BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (7), 1716—1719 (1977)

Ultrasonic Study of Aqueous Solutions of Amines

Sadakatsu Nishikawa, Unpei Otani, and Mitsuo Mashima
Department of Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi, Saga 840

(Received January 31, 1977)

Ultrasonic absorptions in aqueous solutions of allylamine have been measured in the frequency range from 8.5 to 220 MHz at 20 °C. Only a single relaxational absorption has been observed in the concentration range from 0.0562 to 4.00 M; this absorption has been attributed to the proton-transfer reaction. The rate constants and the standard volume change due to the reaction have been determined, and the results are compared with those for aqueous solutions of other amines previously published. It has been elucidated from the ultrasonic absorption data that the presence of the intermediate in the proton-transfer reaction is required in order to analyze the ultrasonic absorption mechanisms quantitatively. The hydrophobic effect in the aqueous solutions of amines has also been discussed.

Ultrasonic absorptions in aqueous solutions of amines are characterized by two kinds of relaxation processes. One is the phenonemon associated with the Peak Sound Absorption Concentration, which is observed in relatively concentrated solutions. Barfield and Schneider,[1] and Andreae *et al.*[2] have attributed the phenomenon to the solute-solvent interactions. However, on the basis of ultrasonic studies in aqueous solutions of several amines, the present authors[3,4] have concluded that the phenomenon is, rather, due to the aggregation reaction of amine molecules not ionized.

The other is the relaxation phenomenon due to the proton-transfer reaction. Maass *et al.*[5,6] have reported the kinetic data of the proton-transfer reaction for various amines; also there have been several discussions for the role of the perturbation of the proton-transfer equilibria of the basic residues of proteins in aqueous solutions.[7,8]

The present authors intend to investigate the correlations between these two kinds of phenomena in ultrasonic absorptions. In this paper the experimental results in an aqueous solution of allylamine will be reported, and the results will be compared with those for other amines.

Experimental

The ultrasonic absorption measurements were made at the odd harmonics of 0.5, 5, and 20 MHz x-cut quartz transducers by using the pulse technique. The frequency range was from 8.5 to 220 MHz. The sound velocity was measured by a sing-around method operated at 1.92 MHz. The major mechanical features of the apparatus have been shown elsewhere.[9] The values of pH were determined by means of Hitachi-Horiba F-5 pH-meter. A saturated solution of $Ca(OH)_2$ was used as the standard reference of the electrode of the pH-meter. All the measurement were made in a dry nitrogen gas atmosphere in order to prevent the contamination of air, for the aqueous solutions of amines are highly basic. The allylamine was distilled once from a commercial product of a G. R. grade. The purity was confirmed by the gas-chromatographic method to be more than 99.9%. NaOH and HCl (guaranteed reagent) were used to obtain the desirable hydroxide concentrations. The measurement cells were immersed in a water bath mantained at a constant temperature within ±0.002 °C. All the measurements were made at 20 °C.

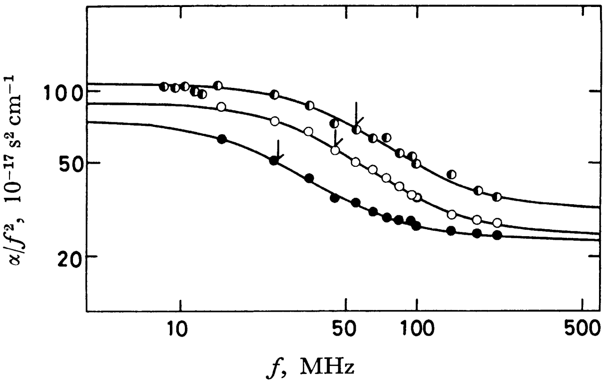

Fig. 1. Representative ultrasonic absorption spectra in aqueous solutions of allylamine at 20 °C. The arrow shows the relaxation frequency. ◐: 2.86 M, ○: 0.435 M, ●: 0.0562 M.

