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Micellar Catalytic Effect on the Base Dissociation of Methylamine Studied by the Ultrasonic Absorption Method

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Micellar catalytic effects on the base dissociation of methylamine have been studied by ultrasonic absorption method. The dissociation constant, the rate constants, and the volume change of the reaction were obtained in the absence and in the presence of SDS. The micellar catalytic effects observed for methylamine was smaller than those for amines of long alkyl chain, which was ascribed to the facts that the former is incorporated into the micellar ionic atmosphere in the concentrated micellar solution while the latters are solubilized into micelles.

In a series of investigations by the ultrasonic absorption method, we have studied the micellar catalytic effects on the acid dissociation of aromatic carboxylic acids[1,2] and the base dissociation of amines.[3-6] In most of these micellar catalyzed reactions, the reactants have been solubilized in the micelles.[1-9] If the solubilization is a prerequisite for the micellar catalysis, one cannot expect micellar catalytic effects for carboxylic acids and alkylamines of short alkyl chain. The present work was intended to examine this problem. Static and kinetic studies were carried out for the base dissociation of methylamine, which has the shortest alkyl group of the alkylamines, in the presence of the SDS micelles. Comparing the results with those for the homologous alkylamines, the dependence of the micellar catalytic effects on the alkyl-chain length of the amines is discussed.

Experimental

Methylamine (MA), in the form of 30% aqueous solution, and propylamine were purchased from Tokyo Kasei and used without further purification. The concentration of MA was determined by pH titration. SDS purchased from Pierce was recrystallized twice in methanol. The critical micelle concentration (cmc) determined by conductivity measurements was found to be 8.0×10^{-3} M§ at 30 °C. All other chemicals were of reagent grade.

pH measurements were carried out with a pH meter (HM-20) using an electrode (GS-135C) of TOA Electronics Ltd. Ultrasonic absorption measurements were carried out by the pulse method in the frequency range of 7.5 to 95 MHz. Details of the apparatus have been described elsewhere.[10] All the absorption data fitted the single relaxation equation[11,12]

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

where α is the absorption coefficient, f the frequency, f_r the relaxation frequency, and A and B are the relaxation and non-relaxation absorptions, respectively. The three parameters, f_r, A, and B, were determined by computer simulation. Experimental errors were within 8%, 5%, and 5% of the corresponding values, respectively. The velocity of sound was measured by the sing-around method at 1.92 MHz.[13] All the measurements were performed under nitrogen atmosphere and thermostated conditions. In the case of MA aqueous solution, the ionic strength, μ, was kept constant at 0.3 by the addition of NaCl.

Results and Discussion

Static and Kinetic Studies of the Base Dissociation of MA in Aqueous Solution. The base dissociation of MA in the absence of SDS was studied first in order to obtain referential data for the MA-SDS system.

For the reaction;

$$CH_3NH_3^+ + OH^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CH_3NH_2 + H_2O\ , \tag{2}$$

the base dissociation constant, $K_b{}^0$, is defined as,

$$K_b{}^0 = \frac{k_b}{k_f} = \frac{\gamma^2[CH_3NH_3^+]\,[OH^-]}{[CH_3NH_2]} = \frac{\gamma^2\sigma^2C_0}{1-\sigma}\ , \tag{3}$$

where γ is the mean activity coefficient, σ the degree of ionization, and C_0 the total concentration of MA. From the pH values in Table 1 and the activity coefficients calculated by the Davies equation,[14] p$K_b{}^0$ was obtained to be 3.44 (±0.02). This is in agreement with the literature value.[15]

Ultrasonic relaxation absorption was observed in the aqueous solution of MA in the MHz frequency range as shown in Fig. 1. The experimental condi-

Table 1. pH and Ultrasonic Absorption Parameters for the Methylamine Aqueous Solution at μ=0.3 and 30 °C

C_0 / M	pH	f_r / MHz	A (10^{-17})	B (10^{-17})
0.01	11.04	24.5	52	18
0.02	11.23	35.0	57	18
0.03	11.32	40.0	65	18
0.04	11.40	49.3	65	18
0.05	11.44	54.7	67	18

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§ 1 M=1 mol dm^{-3}.

