Ultrasonic Properties of Aqueous Solutions of Butylamines

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Ultrasonic absorption and velocity measurements were performed in aqueous solutions of *t*-butylamine and isobutylamine at 20 °C. Two relaxational absorptions were found in both solutions. One is associated with the proton transfer reaction, the rate constants being determined together with the standard volume change of the reaction. No effect was observed on K_f with change in molecular structure. The other, associated with the peak sound absorption concentration, is ascribed to the association-dissociation reaction mechanism of unionized amine molecules. The results are discussed in comparison with those of butylamine.

Ultrasonic investigations for liquid properties provide useful information on kinetic behavior. Two kinds of relaxational processes exist in aqueous solutions of amines, depending upon the concentration and molecular structure.[1,2] One is due to the proton transfer reaction observed in relatively dilute solutions. The other is associated with the peak sound absorption concentration (PSAC). These processes have been treated independently because of the complexity of the interaction between fast and slow processes. A report was given on the ultrasonic absorption of aqueous solutions of some amines. This investigation was undertaken in order to clarify the ultrasonic properties of three butylamines with different molecular structures.

Experimental

Commercial *t*-butylamine and isobutylamine (G. R. grade, Wako Chemicals Industries, Ltd.) were distilled, the purity being confirmed to be higher than 99.9% by gas chromatography. The solutions were prepared with twice distilled water.

The ultrasonic absorption measurement was carried out at the odd harmonics of 0.5, 5, and 20 MHz x-cut quartz transducers by means of pulse technique in the frequency range 6.5—220 MHz, absorption coefficient being reproducible to within ±3%. The sound velocity was measured by a sing-around method operated at 1.92 MHz. The major mechanical features of the apparatus have been reported.[3] The cells for absorption and velocity measurement were immersed in a water bath maintained at a constant temperature within ±0.001 °C. All the measurements were carried out in a dry nitrogen gas atmosphere in order to prevent the contamination of air, since the aqueous solutions of amines are highly basic.

Results and Discussion

In general, the sound absorption caused by several relaxation processes can be expressed by

$$\alpha/f^2 = \sum_i A_i/[1+(f/f_{ri})^2] + B, \quad (1)$$

where α is the absorption coefficient, f frequency, A_i relaxation amplitude for the i-th process, f_{ri} relaxation frequency and B residual absorption amplitude. Figures 1 and 2 show the representative ultrasonic absorption spectra in aqueous solutions of *t*-butylamine and isobutylamine at 20 °C. In both solutions, only a single relaxtional absorption was observed in relatively dilute solutions (less than 0.9 mol dm^{-3}). However, with increasing concentration, the experimental

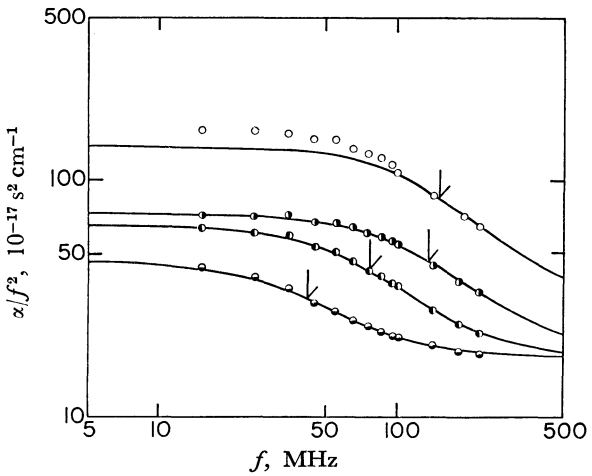

Fig. 1. Ultrasonic absorption spectra in aqueous solution of *t*-butylamine. The solid lines are the best-fit single relaxation curves and the arrows are the relaxation frequencies. ◒: 0.0154 mol dm^{-3}, ◐: 0.154 mol dm^{-3}, ◑: 0.787 mol dm^{-3}, ○: 1.69 mol dm^{-3}.

