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Ultrasonic Absorption Studies of the Micellar Catalyzed Reaction of the Base Dissociation of Ammonia

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Synopsis. The base dissociation of ammonia has been studied by an ultrasonic absorption method in both the absence and presence of SDS micelle in aqueous solution, and kinetic parameters were obtained. The micellar catalyzed reaction mechanism, including the interactions of ammonium ion with SDS micelles, are discussed.

In order to examine the role of the hydrophobic group of the reactant in micellar catalysis we studied the base dissociation of amines by changing their hydrocarbon chain length in the presence of SDS micelles,[1–5] and proposed a micellar catalyzed mechanism for the base dissociation of lower alkylamines.[4,5] In the present work, a study was developed which involved a similar reaction of ammonia.

Experimental

Ammonia was purchased from Wako Chemicals in the form of a 28% aqueous solution; the concentration was determined by acid titration. Sodium dodecyl sulfate (SDS), purchased from Pierce, was recrystallized in methanol; the critical micelle concentration was determined to be 8.0×10^{-3} M (1 M=1 mol dm^{-3}) by a conductivity measurement. Therefore, in the present work, most of the SDS was in the form of micelles. pH measurements were carried out with a pH meter (HM-20) using an electrode (GS-135) of TOA Electronics Ltd. Ultrasonic absorption measurements were carried out by a pulse method over the frequency range 11.5 to 95 MHz.[6] All of the relaxation spectra could be characterized by a single relaxation equation. The velocity of sound was measured by a sing-around method at 1.92 MHz.[7] The measurements were performed under a nitrogen gas atmosphere; further, the surface of the solution was sealed with a plastic plate, and the system was thermostated at 30.0 °C.

Results and Discussion

In an aqueous solution of ammonia, ultrasonic relaxation absorption has been observed over a MHz frequency; the relaxation phenomenon has long been studied and has been ascribed to a base dissociation of ammonia:[8–10]

$$NH_4^+ + OH^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NH_3 + H_2O. \qquad (1)$$

In order to obtain referential data for the micellar catalyzed reaction, the reaction was first studied in the presence of 0.30 M NaCl;[11] the pH and ultrasonic absorption parameters obtained are listed in Table 1. The relaxation frequency, f_r, and the maximum relaxation absorption per wavelength, μ_{max}, for Reaction 1 are related to the kinetic parameters by the following equations:

$$(2\pi f_r)^2 = 4r^2 k_f k_b C_0 + k_b^2 \qquad (2)$$

and

$$\mu_{max} = \frac{\rho u^2 \pi}{2RT} (\Delta V)^2 \Gamma^{-1}, \qquad (3)$$

with

$$\Gamma = [NH_4^+]^{-1} + [OH^-]^{-1} + [NH_3]^{-1}, \qquad (4)$$

where r is the mean activity coefficient, C_0 the initial concentration of ammonia, ρ the density, u the velocity of sound, and ΔV the volume change of the reaction.

With the use of experimental values of f_r and μ_{max}, the values of $(2\pi f_r)^2$ and μ_{max} are plotted against the concentration terms in Eqs. 2 and 3, respectively. Satisfactory linear relationships were observed for each plot; these facts proved that the relaxation absorption is due to Reaction 1. The kinetic parameters, thus

Table 1. pH and Ultrasonic Relaxation Absorption Parameters for Aqueous Solution of Ammonia in the Presence of 0.30 M NaCl at 30.0 °C

C_0	pH	f_r	A	B
M		MHz	10^{-17} s^2 cm^{-1}	
0.10	10.84	17.1	74	18
0.20	11.00	25.0	75	18
0.30	11.08	30.5	74	18
0.40	11.18	35.1	74	18
0.50	11.24	39.1	79	18

Table 2. Kinetic Parameters for the Base Dissociation of Ammonia and Amines in 0.30 M NaCl Solution at 30.0 °C

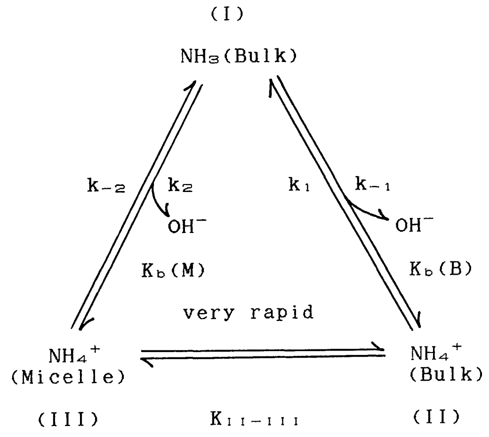
Bases	pK_b	r^2k_f	k_b	ΔV
		10^{10} M^{-1} s^{-1}	10^6 s^{-1}	cm^3 mol^{-1}
Ammonia	4.59	3.4	0.88	29.3
MA	3.21	3.1	19	28.1
DMA	3.06	2.5	22	26.1
EA	3.19	2.5	16	24.1
EN	3.87	2.8	3.8	28.6
EOHA	4.33	2.8	1.3	27.6

MA: methylamine; DMA: dimethylamine; EA: ethylamine; EN: ethylenediamine; EOHA: 2-aminoethanol.

obtained, and the apparent base dissociation constant, $\bar{K}_b$ ($=k_b/r^2k_f$), obtained from the pH measurements, are listed in Table 2, where the corresponding values for lower alkylamines[4,5] are given for a comparison.

