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Kinetic Studies of Fast Reactions in Aqueous Solutions of Amylamine by Means of Ultrasonic Absorption

Sadakatsu NISHIKAWA, Tatsuya YASUNAGA, and Kojiro TAKAHASHI
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730

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The ultrasonic absorptions in aqueous solutions of amylamine were measured in the frequency range of 3.5—220 MHz and in the concentration range of 0.01—3.06 M. Two kinds of relaxations were observed. One was attributed to the 5A—A_5 reaction of non-ionized molecules of amylamine, and the rate constants were determined from the concentration dependence of the relaxation time at various temperatures. The thermodynamic parameters were determined from the temperature dependence of the rate and equilibrium constants. The other was attributed to hydrolysis, which is a diffusion-controlled reaction. In order to clarify the relation between the stability of the aggregate and the length of the hydrophobic group, the ultrasonic absorptions in aqueous solutions of propylamine were also measured. The excess absorption due to the association-dissociation reaction was not observed; only that due to hydrolysis was observed. It was deduced from this investigation that the aggregate formed by the hydrophobic bonding exists in the aqueous solutions of normal amines, the carbon numbers of which are more than 4.

The method of ultrasonic absorption has been successfully applied to the investigation of reaction kinetics which occur rapidly, since the relaxation time and excess absorption determined from the absorption data are related to the kinetic parameters. It is well known that a number of binary mixtures exhibit a maximum in their excess absorptions at an intermediate concentration.[1] It has been previously reported by the present authors[2,3] that there are two kinds of relaxation processes in aqueous solutions of butylamine. One, associated with the maximum excess absorption phenomena, was attributed to the association-dissociation reaction of the non-ionized molecules, and the other, to hydrolysis. Accordingly, the same phenomena may be expected to be observed in aqueous solutions of other amines.

Andreae and his co-workers[1] have explained the excess absorption of ultrasonic waves in aqueous solutions of amylamine as a solute-solvent interaction. However, this analysis employs a rather unusually defined equilibrium constant, and some of the stoichiometries reported appear to be implausible. Moreover, the data reported are insufficient for a reasonable analysis of the excess absorption mechanism.

The purpose of the present investigation is to clarify in detail the excess absorption mechanism of ultrasonic

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[1] J. H. Andreae, P. D. Edmonds, and J. F. McKellar, *Acustica*, **15**, 74 (1965).

[2] S. Nishikawa and T. Yasunaga, This Bulletin, **46**, 1098 (1973).

[3] S. Nishikawa, T. Nakamoto, and T. Yasunaga, *ibid.*, **46**, 324 (1973).

waves in aqueous solutions of amylamine on the basis of that in the aqueous solution of butylamine[2] and to reveal the characteristic properties of the aqueous solutions of amines. This type of information is particularly desirable for an understanding of the more complex biochemical reactions.

Experimental

The amylamine and propylamine were of a guaranteed reagent grade, and KOH was added to them to remove the water because the relatively concentrated solutions were made at the required concentrations by weight. They were distilled after the filtration of KOH. The purities were verified by gas chromatography to be higher than 99.9%. Deionized and distilled water was used as the solvent. The relatively dilute solutions (less than 0.5 M) were prepared by the dilution of the stock solution. The other chemicals used were all of a guaranteed reagent grade. The measurements of the ultrasonic absorption were carried out at the odd harmonic frequencies of 0.5, 5, and 20 MHz X-cut quartz transducers by means of the pulse technique.[4] The frequency range of the measurement was 3.5—220 MHz. Since the aqueous solutions of amines are highly basic, the cell was designed to be air-tight and dry nitrogen gas was passed over the solutions to prevent the contamination of the specimens by oxidation with air. The sing-around method was employed at 1.92 MHz to measure the sound velocity. The densities were measured by means of a standard pycnometer. The pH values of the solutions were measured by means of a Hitachi Horiba type F-5 pH meter. All the measurements for the aqueous solutions of amylamine were made at 15, 20, 25, and 30 °C, and for those of propylamine, at 20 °C.