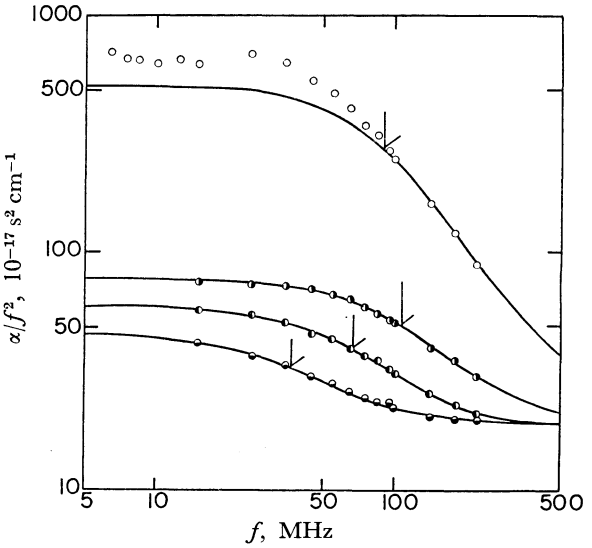

Fig. 2. Ultrasonic absorption spectra in aqueous solution of isobutylamine. ◒: 0.0447 mol dm^{-3}, ◐: 0.158 mol dm^{-3}, ◑: 0.801 mol dm^{-3}, ○: 1.81 mol dm^{-3}.

values of the absorption coefficients deviate from the single relaxational equation, *viz.*, another excess absorption appears in the same frequency range. In the case of the single relaxation process, the ultrasonic parameters, A, f, and B, were determined from the

Table 1. Ultrasonic parameters, density and pH in aqueous solutions of *t*-butylamine and isobutylamine

C_o (mol dm^{-3})	pH	ρ (g cm^{-3})	v (10^5 cm s^{-1})	A (10^{-17} s^2 cm^{-1})	B	f_r (MHz)
			[*t*-butylamine]			
0.0154	11.60	0.9982	1.4847	37	24	42
0.0386	11.76	0.9981	1.4860	55	24	45
0.0772	11.90	0.9970	1.4889	67	25	53
0.154	12.08	0.9962	1.4953	63	24	77
0.184	12.12	0.9962	1.4970	66	24	83
0.202	12.17	0.9955	1.4981	59	24	87
0.268	12.21	0.9946	1.5039	69	24	95
0.508	12.46	0.9917	1.5224	77	22	115
0.681	12.51	0.9883	1.5369	68	27	130
0.787	12.54	0.9868	1.5455	72	26	135
			[isobutylamine]			
0.0203	10.74	0.9982	1.4852	15	23	55
0.0447	11.23	0.9980	1.4870	37	25	37
0.0787	11.48	0.9976	1.4893	41	24	55
0.131	11.75	0.9968	1.4929	51	26	63
0.158	11.74	0.9966	1.4946	57	23	68
0.203	11.84	0.9959	1.4980	56	24	75
0.435	12.22	0.9931	1.5136	72	27	85
0.500	12.25	0.9916	1.5204	79	25	88
0.598	12.29	0.9911	1.5251	77	24	92
0.801	12.47	0.9879	1.5398	81	25	108
0.852	12.45	0.9875	1.5442	77	26	110

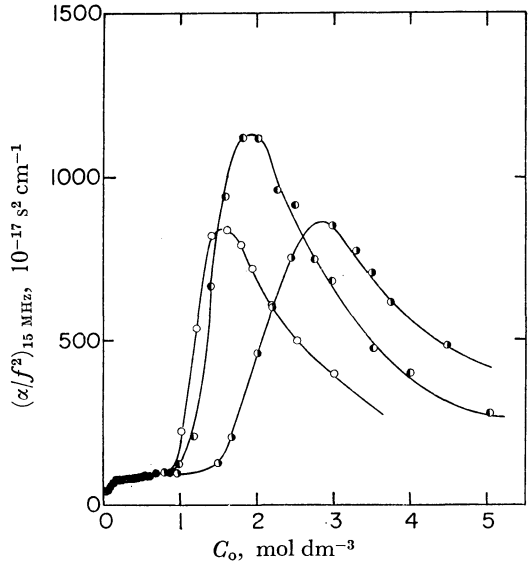

Fig. 3. Plots of α/f^2 *vs.* C_o of aqueous solutions of butylamines. ○: Butylamine, ◑: *t*-butylamine, ◐: isobutylamine.