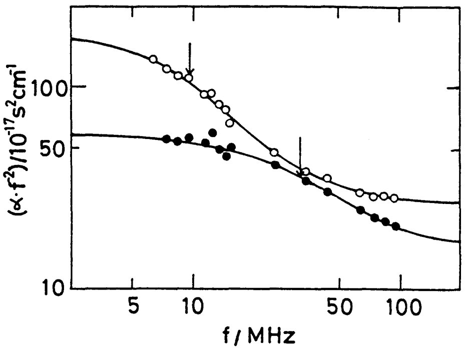

Fig. 1. Representative ultrasonic absorption spectra at 30 °C: ●, MA(0.01 M) aqueous solution at μ=0.3; ○, MA(0.01 M)-SDS(0.30 M) system. The arrows indicate the relaxation frequency.

tions and the relaxation parameters obtained are listed in Table 1. As has been clarified by previous studies on a series of alkylamines,[16,17] the dependence of the relaxation parameters for the concentration and the pH indicates that the relaxation absorption is due to the base dissociation of MA. For Reaction 2, the relaxation parameters are related to the kinetic parameters by the following equations:[11,12]

$$(2\pi f_r)^2 = 4\gamma^2 k_f k_b C_0 + k_b^2, \tag{4}$$

$$(\alpha'\lambda)_{\max} = \frac{\rho u^2 \pi}{2RT} \cdot (\Delta V)^2 \cdot \Gamma^{-1} \tag{5a}$$

with

$$\Gamma = [CH_3NH_3^+]^{-1} + [OH^-]^{-1} + [CH_3NH_2]^{-1}, \tag{5b}$$

where α' is the excess absorption coefficient, λ the wavelength, ρ the density, u the sound velocity, ΔV the volume change of the reaction, and the subscript max indicates maximum value. Plots of $(2\pi f_r)^2$ and $(\alpha' \lambda)_{\max}$ against the concentration terms are shown in Figs. 2a and 2b, respectively. The kinetic parameters were obtained to be $\gamma^2 k_f$=2.7 (±0.4)×10^{10} $M^{-1}s^{-1}$, k_b=2.2 (±0.4)×10^7 s^{-1}, and ΔV=25.8 (±0.8) cm^3 mol^{-1}. The apparent base dissociation constant, K_b (=$k_b/\gamma^2 k_f$), was obtained from the pH data as pK_b=3.09 (±0.02).

Base Dissociation of MA in Micellar Solutions of SDS. The addition of SDS to a MA solution induces an increase of pH as shown in Fig. 3. As seen in this figure, pH changes very little in the region below the cmc, but increases rapidly above the cmc. This result implies that the base dissociation of MA is accerelated by its incorporation into the SDS micelles, and at rather high SDS concentration, the micellar effect, i.e., the incorporation saturates. Similar experiments were carried out also on propylamine. As shown in Fig. 3, the value of pH saturates at a somewhat lower concentration of SDS compared to that in the case of the MA-SDS system, and the change of pH induced by the addition of SDS is larger. These differences in the micellar effects on the two amines are discussed later.

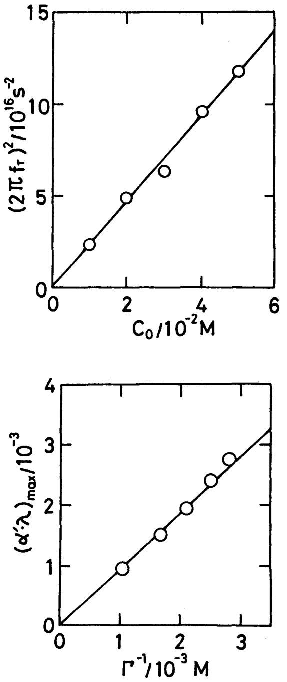

Fig. 2. Plots of (a) $(2\pi f_r)^2$ vs. MA concentration and (b) $(\alpha' \lambda)_{\max}$ vs. Γ^{-1} for MA aqueous solution at μ= 0.3 and 30 °C.

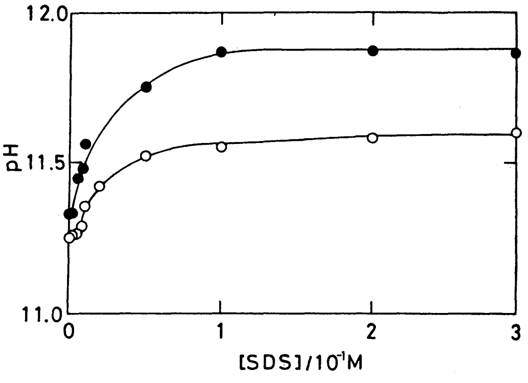

Fig. 3. pH of the alkylamine(0.01 M)-SDS systems at 30 °C: ○, MA; ●, propylamine.

