=0.7$ would give striking coincidence, but a deviation from unity of this size might be insignificant in view of the simplicity of the fundamental model and the consequent uncertainty in the molecular parameters. Here again it may be inferred that a simple concentration effect is the most important factor, and effects specific to micelles would be, if present, of secondary importance. In order to simulate the curve in Fig. 3, it was necessary that 15% of micellar concentration, in addition to the *cmc* and the buffer concentration, be taken as the total counterion concentration C_t: in other words, about 15% of the counterion of a micelle is shared among other micelles.

Inhibition of MOB Hydrolysis by Cationic Surfactant. Although our discussion heretofore has been restricted to the MOB–SDS system, the inhibition of MOB hydrolysis by a cationic surfactant should be briefly referred to. Hydrolysis of MOB is inhibited about 3-fold in the presence of 0.04 M cetyltrimethylammonium bromide.[21] This inhibition can be interpreted in terms of Eq. (16), in which the $\phi_{es}K_Af\exp(-\Phi_0)$ term is neglected because $\exp(-\Phi_0)\ll 1$ in this case.

$$k_2/k_b = 1/(\phi_mK_A+1) \tag{21}$$

Equation (21) predicts about 10-fold inhibition when $\phi_m=0.3\times0.04=0.012$ and $K_A=800$, as a rough estimate, are substituted. Thus the inhibition is explained by the fact that MOB is localized in a micellar region by the hydrophobic interaction, while the protons are expelled out of there by the Coulombic repulsion.

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