Results

The sound absorption caused by a single relaxation process can generally be expressed by

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

where α is the sound absorption coefficient; f, the frequency; f_r, the relaxation frequency; and A and B, the constants. Figure 1 shows some representative ultrasonic absorption spectra in an aqueous solution of allylamine. The spectra in the concentration range up to 4.00 M are all characteristic of a single relaxation process; the ultrasonic parameters, A, B, and f_r, were determined so as to obtain the best fit of the experimental data to Eq. 1. The parameters are listed in Table 1, along with the values of the density, the pH, and the activity coefficient of the solutions used. The activity coefficients were calculated by means of Daviss' equation, $-\log \gamma = 0.5[(\sqrt{I}/(1+\sqrt{I}))-0.3I]$, where I is the ionic strength. The relaxation frequencies and the excess absorptions increase continuously with the solute concentrations, and finally both of them reach their constant values. From these facts it is expected that only a single relaxation process is observed in the frequency range measured. The excess absorption is observed even in relatively dilute solution; thus, the perturbation of the following equilibrium will be considered as the excess absorption mechanism:

$$\text{R-NH}_3^+ + \text{OH}^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{R-NH}_2 + \text{H}_2\text{O}, \tag{2}$$

where k_f and k_b are the forward and backward rate

Table 1. Ultrasonic parameters, density, and activity coefficients in aqueous solutions of allylamine

C_0 M	pH	ρ (g cm^{-3})	γ	A (10^{-17} s^2 cm^{-1})	B (10^{-17} s^2 cm^{-1})	f_r (MHz)	c (10^5 cm s^{-1})
0.0562	11.16	0.9966	0.966	52.3	23.3	26	1.497
0.107	11.43	0.9958	0.966	58.6	24.4	30	1.502
0.247	11.62	0.9950	0.944	63.3	24.4	40	1.507
0.311	11.68	0.9943	0.941	65.6	24.2	40	1.512
0.435	11.80	0.9930	0.933	65.6	24.2	45	1.520
0.508	11.84	0.9927	0.930	70.6	23.1	47	1.524
0.636	11.90	0.9913	0.926	66.2	23.0	55	1.532
0.749	11.95	0.9903	0.922	72.5	23.6	53	1.539
1.15	12.02	0.9873	0.912	75.9	24.9	55	1.561
1.76	12.23	0.9818	0.898	70.3	22.9	65	1.596
2.02	—	—	—	78.1	26.9	54.5	—
2.86	—	—	—	76.6	31.1	55	—
3.00	—	—	—	80.6	36.8	60	—
4.00	—	—	—	81.2	73.0	50	—

Throughout this paper 1 M = 1 mol/dm^3.

constants respectively. The concentration dependences of the relaxation frequency and the maximum excess absorption per wavelength, μ_{max}, for the above mechanism can be written as follows:

$$2\pi f_r = 2k_f\gamma^2[\mathrm{OH}^-] + k_b, \tag{3}$$

and

$$\mu_{max} = Af_rc/2 = \pi\rho c^2(\Delta V)^2\Gamma_c/2RT, \tag{4}$$

where

$$\Gamma_c = (1/[\mathrm{OH}^-] + 1/[\mathrm{R\text{-}NH_3^+}] + 1/[\mathrm{R\text{-}NH_2}])^{-1}, \tag{5}$$

and where γ is the activity coefficient; ρ, the density; c, the sound velocity; ΔV, the standard volume change associated with the reaction. The relaxation frequencies are plotted in Fig. 2 as functions of $\gamma^2[\mathrm{OH}^-]$; the straight line drawn provides the rate constants from the slope and intercept, which are determined by using the least-mean square method. For determining the rate constants, the experimental values in the concentration range below 0.749 M were used because in the concentrated solutions the Daviss equation might not hold and another reaction, such as molecular aggregation with hydrogen-bonding, might affect the reaction of Eq. 2. The standard volume change is determined by Eqs. 4 and 5. The obtained values are listed in Table 2 along with the results of other amines. The equilibrium constants obtained by the $K=k_b/k_f$ relation are abnormally larger than the dissociation constants in the literature, as may be seen in Table 2. The dissociation constant, K_b, was calculated from the pH dependence on the analytical concentration by the equation, $K_b=\gamma^2[\mathrm{OH}^-]/(C_0-[\mathrm{OH}^-])$; we obtained the value of 3.75×10^{-5} M[10] for K_b which was in agreement with that in the literature (see Table 2).