Table 2. pH and Ultrasonic Absorption Parameters for the Methylamine-SDS (0.30 M) System at 30 °C

[MA]/M	pH	f_r/MHz	A (10^{-17})	B (10^{-17})
0.01	11.41	9.9	159	26
0.02	11.60	12.9	237	27
0.03	11.70	16.3	254	27
0.04	11.78	18.4	240	26
0.05	11.83	20.3	272	27

Quantitative measurements of pH and ultrasonic absorption were performed on solutions of various concentrations of MA containing a constant concentration (0.30 M) of SDS. The experimental conditions and the obtained data are summarized in Table 2.

Taking into account small hydrophobicity of MA, it is probable that the base dissociation of MA occurs both in bulk and on the micellar surface, and the following coupled reaction mechanism is proposed:

$$\begin{tikzcd}[column sep=huge, row sep=large]
\text{(i)}\quad CH_3NH_3^+ \arrow[r, shift left, "k_{12}"] \arrow[d, shift left, "\text{(M)}"', "\text{fast}"'] & CH_3NH_2\quad \text{(ii)} \arrow[l, shift left, "k_{21}\ OH^-"] \arrow[d, shift left, "\text{(M)}"', "\text{fast}"'] \\
\text{(iv)}\quad CH_3NH_3^+(M) \arrow[r, shift left, "k_{43}"] \arrow[u, shift left] & CH_3NH_2(M)\quad \text{(iii)} \arrow[l, shift left, "k_{34}\ OH^-"] \arrow[u, shift left]
\end{tikzcd} \qquad (6)$$

where (M) indicates an adsorption site on the micelle and (i)—(iv) mean different states of MA. The apparent dissociation constant of MA in the 0.30 M SDS micellar solution, $\overline{K}_b$ (M), defined as,

$$\overline{K}_b(M) = \frac{\{[CH_3NH_3^+(M)] + [CH_3NH_3^+]\} \cdot [OH^-]}{\{[CH_3NH_2(M)] + [CH_3NH_2]\}}, \quad (7)$$

was obtained from the pH data as p$\overline{K}_b$ (M)=2.18 (±0.01).

Ultrasonic relaxation absorption of the MA-SDS system takes place in a lower frequency range and the relaxation amplitude is larger than those of the pure MA in aqueous solution (Fig. 1). Since the association and dissociation of MA to and from the micelles are very fast,[18] the relaxation time, τ, for the slowest process in Reaction 6 is given by the following equation:[19]

$$\tau^{-1}\ (= 2\pi f_r) =$$

$$\gamma^2 k_{12}\left\{2[CH_3NH_3^+] + \frac{[CH_3NH_2]}{[CH_3NH_2(M)]+[CH_3NH_2]} \cdot K_{12}\right\} + \gamma^2 k_{43}\left\{2[CH_3NH_3^+(M)] + \frac{[CH_3NH_2(M)]}{[CH_3NH_2(M)]+[CH_3NH_2]} \cdot K_{43}\right\}, \quad (8)$$

with

$$K_{12} = \frac{k_{21}}{\gamma^2 k_{12}} = \frac{[CH_3NH_3^+] \cdot [OH^-]}{[CH_3NH_2]} = K_b(W), \quad (9)$$

$$K_{43} = \frac{k_{34}}{\gamma^2 k_{43}} = \frac{[CH_3NH_3^+(M)] \cdot [OH^-]}{[CH_3NH_2(M)]} = K_b(M), \quad (10)$$

where K_b (W) and K_b (M) are the apparent base dissociation constants of MA in the bulk and on the micelle, respectively. If the value of K_b (M) is given, we can calculate the concentrations of MA of the different states with use of Eqs. 7,9, and 10. Then the first term of the right hand side of Eq. 8 was calculated by introducing the kinetic value obtained above for the base dissociation of MA in aqueous solution, and τ^{-1} (=2π f_r) was plotted against the value in the parenthesis of the second term. When K_b (M) is properly assumed, this plot gives a straight line. Then the plot was examined by changing the K_b (M) values in the range of K_b (W) to $\overline{K}_b$ (M). A good linear relationship was obtained only for the K_b (M) values very close to $\overline{K}_b$ (M). The result indicates that Reaction 6 can be approximated by the equilibrium (iv)$\rightleftarrows$(iii), or in other words, all the MA is incorporated into the SDS micelles. The same result was suggested also from the pH saturation behavior at concentrated SDS solution as mentioned above. Consequently, the base dissociation of MA in the 0.30 M SDS solution can be approximated by the reaction,

$$CH_3NH_3^+(M) + OH^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} CH_3NH_2(M) + H_2O. \quad (11)$$

