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Kinetic Studies of the Base Equilibrium of Secondary Amines on the Surface of Sodium Dodecyl Sulfate Micelle by Means of the Ultrasonic Absorption Method

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The ultrasonic relaxation absorption has been measured in aqueous solution of dipentylamine, dihexylamine, dioctylamine, *N*-methylphenethylamine, and *N*-ethylbenzylamine in the presence of the sodium dodecyl sulfate(SDS) micelle. The relaxation absorption has been ascribed to the base equilibrium of the amines on the surface of the micelle: $RR'NH_2^+ + OH^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} RR'NH + H_2O$. The rate constants $\gamma_\pm^2 k_f$, k_b, the apparent base dissociation constant K_b $(=k_b/\gamma_\pm^2 k_f)$, and the volume change in the base equilibrium ΔV were obtained, where $\gamma_\pm$ is the mean activity coefficient for $RR'NH_2^+$ and OH^-. The dependence of the rate constants on K_b revealed that, in the detailed mechanism of the base equilibrium of the amines, $\underset{(I)}{RR'NH_2^+ + OH^-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{(II)}{(RR'NH_2^+ \cdots OH^-)} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{(III)}{RR'NH + H_2O}$, the rate-determining step is the proton-transfer process, (II) $\rightleftharpoons$ (III). The pK_b values of the secondary amines on the surface of the SDS micelle were 0.94—1.26 smaller than the corresponding values in the aqueous solution, and the micellar effect on pK_b was smaller than that of the primary amines. From the standpoint of the micellar effect, the structures of the amines solubilized in the micelle were discussed.

Detergent micelles have been of interest as a peculiar reaction field, and many investigations[1—3] have been carried out to reveal the controlling factors in the promotion or inhibition of various reactions on the surface of the micelle. However, only relatively slow reactions have been studied with the exception of our own previous studies[4,5] of the micellar effect on a rapid base equilibrium of primary amines by the use of the ultrasonic absorption method. In those previous works[4,5] (i) kinetic parameters were obtained for the base equilibrium of primary amines on the surface of the SDS micelle, (ii) linear relationships were observed between the logarithms of the rate constants and that of the base dissociation constant, and (iii) the rate-determining step was ascribed to the proton-transfer process in the ion pair. The purposes of the present work are to study kinetically the micellar effects on the base equilibrium of the secondary amines, to compare the results with those of the primary amines, and to study especially the effect of the *N*-alkyl or aryl groups on the electrostatic interactions between the amine cation and the anionic sulfate group of the micelle forming detergent.

Experimental

The dihexylamine purchased from Tokyo Kasei and *N*-ethylbenzylamine from Aldrich were purified by distillation. The dipentylamine from Katayama Kagaku, dioctylamine from Tokyo Kasei, *N*-methylphenethylamine from Aldrich, and SDS from BDH were used without further purification.

The ultrasonic absorption measurements were performed by the pulse technique over the frequency range of 5—105 MHz. The details of the apparatus were described elsewhere.[6] The velocity of the sound was measured by the sing-around method at 1.92 MHz. The density was measured by means of a pycnometer. The pH of the solution was measured by means of a Kyoto Electronics AT-117-type potentiometer. All the pH and ultrasonic measurements were carried out under a dry nitrogen gas atmosphere at 30 °C.

Results and Discussion

The ultrasonic relaxation absorption was observed for secondary amines of various basicities in a SDS micellar solution. All the absorptions were represented by a single relaxation equation;[7,8]

$$\alpha/f^2 = A/\{1+(f/f_r)^2\} + B, \tag{1}$$

where α is the absorption coefficient, f is the frequency, f_r is the relaxation frequency, and A and B are the relaxing and nonrelaxing absorptions respectively.

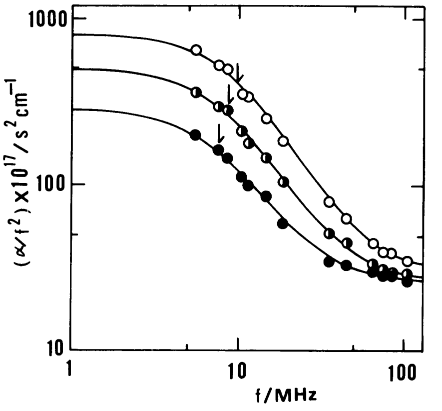

Fig. 1. Representative ultrasonic absorption spectra of the secondary amines (0.050 M[†])–SDS (0.30 M) system at 30.0 °C. ○: Dipentylamine. ◑: *N*-Methylphenethylamine. ●: *N*-Ethylbenzylamine. The arrows indicate the relaxation frequency. ([†] 1 M=1 mol dm^{-3})

Some representative absorption spectra are shown in Fig. 1. The absorption parameters obtained by fitting the data to Eq. 1 by means of a computer simulation are summarized in Table 1, along with the experimental conditions.