The addition of SDS to the ammonia solution induces an increase in the pH, a shift of the ultrasonic relaxation absorption to a lower frequency region, and an increase in the absorption amplitude. These results indicate that the base dissociation of ammonia is catalyzed by SDS micelles. The pH and ultrasonic absorption data (summarized in Table 3) were analyzed using Eqs. 2—4; the obtained kinetic values are listed in Table 4, together with those for the lower alkylamines.[4,5] By comparing the values in Tables 2 and 4, we can say that in the SDS micellar solution: (i) base dissociation is promoted and that the value of $\mathrm{p}\bar{K}_b$ is about 0.8 unit smaller, due to a decrease in k_f and an increase in k_b; (ii) the value of ΔV is about 5 $\mathrm{cm^3 mole^{-1}}$ smaller. These features were similarly observed for the lower alkylamines.[4,5]

Since ammonia has no hydrophobic group, it is very soluble in water and its incorporation into a micellar hydrophobic core is improbable. Therefore, interactions of ammonia with SDS micelles involve the binding of ammonium ions as counter ions of SDS micelles. We can thus propose the following mechanism regarding the base dissociation of ammonia catalyzed by SDS micelles;[12]



Reaction (5)

where (Bulk) and (Micelle) mean that the species is in the bulk out of the micellar atmosphere and on the surface of the micelle, respectively, and that $K_{\mathrm{II-III}}=[\mathrm{NH_4^+(Micelle)}]/[\mathrm{NH_4^+(Bulk)}]$. The apparent base dissociation constant, $\bar{K}_b$, in Table 4 is related to those in bulk, $K_b(\mathrm{B})$, and on the surface of the micelle, $K_b(\mathrm{M})$, as follows:

$$\bar{K}_b = K_b(\mathrm{B}) + K_b(\mathrm{M}). \quad (6)$$

Considering that $K_b(\mathrm{B})$ is equal to K_b in Table 2, $K_b(\mathrm{M})$ is evaluated, and $K_{\mathrm{II-III}}$ is given by

$$K_{\mathrm{II-III}} = K_b(\mathrm{M})/K_b(\mathrm{B}). \quad (7)$$

Since the obtained $K_{\mathrm{II-III}}$ values are much larger than unity, we can say that most of the ammonium ions are on the surface of the SDS micelle, while some part remains in the bulk. Since the association and dissociation of counterions to and from the micelles, $(\mathrm{II}) \rightleftharpoons (\mathrm{III})$, are very rapid,[13,14] the relaxation frequency for the slow process is represented by[5,15]

$$2\pi f_r = 2r^2\left[\frac{k_1k_{-2}(k_{-1}+k_2)}{k_1k_2+k_{-1}k_{-2}}\right]\cdot[\mathrm{OH^-}] + k_2 + k_{-1}. \quad (8)$$

Assuming that the rate constants in bulk (r^2k_1, k_{-1}) are equal to those given in Table 2, the rate constants for a micellar catalyzed reaction, r^2k_{-2} and k_2, were calculated using the above equation with the base dissociation constants in both the absence and presence of SDS. The results are summarized in Table 5 and Fig. 1, together with data for the lower alkylamines. As can be seen in Fig. 1, the reaction of ammonia may be in the same homologues with those of the lower alkylamines, i.e., an introduction of a lower alkyl group (lower than $\mathrm{C_4}$) to ammonia induces no appreciable effect regarding micellar catalysis. We show in Fig. 1, furthermore, that r^2k_f is almost constant and that the K_b dependency of k_b is steep in a solution in the absence of SDS micelles, whereas r^2k_{-2} decreases and k_2 increases gently with an increase of K_b for a micellar catalyzed reaction. This K_b dependency type behavior of the rate constants in the two solutions can well be interpreted by the idea that the rate-determining step of the former is a diffusion process, $(\mathrm{I}) \rightleftharpoons (\mathrm{II})$, while that of the latter is an intramolecular-proton-transfer process, $(\mathrm{II}) \rightleftharpoons (\mathrm{III})$, according to the following stepwise mechanism:

$$\underset{(\mathrm{I})}{\mathrm{NH_4^+ + OH^-}} \rightleftharpoons \underset{(\mathrm{II})}{[\mathrm{NH_4^+\cdots OH^-}]} \rightleftharpoons \underset{(\mathrm{III})}{\mathrm{NH_3 + H_2O}}, \quad (9)$$