Since this reaction is quite similar to Reaction 2, we can apply Eqs. 4 and 5 for the analysis of the relaxation parameters. Each plot of the relaxation parameters is shown in Figs. 4a and 4b. From these plots, the kinetic parameters for Reaction 11 were obtained to be: $\gamma^2 k_f$=3.5 (±0.6)×10^9 M^{-1}s^{-1}, k_b=2.3 (±0.4)×10^{7}s^{-1}, and ΔV=22.4 (±0.7) cm^3 mol^{-1} at 30 °C.

Ultrasonic absorption was measured also in the MA-SDS system with changing pH. Experimental conditions and the results are listed in Table 3. For Reaction 11, f_r is related to the rate constants as follows:[11,12,19]

$$2\pi f_r = \gamma^2 k_f\{[CH_3NH_3^+(M)] + [OH^-]\} + k_b. \quad (12)$$

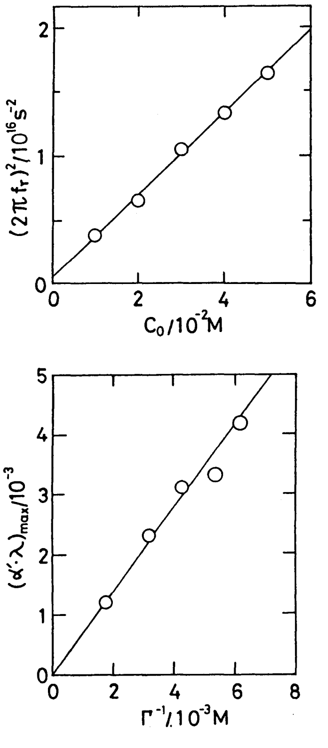

Fig. 4. Plots of (a) (2π f_r)^2 vs. MA concentration and (b) (α' λ)$_{max}$ vs. Γ^{-1} for MA-SDS(0.30 M) system at 30°C.

Table 3. Ultrasonic Absorption Parameters for the Methylamine (0.03 M)-SDS (0.30 M) System at Various pH and 30 °C

pH	f_r / MHz	A (10^{-17})	B (10^{-17})
10.80	18.0	36	30
11.14	16.8	88	28
11.43	13.4	152	30
11.73	16.5	195	28
12.18	26.2	98	26

The concentrations of the MA cation and OH$^-$ were calculated from the pH, C_0, and K_b (M). Then, the value of ($2\pi f_r$) was plotted against the concentration term of Eq. 12, and the rate constants were obtained to be; $\gamma^2 k_f=3.6\,(\pm0.6)\times10^9\,\text{M}^{-1}\,\text{s}^{-1}$ and $k_b=2.4\,(\pm0.4)\times10^7\,\text{s}^{-1}$. For the relaxation absorption amplitude analysis, Eq. 5 can be applied. From the plot of $(\alpha'\lambda)_{\max}$ vs. the concentration term, the value of ΔV was given to be 20.0 (±0.6) cm^{3}mol^{-1}. The fact that the absorption parameters can be satisfactorily analyzed by Eqs. 12 and 5 supports the assignment of the relaxation absorption to Reaction 11. Furthermore, the kinetic values were in reasonable agreement with the corresponding value obtained in the above experiments of MA concentration change.

Dependence of the Micellar Catalytic Effects on the Alkyl-Chain Length of the Amines. Magnitude of the micellar catalytic effects on the base dissociation of amines depends on their alkyl-chain length, e.g., as seen above, the pH change induced by the addition of SDS is larger for propylamine than for MA. Further examinations are performed in the following way.

Comparison of the values of $\text{p}K_b^0$ and $\text{p}K_b$ (M) obtained above shows that the dissociation of MA is promoted by 1.26 $\text{p}K_b$ unit in the micellar solution. Since the micellar effect has been about 1.5 $\text{p}K_b$ unit for a series of amines of long alkyl chain in a 0.30 M detergent solution,[3—6] the micellar effect is smaller for MA.