The ultrasonic behavior of the secondary amines in the SDS micellar solution was similar to that of the primary amines, which implies that the relaxation absorption can be assigned to the following reaction;

Table 1. Ultrasonic absorption parameters for various concentrations of secondary amines in the presence of SDS (0.30 M) at 30.0 °C

Σ[Amine] / M	pH	A / 10^{-17} s^2 cm^{-1}	B / 10^{-17} s^2 cm^{-1}	f_r / MHz	σ[a]
	Dipentylamine				
0.015	11.83	339	26	5.6	0.60
0.020	11.89	337	28	6.3	0.55
0.025	11.91	472	30	6.9	0.51
0.030	11.97	532	30	7.3	0.48
0.036	12.01	588	27	8.5	0.45
0.043	12.06	638	30	8.9	0.43
0.050	12.11	785	29	9.7	0.40
	Dihexylamine				
0.015	11.78	505	26	5.9	0.57
0.020	11.83	586	28	6.6	0.52
0.025	11.85	596	29	7.3	0.49
0.030	11.90	597	27	8.1	0.46
0.036	11.97	613	25	8.6	0.43
0.043	12.04	621	26	9.5	0.40
0.050	12.09	777	25	10.1	0.38
	Dioctylamine				
0.015	11.70	358	30	6.4	0.52
0.020	11.76	382	31	7.2	0.48
0.025	11.83	429	33	8.1	0.44
0.030	11.88	441	29	8.6	0.41
0.036	11.95	453	29	9.6	0.39
0.043	12.00	522	25	10.3	0.36
0.050	12.07	558	26	11.2	0.34
	N-Methylphenethylamine				
0.015	11.57	328	26	4.9	0.33
0.020	11.66	348	24	6.1	0.30
0.025	11.69	352	26	6.6	0.27
0.030	11.75	378	26	7.0	0.25
0.036	11.80	410	26	7.6	0.23
0.043	11.83	421	26	8.4	0.21
0.050	11.88	471	26	8.7	0.20
	N-Ethylbenzylamine				
0.020	11.45	207	25	4.9	0.19
0.025	11.52	217	26	5.6	0.17
0.030	11.53	222	26	6.2	0.16
0.036	11.58	246	25	6.6	0.14
0.043	11.63	246	28	7.3	0.13
0.050	11.69	264	26	7.6	0.12

a) Degree of ionization.

$$\mathrm{RR'NH_2^+ + OH^-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{RR'NH + H_2O}, \tag{2}$$

where the hydrocarbon groups of an amine are solubilized in the core of the SDS micelle. The base dissociation constant, K_b^0, is given as;

$$K_b^0 = \frac{k_b}{k_f} = \frac{\gamma_\pm^2[\mathrm{RR'NH_2^+}][\mathrm{OH^-}]}{[\mathrm{RR'NH}]} = \frac{\gamma_\pm^2\sigma^2C_0}{1-\sigma}, \tag{3}$$

where σ is the degree of ionization, C_0 is the total concentration of the amine, and $\gamma_\pm$ is the mean activity coefficient. The relaxation frequency and the maximum relaxation absorption per wavelength, $\mu_{\max}$, for Reaction 2 are expressed by;[7,8]

$$2\pi f_r = \gamma_\pm^2 k_f([\mathrm{RR'NH_2^+}]+[\mathrm{OH^-}]) + k_b, \tag{4}$$

$$\mu_{\max} = \frac{\rho u^2\pi(\Delta V)^2}{2RT}\cdot\Gamma^{-1},$$

$$= \frac{\rho u^2\pi(\Delta V)^2}{2RT}\cdot\frac{\sigma(1-\sigma)}{2-\sigma}\cdot C_0, \tag{5}$$

with;

$$\Gamma = [\mathrm{RR'NH_2^+}]^{-1} + [\mathrm{OH^-}]^{-1} + [\mathrm{RR'NH}]^{-1}, \tag{6}$$

where ρ is the density of the solution, u is the velocity of sound, and ΔV is the volume change in the base equilibrium of the amine. Equation 4 can be rewritten as follows in terms of C_0 by using Eq. 3;

$$(2\pi f_r)^2 = 4\gamma_\pm^2 k_f k_b C_0 + k_b^2. \tag{7}$$

The experimental values of $(2\pi f_r)^2$ are plotted against C_0 in Fig. 2. The plots give a straight line, as predicted by Eq. 7; the result indicates that the relaxation absorption is due to Reaction 2. From the slope and the intercept of the straight line, the values of $\gamma_\pm^2 k_f$ and k_b respectively were obtained, and from their ratio, the apparent base dissociation constant, K_b $(=k_b/\gamma_\pm^2 k_f)$, was obtained; all these parameters are listed in Table 2. The plots of $\mu_{\max}$ against the Γ^{-1} calculated from the K_b obtained above and C_0 gave a straight line which goes through the point of origin of the coordinates, as shown