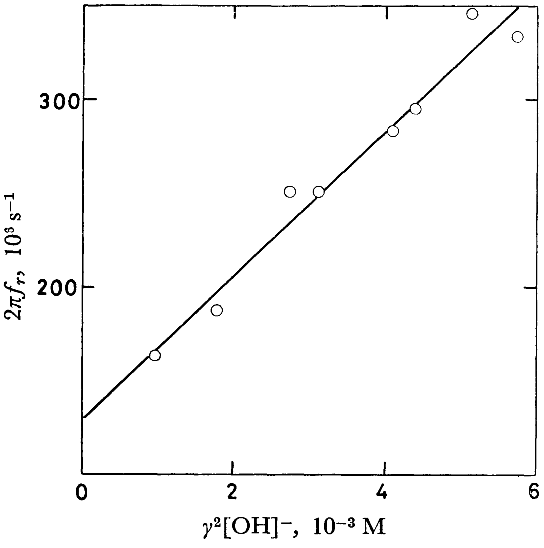

Fig. 2. The plots of $2\pi f_r$ vs. $\gamma^2[\mathrm{OH}^-]$ in aqueous solutions of allylamine at 20 °C.

In order to ascertain the excess absorption mechanism associated with the reaction expressed by Eq. 2, the pH dependence of the absorption at a constant concentration of allylamine has been investigated by adding small amounts of NaOH or HCl. However, the relaxation frequencies obtained did not agree with those calculated by means of Eq. 3; also the pH dependence of μ_{max} was not in accordance with the theory. These facts indicate the presence of another equilibrium in the aqueous solutions of amines.

Discussion

The investigations of a number of proton-transfer reactions of compounds containing the $-\mathrm{NH_2}$ group have been performed and the kinetics have been rationalized in terms of the following mechanism:[7,8,13]

$$\mathrm{R\text{-}NH_3^+ + OH^-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{R\text{-}NH_3^+\cdots OH^-} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{R\text{-}NH_2 + H_2O}. \tag{6}$$

If the second step is faster than the first one, we get the following relations for each process:

$$2\pi f_{r1} = k_{12}\gamma^2([\mathrm{R\text{-}NH_3^+}] + [\mathrm{OH}^-]) + k_{21}(1+K_{23}^{-1})^{-1}, \tag{7}$$

TABLE 2. RATE CONSTANTS AND STANDARD VOLUME CHANGE OF PROTON-TRANSFER REACTIONS IN AQUEOUS SOLUTIONS OF AMINES

Solute	k_f (10^{10} M s^{-1})	k_b (10^7 s^{-1})	$K(k_b/k_f)$ (10^{-3} M^{-1})	ΔV (cm^3 mol^{-1})	K_b a) (10^{-4} M^{-1})	Ref.
Propylamine	2.5	3.7	1.5	21	3.73	5)
	3.0	1.2	0.4	24	3.73	4)
Allylamine	1.9	13	6.8	29	0.368	This work
Butylamine	4.1	12	2.9	32	4.44	16)
Pentylamine	3.0	7.5	2.5	25	4.94	4)
Octylamine	1.0	7.6	7.6	32	4.5	17)

a) The dissociation constants, K_b, are taken from Refs. 10 and 11.

TABLE 3. REEXAMINED RATE AND EQUILIBRIUM CONSTANTS OF PROTON-TRANSFER REACTIONS

Solute	k_{12} (10^{10} M s^{-1})	k_{21} (10^7 s^{-1})	K_{12} (10^3 M)	K_{23}
Propylamine	2.5	4.7	0.53	4.0
Allylamine	1.9	13	0.15	190
Butylamine	4.1	14	0.30	6.5
Pentylamine	3.0	8.8	0.33	5.1
Octylamine	1.0	8.1	0.12	17