Ultrasonic relaxation absorption spectrum reflects the difference of the alkyl-chain length of the amines in micellar solution. As shown in Fig. 5, f_r shifts to the lower frequency region and the absorption amplitude increases with increase of the alkyl-chain length of the amine. However, these dependences on the alkyl-chain length saturate rapidly and the absorption spectra for the systems of amines of C_{4-10}-SDS are almost indistinguishable from each other.[3—6]

For the base dissociation of alkylamines in a micellar solution, we have found that $\gamma^2 k_f$ and k_b are both dependent on the base dissociation constant.[1—6] These situations are shown in Fig. 6 where the rate constants for MA obtained in this work are also plotted. Looking into this figure, we can discover the following features. (i) The rate constants for MA in an aqueous solution fall on the line expected from the corresponding literature values for the homologous amines.[16,17] (ii) The rate constants for MA in the micellar solution are much smaller than the corresponding values in aqueous solution at the same $\text{p}K_b$ but larger than those for the amines of long alkyl chain in the micellar solution.[3,4] These results indicate that the base dissociation of MA is catalyzed by the SDS micelles but the catalytic effects are smaller than those for the amines of long alkyl chain.

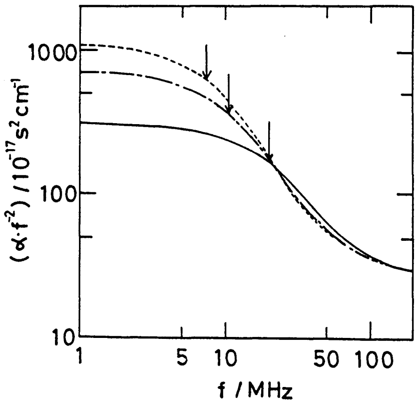

Fig. 5. Representative ultrasonic absorption spectra of the alkylamine(0.05 M)-SDS(0.30 M) solutions at 30 °C: (——), MA; (—·—·—), propylamine; (– – – –), amines of alkyl chain of C_{4-10}.

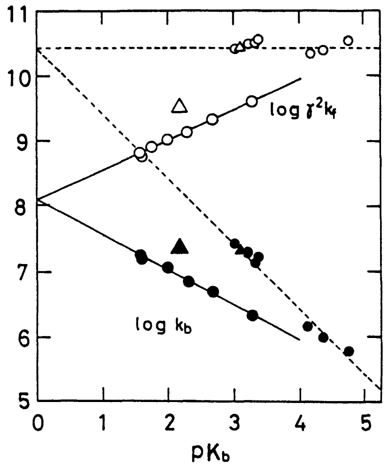

Fig. 6. $\text{p}K_b$ dependencies of the rate constants for the base dissociation of the amines in the presence of 0.30 M SDS (large signs, data from Refs. 3—6) and in the absence of the micelles (small signs, data from Refs. 16 and 17): triangle indicates MA. The amines cited for the two conditions are not corresponding to each other.

Taking into consideration the fact that the $\text{p}K_b$ values of alkylamines are almost the same in aqueous solution,[15] dependence of the micellar catalytic effects on the alkyl-chain length of amines should be ascribed to the position of the amino group in the micellar atmosphere. Judging from the behavior of saturation of the effects with the alkyl-chain length, the amino group of the amines of alkyl chains longer than C_4 is in the Stern layer due to the solubilization of the alkyl chain into the micellar core. For the amines of alkyl chain shorter than C_4, the solubilization is inadequate, and the amino group may be outside of the Stern layer. Especially in the case of MA, ordinary solubilization is not conceivable. Then, the smaller micellar catalytic effects for MA are interpreted as follows.

The MA cation can be incorporated into the micellar atmosphere as a counter ion because of its small predominance in the hydrophobicity compared to Na^+.20) On the other hand, undissociated MA may not be solubilized preferentially into the micelle. In a rather concentrated detergent solution, however, the micelle-micelle interaction becomes predominant because of the high cocentration of micellar aggregates,21,22) and the free bulk will essentially disappear. Therefore, both dissociated and undissociated MA, which were in the bulk at lower detergent concentration are now incorporated into the micellar ionic atmosphere, i.e., Gouy-Chapman double layer. In fact, in recent investigations, we have found that noncharged amphiphilic molecules of short alkyl chain, e.g., methyl or ethyl group, can be incorporated into micelles at high detergent concentration.23) As a consequence, we conclude that, in a concentrated SDS solution as in the present case, all the MA are incorporated into the micellar ionic atmosphere and the base dissociation is catalyzed moderately.

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