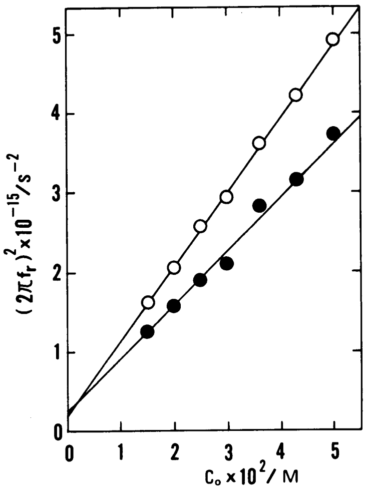

Fig. 2. Plots of $(2\pi f_r)^2$ *vs.* concentration of secondary amines in the presence of SDS (0.30 M) at 30.0 °C. ○: Dioctylamine. ●: Dipentylamine.

TABLE 2. KINETIC PARAMETERS FOR THE BASE EQUILIBRIUM OF SECONDARY AMINES ON THE SURFACE OF THE SDS MICELLE AT 30.0 °C

Amine	$\frac{\gamma_\pm^2 k_f}{10^8\,M^{-1}\,s^{-1}}$	$\frac{k_b}{10^7\,s^{-1}}$	$\frac{\Delta V}{cm^3\,M^{-1}}$	pK_b[a)]	pK_b[b)]	$pK_{b(w)}$[c)]
Dipentylamine	11.2	1.5	20.6	1.87	1.79	2.82
Dihexylamine	13.0	1.5	23.4	1.94	1.94	3.00
Dioctylamine	16.3	1.4	21.4	2.06	2.06	3.00
N-Methylphenethylamine	25.1	0.6	21.2	2.60	2.43	3.86
N-Ethylbenzylamine	37.2	0.3	18.6	3.07	2.89	4.32

a) The value of $pK_b = -\log(k_b/\gamma_\pm^2 k_f)$. b) The value evaluated from the values of C_0 and pH. c) Ref. 16.

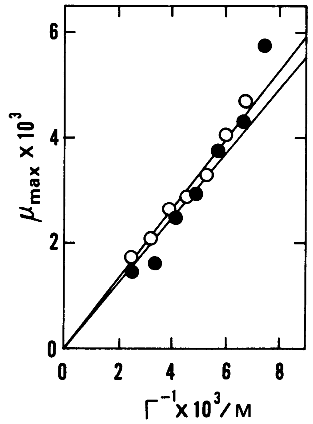

Fig. 3. Plots of μ_{max} *vs.* Γ^{-1} for the secondary amines in the presence of SDS (0.30 M) at 30.0 °C. ○: Dioctylamine. ●: Dipentylamine.

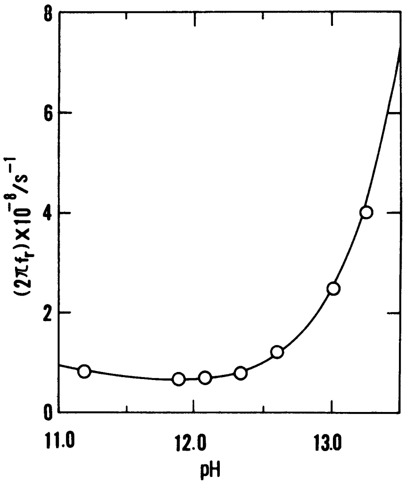

Fig. 4. pH dependence of the value of $2\pi f_r$ for the dioctylamine (0.050 M)–SDS (0.30 M) system at 30.0 °C. The solid line is the curve calculated by Eq. 4 with the values of $\gamma_\pm^2 k_f$, k_b, and K_b in Table 2. Circles are the experimental data.