$$2\pi f_{r2} = k_{23} + k_{32}, \tag{8}$$

where f_{r1} and f_{r2} are the relaxation frequencies associated with the first and second step respectively, and where $K_{23}=k_{23}/k_{32}$. Comparing Eq. 3 with Eq. 7, the rate constants obtained from the plots of $2\pi f_r$ *vs.* γ^2-[OH$^-$] may easily be written as follows:

$$k_f = k_{12}, \quad k_b = k_{21}(1+K_{23}^{-1})^{-1}. \tag{9}$$

The dissociation constant, K_b, which is determined by the static method, may be expressed by the following equation, considering the detailed equilibrium of Eq. 6:

$$K_b^{-1} = K_{12} + K_{12}K_{23}, \tag{10}$$

where $K_{12}=k_{12}/k_{21}$. The following relation is derived from Eqs. 9 and 10:

$$K_{23} = k_b K_b^{-1}/k_f. \tag{11}$$

The values of the rate constants, k_{12} and k_{21}, and the equilibrium constants, K_{12} and K_{23}, as calculated from Eqs. 9 and 11, are listed in Table 3. The absorption data in aqueous solutions of other amines reported previously[4,16,17] were reexamined by using the above treatment; these results are also listed in Table 3. The values of K_{23} are larger than unity, which reflects the fact that the intermediate of the hydrolysis of amines is not very stable.

Debye[14] has derived an expression for the diffusion-controlled rate of the reactions of ions in solutions and Eigen[15] has considered the reverse process of dissociation to form ions. The rate constant, k_{12}, of the first step in Eq. 6 is reasonable for the diffusion-controlled reaction, because the rate constant determined agrees very closely with the results obtained experimentally and theoretically for other compounds.[4,7] However, the rate constant of the reverse process is too low because its order should be 10^{10} s^{-1} according to Eigen's theory;[7] the similar discrepancies have also been found by Applegate *et al.*[7] for some aminoacids and polypeptides.

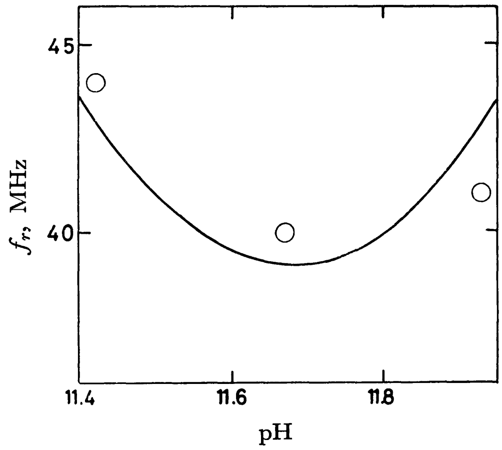

Fig. 3. The pH dependence of the relaxation frequency associated with the proton-transfer reaction. The solid curve is the theoretical value.

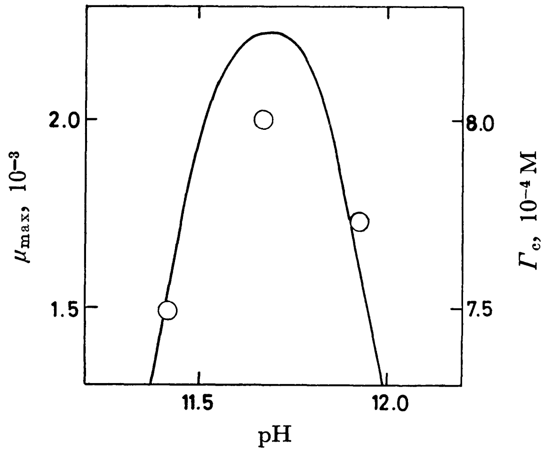

Fig. 4. The pH dependence of μ_{max} and Γ_c. The solid curve is the calculated value of Γ_c.