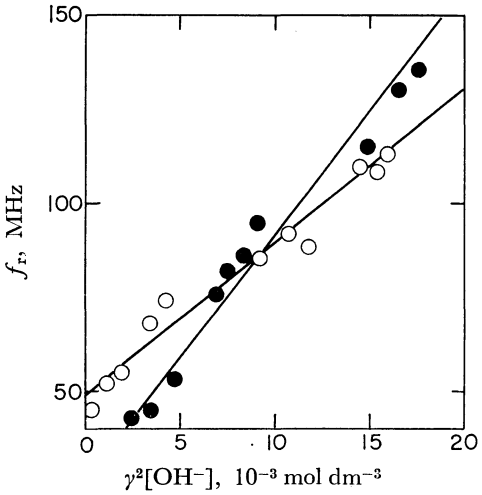

Fig. 4. Plots of f_r *vs.* γ^2[OH$^-$]. ●: *t*-Butylamine, ○: isobutylamine.

plots of α/f^2 *vs.* $[1+(f/f_r)^2]^{-1}$ so as to obtain a straight line. On the other hand, the ultrasonic parameters associates with more than one process are not easily determined because the two processes are close together. In Fig. 3 only the concentration dependence of α/f^2 at 15 MHz in the aqueous solutions is shown along with that of butylamine.[5] The most plausible mechanism of the excess absorption in the lower concentration range is the perturbation of the equilibrium associated with proton transfer[1,2,6,7] expressed by the formula

$$R\text{-}NH_3^+ + OH^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R\text{-}NH_2 + H_2O. \quad (2)$$

The relaxation frequency for the above process can be related to the forward and backward rate constants, k_f and k_b, as repredented by

$$2\pi f_r = k_f\gamma^2([R\text{-}NH_3^+]+[OH^-]) + k_b, \quad (3)$$

$$= 2k_f\gamma^2[OH^-] + k_b, \quad (3')$$

where γ is the mean activity coefficient, which is assumed to be identical for $R\text{-}NH_3^+$ and OH^- ions,[8] and is calculated from the equation, $-\log\gamma=0.5[\sqrt{I}/(1+\sqrt{I})-0.3I]$ where I is the ionic strength. Equation 3 can be rewritten as follows, using the analytical

Table 2. Rate constants and standard volume change of proton transfer reaction of butylamines

	k_f (mol dm^{-3} s^{-1})		k_b (s^{-1})			K_b (mol^{-1})	ΔV (cm^3 mol^{-1})	Ref.
	(a)	(b)	(a)	(b)	(c)			
Butylamine	4.1×10^{10}	2.5×10^{10}	1.4×10^{8}	1.1×10^{8}	1.1×10^{7}	4.44×10^{-4}	32	4
Isobutylamine	1.2×10^{10}	3.4×10^{10}	3.2×10^{8}	3.0×10^{8}	1.1×10^{7}	3.22×10^{-4}	29	This work
t-Butylamine	1.9×10^{10}	2.0×10^{10}	2.1×10^{8}	2.9×10^{8}	1.0×10^{7}	5.17×10^{-4}	24	This work

The values in column (a) were determined from the slope and intercept using Eq. 3, those in column (b) from Eq. 4, and the backward rate constants in column (c) were calculated using the dissociation constant.

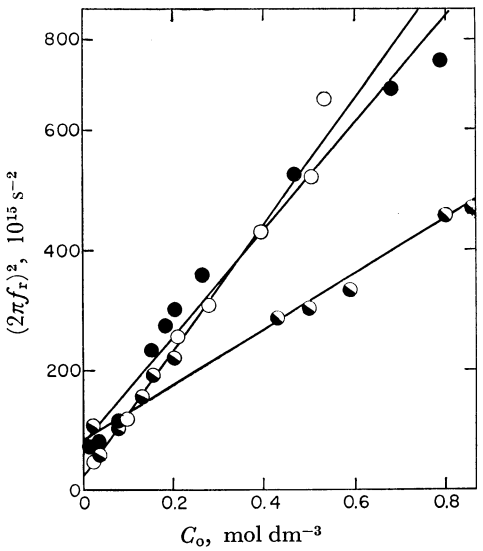

Fig. 5. Plots of $(2\pi f_r)^2$ *vs.* C_o. ○: Butylamine, ●: *t*-butylamine, ◔: isobutylamine.