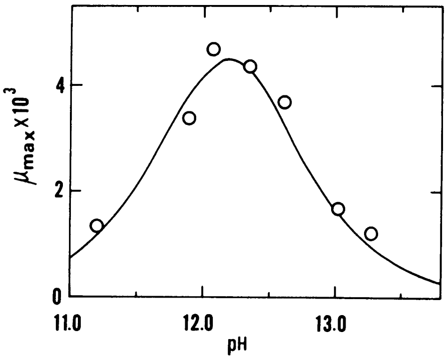

Fig. 5. pH dependence of μ_{max} for the dioctylamine (0.050 M)–SDS (0.30 M) system at 30.0 °C. The solid line is the curve calculated by Eq. 5 with the values of K_b and ΔV in Table 2. Circles are the experimental data.

in Fig. 3. A comparison with Eq. 5, also supports the idea that the relaxation absorption is due to Reaction 2. The value of ΔV was calculated from the slope of the straight line in Fig. 3.

The values of K_b can also be evaluated statically from the values of C_0 and pH in Table 1, together with the activity coefficient calculated by the use of the Davies equation;[9] they are listed in Table 2. As can be seen in the table, the value for each amine is in satisfactory agreement with that obtained above kinetically.

Further support of the assignment of the present relaxation absorption was given by the pH-dependences of the ultrasonic parameters. As a sample, the data for dioctylamine were obtained; the pH-dependences of f_r and μ_{max} are shown in Figs. 4 and 5 respectively. As can be seen in the figures, f_r and μ_{max} depend strongly on the pH, and the curves as calculated from Eqs. 3—6 by using the values of C_0, and the rate constants, K_b and ΔV obtained above express the experimental data satisfactorily. These results lead to the conclusion that the assignment of the absorption and the kinetic parameters obtained is reasonable.

The results demonstrate, among other things, the basicity dependence of the rate constants. As shown in Fig. 6, linear relationships were established for the plots of $\log \gamma_\pm^2 k_f$ *vs.* $\log K_b$ and $\log k_b$ *vs.* $\log K_b$. These relationships are expressed as;

$$\gamma_\pm^2 k_f = 10^{8.3} K_b^{-0.40} = 10^{8.3}(K_w/K_a)^{-0.40} = 10^{13.8} K_a^{0.40}, \tag{8}$$

$$k_b = 10^{8.3} K_b^{0.60}, \tag{9}$$

where K_w is the ionization constant of water and where K_a is the acid dissociation constant of an amine. These relationships are in contrast to those for the base equilibrium of amines in an aqueous solution,[10—14] where k_f is independent, while k_b is dependent on K_b(w);

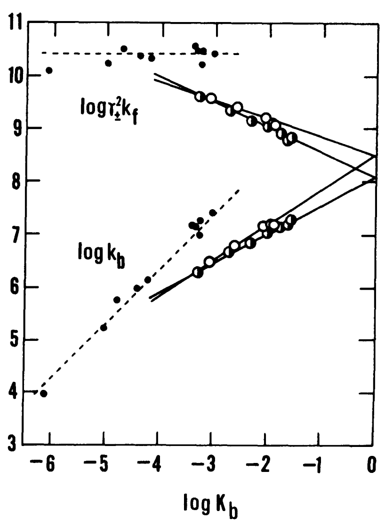

Fig. 6. Plots of the logarithms of the rate constants *vs.* $\log K_b$ for secondary amines (○) and primary amines[4,5] (◑) in the presence of SDS (0.30 M), and various amines in the absence of the micelle[11] (●).

$$k_{f(w)} = 10^{10.5}, \tag{10}$$

$$k_{b(w)} = 10^{10.5} K_{b(w)}, \tag{11}$$

where the subscript, (w), indicates the aqueous solution.

In general, the detailed mechanism of Reaction 2 has been described as;

$$\underset{\text{(I)}}{RR'NH_2^+ + OH^-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{\text{(II)}}{(RR'NH_2^+ \cdots OH^-)}$$

$$\underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{\text{(III)}}{RR'NH + H_2O.} \tag{12}$$

The (I)⇌(II) process is an ion pair formation and dissociation (diffusion process), and the rate constants, k_{12} and k_{21}, are dependent on the electric charge, the volume, and state of hydration, *etc.* of the ions; the proton-transfer still does not occur in the (I)⇌(II) process. Accordingly, k_{12} and k_{21} do not depend on the electron-donating (or-attracting) property of amines. On the other hand, the (II)⇌(III) process is a proton-transfer process in the ion pair, and the rate constants, k_{23} and k_{32}, are dependent mainly on the electron-donating (or-attracting) property of amines; that is k_{23} and k_{32} are dependent on K_b.