Results

In Fig. 1 the plots of α/f^2 *vs.* the concentration for the aqueous solutions of amylamine at 20 °C are shown, where α is the sound absorption coefficient, and f, the frequency. As may be seen in this figure, the absorption and the peak sound absorption concentration (P.S.A.C) depend on the frequency. This behavior leads us to predict the existence of the relaxation phenomena. In general, the sound absorption caused by the several relaxation processes can be described by the following equation:

$$\alpha/f^2=\sum_i \frac{A_i}{1+(f/f_{ri})^2}+B \qquad (1)$$

where f_{ri} is the relaxation frequency for the i-th process and where A_i and B are constants. Figure 2 shows the representative ultrasonic absorption spectra of the aqueous solutions of amylamine at 20 °C. The spectra in the concentration range of more than 1 M and less than 0.4 M show the characteristic behavior due to the single relaxation process, which is expressed by the case of $i=1$ in Eq. (1). On the other hand, the spectra in the concentration range between 1.0 and 0.4 M can be represented by the double relaxation process, which correspond to the case of $i=2$ in Eq. (1). These facts indicate that there are two kinds of relaxation processes in the aqueous solution of amylamine. The relaxation parameters, A_i, B, and f_{ri}, were determined so as to obtain the best fit of the

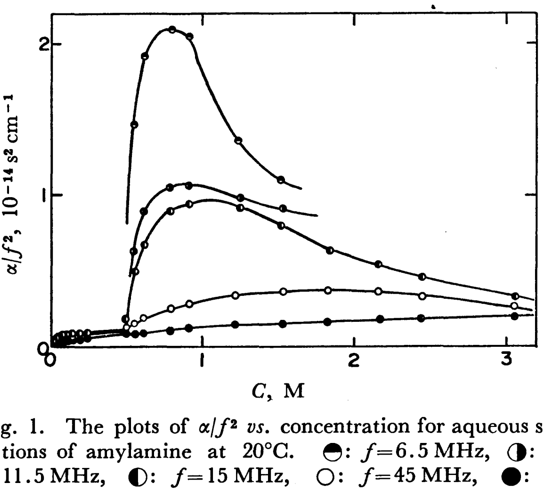

Fig. 1. The plots of α/f^2 *vs.* concentration for aqueous solutions of amylamine at 20°C. ◓: f=6.5 MHz, ◑: f=11.5 MHz, ◐: f=15 MHz, ○: f=45 MHz, ●: f=100 MHz.

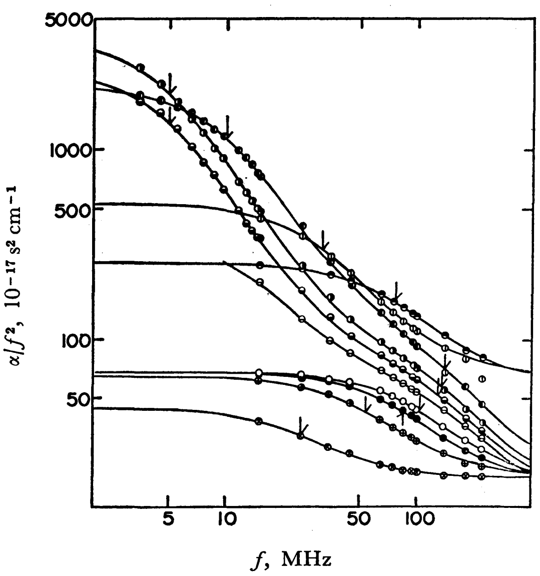

Fig. 2. Ultrasonic absorption spectra in aqueous solutions of amylamine at 20°C. ⊗: 0.00918 M, ⊕: 0.0685 M, ●: 0.147 M, ○: 0.245 M, ⊖: 0.490 M, ◒: 0.551 M, ◑: 0.612 M, ◐: 0.918 M, ⦶: 1.84 M, ◓: 3.06 M.