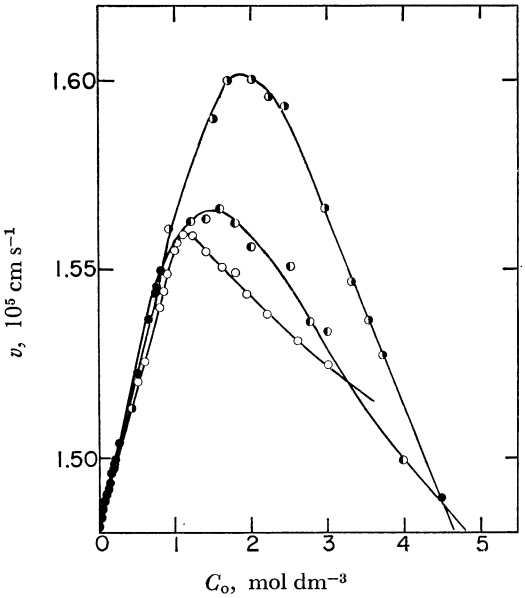

Fig. 6. Concentration dependence of the sound velocity. ○: Butylamine, ◑: *t*-butylamine, ◐: isobutylamine.

concentration, C_o, on the assumption that the activity coefficient is unity and only one equilibrium exists in the aqueous solution.

$$(2\pi f_r)^2 = 4k_f k_b C_o + k_b^2 \quad (4)$$

Figure 4 shows the plots of f_r *vs.* $\gamma^2[OH^-]$, the slope and intercept of which provide the rate constants. Figure 5 shows those of $(2\pi f_r)^2$ *vs.* C_o, from which the rate constants were also determined. In proton transfer investigations so far, the latter procedure of rate determination was carried out by means of the dissociation constants in the literature because of the uncertainty of the intercept. The forward rate constants are approximately the same in both determinations and reasonable values are obtained for the diffusion-controlled reaction. However, there are some questions in the latter determination of the backward rate constants for the following reasons. First, Eq. 4 is derived with numerous approximations. Second, the backward rate constant is determined from Eq. 4 without use of dissociation constant. However, ratio k_b/k_f is not in line with the dissociation constant even when the experimental error is taken into account. The cause of disagreement has been interpreted by the introduction of intermediate of Eq. 5.[2]

$$R\text{-}NH_3^+ + OH^- \rightleftharpoons R\text{-}NH_3^+\cdots OH^- \rightleftharpoons R\text{-}NH_2\cdots H_2O \rightleftharpoons R\text{-}NH_2 + H_2O \quad (5)$$

Actually, the rate constants, k_f and k_b, can be related by those of each steps of Eq. 5, assuming that the second and third steps equilibrate so rapidly or the stationary states are established. However, detailed discussions for each step of Eq. 5 from the rate constants obtained may not be appropriate at this stage since the rationalized mechanisms are too complicated.

The determination of the rate constants from Eq. 3, on the other hand, is a direct procedure even if the intermediate exists. The dissociation constants were calculated from the concentration dependence on pH and are very close those in the literature.[9] This means that the determination of the concentration of OH^- ion in the solutions is correct. The rate constants calculated from the above two methods (from Eqs. 3 and 4) are given in Table 2 along with the dissociation constants and the standard volume changes of the reaction which are determined from the maximum excess absorption per wavelength.[2] It can be concluded that the diffusion-controlled rate constants of butylamines may be independent of the molecular structures, *viz.*, the mobilities of butylamine molecules in aqueous solvent are approximately the same.

We consider next the absorptions which appear in the concentrated solutions of the amines. Figure 6 shows the concentration dependence of the sound velocity at 20 °C. The values of α/f^2 increase rapidly near the maximum of the sound velocity, reaching a maximum in all the solutions. The peak sound veloc-

ity concentration increases in the order, butylamine, isobutylamine and *t*-butylamine. The peak sound absorption concentration stands in the same order. We have proposed an association-dissociation reaction of unionized amine molecules as the cause of the excess absorption mechanism, since no peak sound absorption concentration is observed in aqueous solutions of amines with low hydrophobicity,[2] nor excess absorption in aqueous solution of the amine hydrochloride and in organic solvent.[1] In the cases of aqueous solutions of butylamine and pentylamine, the two relaxation processes could be treated independently since the two relaxation frequencies are far apart. However, in the aqueous solutions of *t*-butylamine and isobutylamine, the relaxation times are close to each other and can not be determined precisely. It is likely that the structure of liquid solution is altered by addition of solute molecules near the peak sound velocity concentration and the solute molecules with hydrophobicity aggregate in aqueous media. The hydrophobicity seems to be in the order of peak sound velocity concentration or peak sound absorption concentration. Williams *et al.*[10] reported the ultrasonic absorption data of various amines in the liquid phases and interpreted them in terms of conformational changes of molecules. However, no excess absorption has been observed in the pure liquids of amines. Thus, the absorption mechanism with conformational change has been ruled out from the cause of the excess absorption.

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