If (I)⇌(II) is the rate-determining step, the overall rate constants are expressed as;[10—14]

$$k_f = k_{12}, \tag{13}$$

$$k_b = k_{21} \cdot \frac{k_{32}}{k_{23}}. \tag{14}$$

These equations predict an independency of K_b from k_f and a linear dependency of K_b on k_b; these predictions are in good agreement with the results for the base equilibrium of amines in aqueous solutions, as seen in Eqs. 10 and 11 and in Fig. 6. However, the results of the present work, the K_b dependencies of k_f and k_b, *i.e.*, Eqs. 8 and 9, cannot be realized at all by means of Eqs. 13 and 14.

If (II)⇌(III) is the rate-determining step, on the other hand, k_f and k_b are given as follows;[5]

$$k_f = \frac{k_{12}}{k_{21}} \cdot k_{23}, \tag{15}$$

$$k_b = k_{32}. \tag{16}$$

Since (II)⇌(III) is a proton-transfer process in the ion pair, k_{23} will decrease and k_{32} will increase with an increase in K_b. Accordingly, Eqs. 15 and 16 provide a satisfactory interpretation of the K_b dependences of the rate constants in the base equilibrium of amines in a micellar solution. Then, the rate-determining step in Reaction 12 on the surface of a micelle is clarified to be the proton-transfer process in the ion pair, (II)⇌(III).

As can be seen in Eqs. 8 and 9, the kinetics of the base equilibrium of amines in the micellar system are in the form of the Brönsted catalysis law.[15] According to the Brönsted catalysis law, the right-hand side is composed of a constant and a term of a contribution of K_b, where the index (the Brönsted coefficient) expresses the degree of proton-transfer at the rate-determining step. The constant in Eqs. 8 and 9 corresponds to the rate constant of k_f (or k_b) when $K_b=1$; in other words, it reflects the magnitude of the activation energy of a reaction when the energy difference of the reactant and the product is zero. As can be seen in Eqs. 8—11, in the base equilibrium of amines on the surface of the SDS micelle, the value of the constant is more than two orders of magnitude smaller than that in the aqueous solution. This means that the former has a larger activation energy than the latter; the difference between them was found to be 3.0 kcal mol^{-1} by the use of the equation of $-RT \ln 10^{8.3-10.5}$. The indices of the primary and the secondary amines in the micellar system were found to be about 0.5, which indicates that about half of the proton-transfer is performed at the rate-determining step. This fact supports the above-mentioned conclusion that the rate-determining step exists between (II) and (III) in Reaction 12.

As can be seen in Table 2, the pK_b values of the amines in an SDS micellar solution are much smaller than the corresponding values in an aqueous solution. This micellar effect on pK_b can be explained in terms of the cationic amino group being stabilized electrostatically by the surrounding anionic sulfate groups of the micelle and the dissociation of the amine being accelerated. Since the electrostatic interaction is proportional to the distance of the amino group and the anionic surface of the micelle, the difference in the pK_b values between the two solutions, ΔpK_b, will be used as a measure of the degree of penetration of an amine into the micelle. In fact, in a series of primary amines,[5] the largest of the ΔpK_b values, 1.77, was observed for octylamine, where a long alkyl chain causes the amine to be well solubilized in the micelle and causes the amino group to be close to the anionic surface of the micelle, while in the case of benzylamine, the hydrophobic group is small and the penetrates little into the micelle, and the micellar effect on pK_b is smaller, ΔpK_b=1.35. In the present study, the ΔpK_b values of the secondary amines (shown in Table 2) were smaller than those for the primary amines, 1.35—1.77. Especially in the cases of the amines with two long alkyl groups, the ΔpK_b values were the smallest among those of the amines studied. From the standpoint of the micellar effect on pK_b, the secondary amines are not so deeply solubilized in the micelle as the primary amines because of the specific structures of the two hydrophobic groups. A similar picture can also be deduced from the kinetic results; as may be seen in Fig. 6, the K_b dependencies of k_f and k_b in the present work are a little closer to those in the aqueous solution than those for the primary amines in the SDS micellar solution. Therefore, the amino group of secondary amines might be located a little far from the anionic sulfate group of the micelle and closer to the bulk water, and the micellar effect on the base equilibrium seems to be a little smaller than that of primary amines.

In conclusion, the fundamental difference between the primary and secondary amines was not established in the reaction mechanism of the base equilibrium on the SDS micelle. However, small differences in the micellar effect on pK_b and in the K_b dependencies of the rate constants provided a picture of a little shorter penetration of the secondary amines into the SDS micelle than that of the primary amines.

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