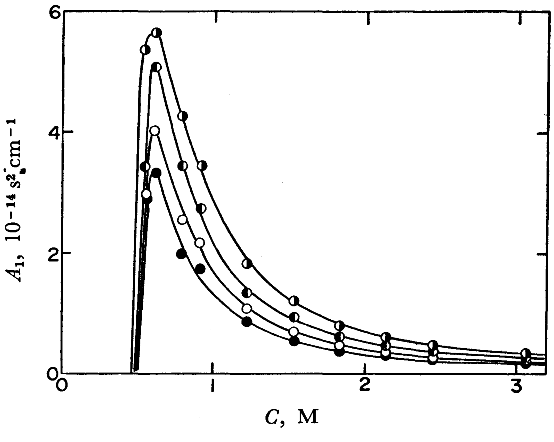

Fig. 3. Concentration dependence of the excess absorption A_1 in aqueous solutions of amylamine. ◐: 15 °C, ◐: 20 °C, ○: 25°C, ●: 30 °C.

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[4] N. Tatsumoto, *J. Chem. Phys.*, **47**, 4561 (1967).

Table 1. Relaxation parameters, sound velocity and density in the aqueous solutions of amylamine and propylamine at 20°C

C (M)	pH	γ	ρ (g·cc^{-1})	c (m·s^{-1})	f_{r1} (MHz)	f_{r2} (MHz)	A_1 (10^{-17} s^2 cm^{-1})	A_2 (10^{-17} s^2 cm^{-1})	B
				(amylamine)					
3.06	12.54	0.8276	0.9300	1470.8	77	—	257	—	80.7
2.45	12.53	0.8295	0.9446	1479.1	54	—	386	—	69.2
2.14	12.52	0.8302	0.9535	1483.7	48	—	490	—	86.5
1.84	12.51	0.8315	0.9597	1488.8	32	—	604	—	92.1
1.53	12.50	0.8328	0.9685	1494.0	25	—	992	—	107
1.22	12.48	0.8353	0.9753	1498.9	18	—	1338	—	138
0.918	12.46	0.8379	0.9824	1505.0	10	140	2763	115	23.0
0.796	12.44	0.8404	0.9845	1506.6	8.5	120	3454	109	23.0
0.612	12.42	0.8429	0.9887	1511.5	5.0	133	5066	98.0	21.3
0.551	12.41	0.8442	0.9904	1514.8	5.0	130	3454	86.0	19.5
0.245	12.31	0.8565	0.9943	1506.5	—	105	—	64.9	23.0
0.196	12.24	0.8650	0.9950	1501.9	—	95	—	63.0	24.3
0.147	12.15	0.8749	0.9954	1497.4	—	85	—	64.2	23.9
0.107	12.06	0.8908	0.9961	1493.2	—	70	—	60.3	23.9
0.0685	11.93	0.8977	0.9971	1490.0	—	55	—	59.4	25.2
0.0300	11.64	0.9228	0.9978	1487.0	—	35	—	48.4	25.8
0.00918	11.20	0.9509	0.9989	1485.3	—	25	—	32.7	25.0
				(propylamine)					
0.201	12.37	0.8492	0.9949	1497.0	—	100	—	61.0	23.0
0.161	12.30	0.8577	0.9955	1494.6	—	85	—	61.0	23.6
0.121	12.23	0.8659	0.9961	1491.7	—	73	—	63.6	24.0
0.0805	12.11	0.8793	0.9964	1490.2	—	60	—	59.3	24.8
0.0604	12.03	0.8879	0.9969	1488.2	—	53	—	58.7	24.8
0.0403	11.82	0.9079	0.9969	1485.6	—	35	—	43.3	22.3
0.0121	11.47	0.9350	0.9975	1485.7	—	25	—	29.1	25.0

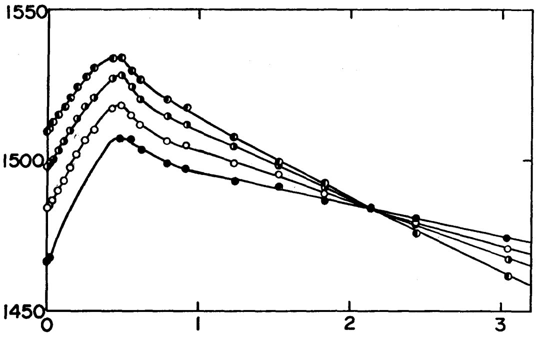

Fig. 4. Concentration dependence of the sound velocity in aqueous solutions of amylamine, ●: 15 °C, ○: 20 °C, ◑: 25 °C, ◐: 30 °C.