Though the pH dependences of f_r and μ_{max} are difficult to be interpreted only in terms of the process of Eq. 2, the introduction of the intermediate expressed by Eq. 6 allows us to analyze the dependences quantitatively. Figure 3 shows the pH dependences of the relaxation frequencies. The solid line represents the relaxation frequencies calculated by Eq. 7, where the analytical concentration has to be written as $C_0=$[R–NH$_3^+$]+[R–NH$_3^+\cdots$OH$^-$]+[R–NH$_2$]. The pH dependence of μ_{max} is also shown in Fig. 4, along with that of Γ_c

which is nearly dependent on μ_{max} (see Eqs. 4 and 5). Though the contribution from the fast process to the slow one for μ_{max} should be taken into account, the effects were very small. As may be seen in Fig. 4, the tendency of the pH dependence of μ_{max} is similar to that of Γ_{e}. These facts confirm that the excess absorption mechanism in the aqueous solution of allylamine is due to the perturbation of the equilibrium of Eq. 6.

In aqueous solutions of allylamine, only one kind of excess absorption is found in the frequency range investigated here; the character of the excess absorption is similar to that obtained for propylamine.[4)] However, another excess absorption in aqueous solutions of butyl,[3)] pentyl,[4)] and octylamine[18)] has been observed in addition to that due to the proton-transfer reaction. The cause of the latter excess absorption has quantitatively interpreted by the molecular aggregation theory,[4,18)] and this excess absorption may be the main cause of the phenomenon associated with the Peak Sound Absorption Concentration. These results lead us to predict that the characteristic ultrasonic absorption due to the molecular aggregation reaction is associated with the hydrophobicity in amine molecules; that is, the aggregate may be formed by hydrophobic effects. With decrease in the hydrophobic effects, the excess absorption disappears in the frequency range measured except for the absorption due to the proton-transfer reaction.

The background absorption, B, in Eq. 1 increases with the analytical concentration. This means that the other excess absorption, *e. g.*, that due to the aggregation reaction with hydrogen-bondings, may exist in the higher-frequency range. However, this is beyond the scope of this paper.

In conclusion, the present ultrasonic study has revealed that the excess absorption mechanism in aqueous solutions of allylamine is attributable to the hydrolysis which proceeds through an intermediate, and the excess absorption associated with the Peak Sound Absorption Concentration has not been observed.

This work was partially supported by the Sakkokai Foundation.

References

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

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

3) S. Nishikawa and T. Yasunaga, *Bull. Chem. Soc. Jpn.*, **45**, 1262 (1972).

4) S. Nishikawa, T. Yasunaga, and K. Takahashi, *Bull. Chem. Soc. Jpn.*, **46**, 2992 (1973).

5) G. Maass, Ph. D. Thesis, Univ. of Göttingen (1962).

6) M. Eigen, G. Maass, and G. Schwarz, *Z. Phys. Chem. (Frankfurt am Main)*, **74**, 319 (1971).

7) K. Applegate, L. J. Slutsky, and R. C. Parker, *J. Am. Chem. Soc.*, **90**, 6909 (1968).

8) R. D. White, L. J. Slutsky, and S. Pattion, *J. Phys. Chem.*, **75**, 161 (1971).

9) N. Tatsumoto, *J. Chem. Phys.*, **47**, 4561 (1967).

10) This dissociation constant was calculated in the concentration range below 0.749 M.

11) M. C. Cox, D. H. Everett, D. A. Lansman, and R. J. Munn, *J. Chem. Soc.*, *B*, **1968**, 1373.

12) J. J. Christensen, R. M. Izatt, D. P. Wrathall, and L. D. Hansen, *J. Chem. Soc.*, *B*, **1969**, 1212.

13) M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry," Vol. VIII, Part 2, ed by A. Weissberger, Jr., Wiley, New York, N. Y. (1961).

14) P. Debye, *Trans. Electrochem.*, **82**, 256 (1942).

15) M. Eigen, *Z. Phys. Chem. (Frankfurt am Main)*, **1**, 176 (1954).

16) S. Nishikawa, T. Nakamoto, and T. Yasunaga, *Bull. Chem. Soc. Jpn.*, **46**, 324 (1973).

17) S. Nishikawa, T. Yasunaga, and N. Tatsumoto, *Bull. Chem. Soc. Jpn.*, **46**, 1657 (1973).

18) S. Nishikawa, *J. Colloid Interface Sci.*, **45**, 259 (1973).