Table 3. pH and Ultrasonic Relaxation Absorption Parameters for Aqueous Solution of Ammonia in the Presence of 0.30 M SDS at 30.0 °C

C_0	pH	f_r	A	B
M		MHz	$10^{-17}\,\mathrm{s^2\,cm^{-1}}$	
0.10	11.27	11.7	182	28
0.20	11.42	16.8	190	27
0.30	11.51	20.2	193	27
0.40	11.57	23.2	188	27
0.50	11.62	25.6	189	27

Table 4. Apparent Kinetic Parameters for the Base Dissociation of Ammonia and Amines in the Presence of 0.30 M SDS at 30.0 °C

Bases	$\mathrm{p}\bar{K}_b$	r^2k_f	k_b	ΔV
		$10^9\,\mathrm{M^{-1}\,s^{-1}}$	$10^6\,\mathrm{s^{-1}}$	$\mathrm{cm^3\,mol^{-1}}$
Ammonia	3.77	8.8	1.5	24.0
MA	2.19	3.5	23	21.5
DMA	2.08	3.5	29	22.4
EA	2.15	2.9	20	22.7
EN	2.95	6.4	7.2	21.9
EOHA	3.38	8.4	3.5	19.8

Table 5. Kinetic Parameters for the Base Dissociation of Ammonia and Amines on the Surface of SDS Micelles at 30.0 °C

Bases	pK_b	r^2k_{-2}	k_2
		10^8 M^{-1} s^{-1}	10^6 s^{-1}
Ammonia	3.84	44	0.64
MA	2.23	6.0	3.4
DMA	2.13	10	7.4
EA	2.19	6.0	3.9
EN	3.01	34	3.8
EOHA	3.43	58	2.2

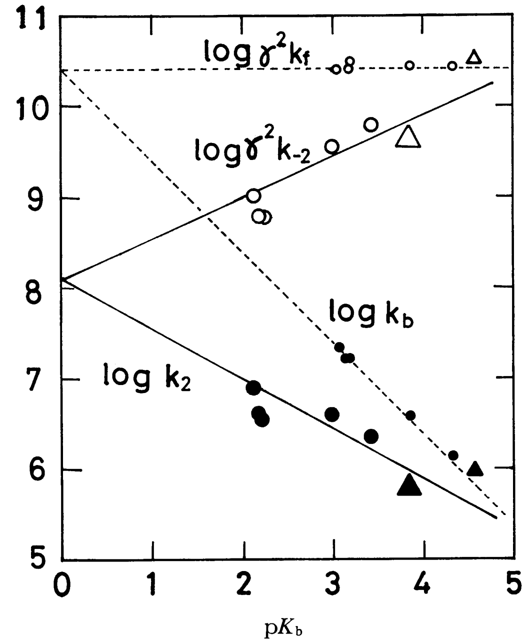


Fig. 1. K_b dependencies of the rate constants for the base dissociation of ammonia and amines in the absence (small signs) and in the presence of 0.30 M SDS (large signs); triangle indicates ammonia. Solid lines are the corresponding data for the amines of higher alkyl chain.[1-3]

where species (II) is an ion-paired intermediate. In a micellar-catalyzed reaction, the K_b(M) dependencies of the rate constants of ammonia and the lower alkylamines are similar to those of the higher alkylamines,[1-3] which is shown by the solid lines in Fig. 1. From these trends regarding the rate constants, it appears that the primary factor concerning micellar catalysis consists of an interaction of ammonium ion with the anionic surface of the micelle as their counter ions; the hydrophobic interaction plays a secondary role.

We have consequently clarified that: (i) the ammonium ions bind predominantly to the SDS micelles as counter ions exchanged with Na$^+$ ions; (ii) the rate-determining step of the base dissociation of ammonia is different for reactions in both the absence and presence of SDS micelles; and (iii) ΔV is smaller in a micellar solution. All of these features can be well interpreted by the idea that ammonium and the lower alkylammonium ions bind relatively tightly to SDS micelles, mainly by an electrostatic force and partly by some additional force, e.g., hydrogen-bonding. Detailed discussions concerning this problem will be developed elsewhere.[5]

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11) In the micellar solution, Reaction 1 is composed of three reactions occuring (i) in the bulk out of the micellar atmosphere, (ii) between the bulk and the surface of the micelle, and (iii) on the surface of the micelle; the ionic strength of these conditions might be different considerably. Therefore, as a referential condition of 0.30 M SDS solution, ionic strength was chosen as to equal to an average condition of (i), (ii), and (iii), i.e., apparent ionic strength of the micellar solution.

12) In our preliminary work for methylamine-SDS system,[4] we have proposed four state model where not only dissociated methylamine but also undissociated one is supposed to be incorporated partly into SDS micelles. However, detailed examination of the pH and ultrasonic data of the present experiments clarified that the incorporation of the undissociated ammonia is negligible.

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