data to Eq. (1). However, the spectrum at 0.490 M could not be analyzed because the absorption coefficients at low frequencies could not be observed. The excess absorptions, A_1, which were observed in the concentration range of more than 0.5 M in the lower frequency range are shown in Fig. 3. As may be seen in this figure, the positions of the P.S.A.C are independent of the temperature. The sound velocity also shows the peak at an intermediate concentration, as may be seen in Fig. 4. The concentration at which the sound velocity shows its maximum is lower than that of the excess absorption.

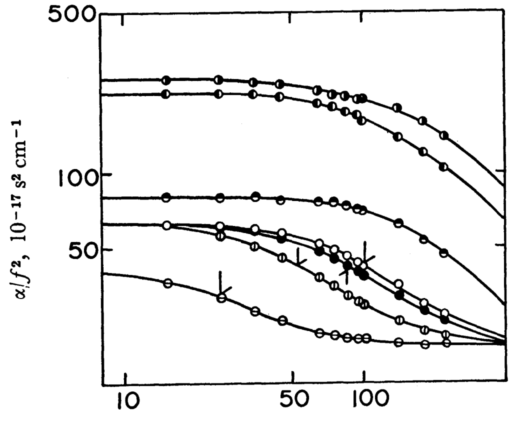

Fig. 5. Ultrasonic absorption spectra in aqueous solutions of propylamine at 20 °C. ⊖: 0.0121 M, ⦶: 0.0604 M, ●: 0.161 M, ○: 0.201 M, ◓: 2.07 M, ◐: 3.05 M, ◑: 4.04 M.

The ultrasonic absorptions in aqueous solutions of propylamine were also measured; same representative spectra are shown in Fig. 5. As may be seen in this figure, no double relaxation processes were observed, but only a single one was observed; no characteristic excess absorption such as is observed in the relatively concentrated solutions of butylamine and amylamine was found. In Table 1, the ultrasonic parameters and sound velocity obtained for the aqueous solutions of amylamine and propylamine are listed, together with the density, the pH, and the activity coefficient of the ions, the last of which was calculated by means of Davies equation:[5] $-\log\gamma=0.5[\{\sqrt{I}/(1+\sqrt{I})\}-0.3I]$, where γ is the activity coefficient, and I, the ionic strength.

Interpretation of Results

First, for the excess absorption observed in the lower frequency range in the aqueous solution of amylamine, the following reaction is considered.

$$nA \underset{k_b}{\overset{k_f}{\rightleftharpoons}} A_n \tag{2}$$

where A is the monomer, A_n, the aggregate, n, the aggregation number, and k_f and k_b, the forward and backward rate constants respectively. If one denotes the molar concentrations of the A and A_n components by C_1 and C_2, the relaxation time, τ_1, and the maximum excess absorption per wavelength, $\mu_{\max 1}$, can be written as follows:

$$2\pi f_{r_1} = {\tau_1}^{-1} = \overline{k_f} n^2 (\overline{C}_1)^{n-1} + \overline{k_b} \tag{3}$$

$$\mu_{\max 1} = \frac{1}{2} A_1 f_{r_1} c = \frac{\pi\rho c^2}{2} \cdot \frac{(\Delta {V_1}^{\circ})^2}{RT} \overline{k_f} \cdot (\overline{C}_1)^n \cdot \tau_1 \tag{4}$$

where ρ is the density, c, the velocity of sound, $\Delta {V_1}^{\circ}$, the standard volume change, R, the gas constant, and T, the absolute temperature. The equilibrium values of the rate constants and the concentrations are indicated by a bar over each symbol. The detailed derivatives of Eqs. (3) and (4) were reported in a previous paper.[2] In aqueous solutions of amines, there also exists the following equilibrium:

$$\text{R-NH}_3^+ + \text{OH}^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{R-NH}_2 + \text{H}_2\text{O} \tag{5}$$

where k_1 and k_2 are the forward and backward rate constants respectively. The dissociation constant, K_b, is defined by:

$$K_b = \frac{\overline{k_2}}{\overline{k_1}} = \frac{\gamma^2[\text{OH}^-]^2}{[\text{R}-\text{NH}_2]} \tag{6}$$

where γ is the mean activity coefficient of the ion. If the non-ionized molecules are associated with the aggregation, Eqs. (3) and (4) can be expressed in terms of K_b and $\gamma[\text{OH}^-]$ as follows:

$$2\pi f_{r_1} = {\tau_1}^{-1} = \overline{k_f} n^2 \left(\frac{\gamma^2[\text{OH}^-]^2}{K_b}\right)^{n-1} + \overline{k_b} \tag{7}$$

$$\mu_{\max 1} = \frac{\pi\rho c^2}{2} \cdot \frac{(\Delta {V_1}^{\circ})^2}{RT} \cdot \overline{k_f} \left(\frac{\gamma^2[\text{OH}^-]^2}{K_b}\right)^n \cdot \tau_1 \tag{8}$$

The aggregation number was determined from the slope of the plots of $\log(\mu_{\max 1}/\rho c^2 \tau_1)$ *vs.* $\log(\gamma^2[\text{OH}^-]^2)$; the result was $n=5$. Figure 6 shows the plots of f_{r_1} *vs.* $(\gamma^2[\text{OH}^-]^2)^4$ for the aqueous solution of amylamine at 20 °C. If the dissociation constant, K_b, is known, the rate constants, $\overline{k_f}$ and $\overline{k_b}$, may be determined from the slope and intercept respectively. However, no dissociation constant has been reported except for one at 25 °C,[6] and the intercept of these plots in Fig. 6 is close to zero. Therefore, the rate constants were determined in the following manner. Equation (7) can be rewritten as:

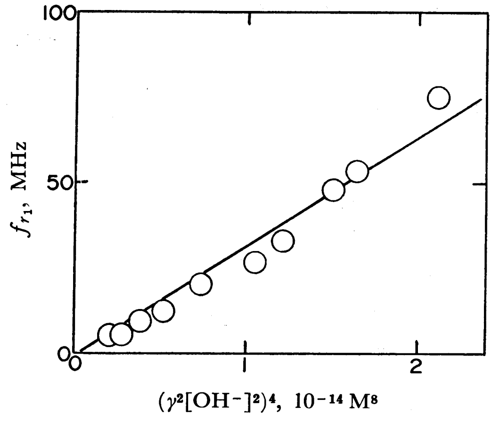

Fig. 6. The plots of f_{r_1} *vs.* $(\gamma^2[\text{OH}^-]^2)^4$ for aqueous solutions of amylamine at 20 °C.

$$2\pi f_{r_1} = {\tau_1}^{-1} = n\overline{k_b} K_b \cdot \frac{C_0}{\gamma^2[\text{OH}^-]^2} - (n-1)\overline{k_b} \tag{9}$$

where $C_0=[\text{R}-\text{NH}_2]+n[(\text{R}-\text{NH}_2)_n]$. Then, one can determine the values of $\overline{k_b}$ and $\overline{K_b}$ from the intercept and the slope of the plots of f_{r_1} *vs.* $C_0/\gamma^2[\text{OH}^-]^2$, which are shown in Fig. 7. The value of $\overline{k_f}$ was obtained using the slope of the plots of f_{r_1} *vs.* $(\gamma^2[\text{OH}^-]^2)^4$ in Fig. 6. The standard volume change was calculated by means of Eq. (4). In Table 2, the rate constants, the dissociation constant, and the standard volume change obtained are listed, together with the free energy, ΔF, which was calculated by means of: $K=\overline{k_b}/\overline{k_f}=\exp(-\Delta F/RT)$. The dissociation constant, K_b, was also determined from the $K_b=\gamma^2[\text{OH}^-]^2/(C_0'-[\text{OH}^-])$ relation in the concentration range of less than 0.25 M, in which it is expected that only the equilibrium expressed by Eq. (5) exists, where $C_0'=[\text{R}-\text{NH}_2]+[\text{R}-\text{NH}_3^+]$. These dissociation constants are indicated by K_b' in Table 2.

Secondly, for the sake of explaining the excess absorption observed in the aqueous solution of propylamine and the other one observed in the aqueous solution of amylamine, let us consider the hydrolysis which is expressed by Eq. (5). The relation between the relaxation time, τ_2, and the concentration can be

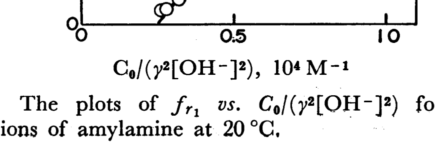

Fig. 7. The plots of f_{r_1} *vs.* $C_0/(\gamma^2[\text{OH}^-]^2)$ for aqueous solutions of amylamine at 20 °C.

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[5] C. W. Davies, "Ion Association," Butterworths, London (1962).

[6] C. W. Hoerr, M. R. McCorkle, and A. W. Ralston, *J. Amer. Chem. Soc.*, **65**, 328 (1943).

Table 2. The rate and thermodynamic constants obtained for the association-dissociation reaction of amylamine

T (°C)	$\bar{k}_f$ (10^7 M^4 s^{-1})	$\bar{k}_b$ (10^7 s^{-1})	ΔV_1° (ml mol^{-1})	ΔF (kcal mol^{-1})	K_b	K_b' (10^{-4} M)	K_b[a]
15	0.64	5.5	17	−1.2	6.6	6.2	—
20	0.88	4.9	16	−1.0	3.2	4.8	—
25	1.2	5.0	17	−0.87	4.2	5.5	4.3
30	1.5	5.5	15	−0.80	3.0	3.6	—

a) Ref. 6).

Table 3. Rate constants and standard volume changes of hydrolysis at 20°C

System	$\bar{k}_1$ (M^{-1} s^{-1})	$\bar{k}_2$ (s^{-1})	ΔV_2° (ml mol^{-1})	Reference
$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$	3.6×10^{10}	6.0×10^5	26.8	(11)
$CH_3NH_3^+ + OH^- \rightleftharpoons CH_3NH_2 + H_2O$	3.7×10^{10}	1.6×10^7	26.1	(11)
$C_2H_5NH_3^+ + OH^- \rightleftharpoons C_2H_5NH_2 + H_2O$	3.2×10^{10}	1.4×10^7	24.3	(11)
$C_3H_7NH_3^+ + OH^- \rightleftharpoons C_3H_7NH_2 + H_2O$	3.0×10^{10}	1.2×10^7	24.0	(14)
	2.5×10^{10}	3.7×10^7	21	this work
$C_4H_9NH_3^+ + OH^- \rightleftharpoons C_4H_9NH_2 + H_2O$	4.1×10^{10}	1.2×10^7	32	(3)
$C_5H_{11}NH_3^+ + OH^- \rightleftharpoons C_5H_{11}NH_2 + H_2O$	3.0×10^{10}	7.5×10^7	25	this work
$C_8H_{17}NH_3^+ + OH^- \rightleftharpoons C_8H_{17}NH_2 + H_2O$	1.0×10^{10}	7.6×10^7	32	(13)

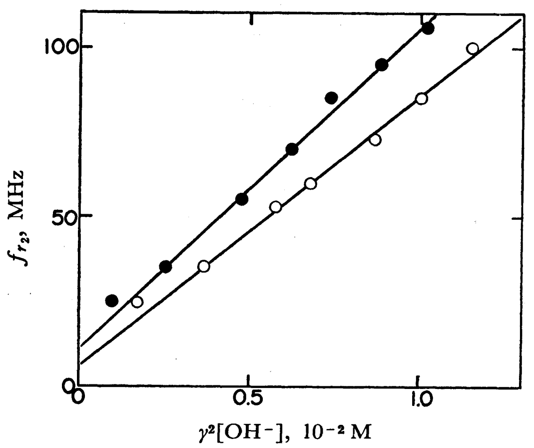

Fig. 8. The plots of f_{r_2} vs. $\gamma^2[OH^-]$ at 20°C. ●: aqueous solutions of amylamine, ○: aqueous solutions of propylamine.

expressed as follows:

$$2\pi f_{r_2} = \tau_2^{-1} = 2\bar{k}_1\gamma^2[OH^-] + \bar{k}_2 \tag{10}$$

The excess absorption per wavelength can be written as:

$$\mu_{\max_2} = \frac{1}{2}A_2 f_{r_2}c = \frac{1}{2}\pi\rho c^2\frac{(\Delta V_2^\circ)^2}{RT}\Gamma_c \tag{11}$$

where $\Gamma_c = (1/[OH^-]+1/[R-NH_3^+]+1/[R-NH_2])^{-1}$. Figure 8 shows the plots of f_{r_2} vs. $\gamma^2[OH^-]$ for the aqueous solutions of amylamine and propylamine. The forward and backward rate constants were determined from the slope and intercept respectively. The standard volume change associated with the hydrolysis was calculated by means of Eq. (11). In Table 3, the rate constants and standard volume change obtained in the present investigation are listed, together with the results for other monoamines.

Discussion

First, the excess absorption mechanism observed in an aqueous solution of amylamine in the lower frequency range will be discussed. For the mechanism associated with the peak sound absorption, several models have been proposed, such as AA+BB→2AB[7] and A+nB→AB$_n$,[1] where A is the solute, and B, the solvent molecules. All these models are due to the solute-solvent interaction. However, they are not acceptable in the case of the aqueous solutions of amines, as has been discussed in a previous paper.[2] In addition, if the cause of this excess absorption is associated with this solute-solvent interaction, the same absorption should be observed in any aqueous solution of amines. The fact that no excess absorption due to this mechanism was observed in the aqueous solution of propylamine also rules out these models. As is shown in Figs. 6 and 7, the linearities of the plots of f_{r_1} vs. $(\gamma^2[OH^-]^2)^4$ and f_{r_1} vs. $C_0/\gamma^2[OH^-]^2$ and the reasonable values of the dissociation constants, K_b, lead to the conclusion that the cause of the excess absorption is the association-dissociation reaction of amine. The theoretical maximum excess absorption per wavelength, which was calculated by Eq. (4) using the obtained values of $\bar{k}_f$ and ΔV_1°, are shown in Fig. 9, together with the experimental results. The agreement between the observed and calculated values also confirms the present model. In order to ascertain the natures of the aggregate, the ultrasonic absorptions were measured in aqueous solutions of butylamine hydrochloride and amylamine hydrochloride and in cyclohexane solutions of butylamine and amylamine. However, no excess absorptions were observed, as may be seen in Fig. 10. These facts lead us to the conclusions that the aggregate considered here consists of non-ionized amine molecules and that the water molecules participate in the aggregation of amines. In general, the molecules which consist of hydrophilic and hydrophobic groups have a tendency to aggregate in an aqueous solution. This aggregate is formed

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[7] R. N. Barfield and W. G. Schneider, *J. Chem. Phys.*, **31**, 488 (1959).

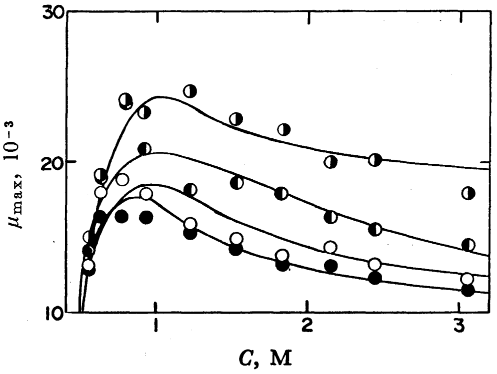

Fig. 9. Comparison of the experimental values of $\mu_{\max_1}$ with the theoretical ones for aqueous solutions of amylamine. ◑: 15 °C, ◐: 20 °C, ○: 25 °C, ●: 30°C.

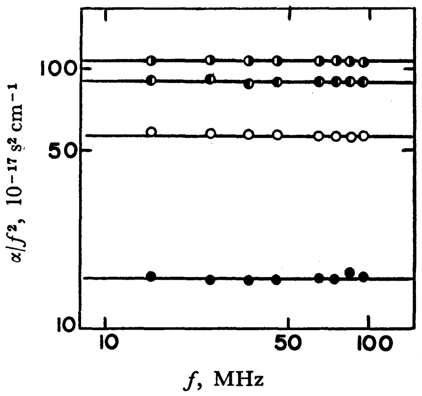

Fig. 10. Ultrasonic absorption spectra at 25 °C.
◑: cyclohexane solution of amylamine, 1.0 M.
◐: cyclohexane solution of butylamine, 2.3 M.
○: aqeous solution of butylamine hydrochloride, 2.0 M
●: aqeous solution of amylamine hydrochloride, 1.0 M.

by hydrophobic bonding, by which the ice berg structures of water which are formed around the nonpolar group of the molecule are broken and change to the normal structures of water. Since the standard volume change associated with the association-dissociation reaction of amines is comparatively large, this may be due to the change in the structure of the solvent water. The relaxation time[8] associated with this structural change in water is so small that the contribution of this relaxation to the association-dissociation reaction of amines may be neglected.

The thermodynamic parameters can be determined from the temperature dependence of the rate constants and the equilibrium constant obtained for the association-dissociation reaction of amylamine. According to the rate theory of reaction, the rate constant, k_i, is expressed by:

$$k_i = PT\exp\left(-\frac{\Delta F_i{}^{\neq}}{RT}\right) = PT\exp\left(-\frac{\Delta H_i{}^{\neq} - T\Delta S_i{}^{\neq}}{RT}\right) \tag{12}$$

where $\Delta H_i{}^{\neq}$ is the activation enthaply, $\Delta S_i{}^{\neq}$, the activation entropy, and P, the constant. The activation enthalpy is determined from the slope of the plots of $\ln(k_i/T)$ vs. $1/T$; the results are $\Delta H_i{}^{\neq}=8.7$ kcal/mol and $\Delta H_b{}^{\neq}=0$ kcal/mol. The enthalpy change was found to be −9.0 kcal/mol from the plots of $\ln K$ vs. $1/T$. Furthermore, through $\Delta F = \Delta H - T\Delta S$ the entropy change was calculated to be $\Delta S = -14$ e.u. It is well known that surface-active agents form a micelle by hydrophobic bonding in an aqueous solution with more than critical micelle concentration.[9] The thermodynamic parameters for micelle formation show the same temperature dependence as those of the association of amylamine, though the enthalpy change that in the latter is comparatively large. This confirms the aggregate of amylamine is formed by hydrophobic bonding. Compared with the case of the aqueous solution of butylamine,[2] the aggregation number increases with an increase in the chain length of the hydrophobic group and the dissociation rate constant of the aggregate for amylamine is smaller than that of butylamine. These facts mean that the aggregate is stabilized with an increase in the chain length of the hydrophobic group. It is also noteworthy that the aqueous solution of octylamine forms a mesomorphic phase, which consists of highly associated molecules. The ultrasonic investigation for this phase has previously been done by the present authors.[10]

Next, let us discuss the excess absorption mechanism in the aqueous solution of propylamine and the other one in the aqueous solution of amylamine. It has been reported by many authors[11–14] that there exists an excess absorption associated with hydrolysis in aqueous solutions of amines. As may be seen in Fig. 8, the linearities of the plots of f_{r_2} vs. $\gamma^2[\mathrm{OH}^-]$ show that the cause of the excess absorption mechanism is attributed to the perturbation of the equilibrium expressed by Eq. (5). The obtained values of the rate constant, k_1, are pertinent for the proton transfer reaction. As may be seen in Table 3, the rate constants for the proton transfer reaction for normal amines are not appreciably dependent on the hydrophobic chain length, though the long chain length may affect the rate of the reaction.[13]

Finally, since there exist two types of equilibria in the solution of amylamine, it may be necessary to consider precisely the following two step mechanism, that is, the reaction which is coupled by Eqs. (2) and (5):

$$\mathrm{A}^+ + \mathrm{B}^- \rightleftharpoons \mathrm{A} \rightleftharpoons \frac{1}{n}\mathrm{A}_n \tag{13}$$

However, as has been described in the previous paper,[2] it has been verified that the contribution of the faster process, which is associated with hydrolysis, to the slower one, which is associated with the association-dissociation reaction, is so small that two different relaxation processes can be interpreted independently.

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