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Analysis of Proton-Transfer Reaction in Aqueous Solutions of Butylamines by Ultrasonic Methods

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Ultrasonic absorption has been measured in an aqueous solution of *s*-butylamine over the frequency range 6.5—220 MHz and the concentration range 0.0115—3.18 mol dm^{-3} at 25 °C. The single relaxational phenomenon observed in a range less than 1 mol dm^{-3} was found to be associated with a perturbation of the equilibrium; $\mathrm{R\text{-}NH_3^+ + OH^- \rightleftharpoons R\text{-}NH_3^+ \cdots OH^-}$. The rate constants of the forward and backward reactions, k_{12} and k_{21}, have been determined to be 2.1×10^{10} s^{-1} mol^{-1} dm^3 and 1.8×10^8 s^{-1}, respectively. It was also determined that the next step, $\mathrm{R\text{-}NH_3^+ \cdots OH^- \rightleftharpoons R\text{-}NH_2 + H_2O}$, which had been thought to have a considerable influence on the first step, was not very effective regarding the ultrasonic absorption observed in the MHz frequency range. The equilibrium constant in the second step, K_{32}, has been determined to be 3.5×10^{-2}. The standard volume change of the reaction has been calculated to be 26 cm^3 mol^{-1} from the concentration dependence of the maximum excess absorption per wavelength. The relaxation observed in a range greater that 1 mol dm^{-3} has been estimted to be associated with a molecular aggregation reaction. An ultrasonic study in an aqueous solution of butylamine has also been performed in order to determine the rate constants associated with a proton-transfer reaction at 25 °C.

The hydrogen atom has the simplest atomic structure and its properties have been experimentally and theoretically investigated.[1,2] Kinetic studies concerning proton-transfer reactions of amino acids, amines and carboxylic acids,[3–5] as well as the catalytic effect on the reaction[6–8] have been published using relaxation methods. Such information is very important in relation to biological reactions. It has been known that the proton-transfer process in aqueous amine solutions can be observed within the range of the ultrasonic pulse frequency 1—250 MHz. A theoretical approach which was originally proposed by Eigen,[9] seems to have become established. However, an analysis of the absorption associated with a proton-transfer may give us some unreasonable results, though the present authours[10,11] have also reported kinetic results regarding proton-transfer reaction in aqueous solutions of some amines according to his theory. In this situation, we consider that a reexamination of the analysis procedure should be undertaken. Another purpose of this report is to examine the isomeric effect of a proton-transfer reaction of butylamines. To this end, *s*-butylamine was chosen and the ultrasonic absorption and velocity results are given in this paper.

Experimental

s-Butylamine and butylamine were purchased from Tokyo Kasei Co. Ltd and Wako pure Chemicals, respectively, and distilled once. The desired concentrations of the aqueous solutions were prepared with doubly distilled water by weight. An improved ultrasonic pulse method was used for absorption measurements in the frequency range 6.5 to 220 MHz with 0.5, 5, and 20 MHz X-cut quartz transduceres. The procedure of the semiautomatic absorption measurement has been described elsewhere.[12] The sound velocity was measured by a sing around meter at 1.92 MHz and an interferometer at 2.5 MHz. The density of the solution was determined by a standard pyconometer of about 4 cm^3. The pH of the solution was measured by a HITACHI-HORIBA pH meter with a glass electrode. A saturated aqueous solution of $\mathrm{Ca(OH)_2}$ was used as the standard reference of the electrode at pH=12.45 along with a standard buffer solution at 9.18 at 25 °C. All pH and ultrasonic measurements were carried out under a dry nitrogen gas because of the high basicity of the solution. They were all measured at 25 °C.

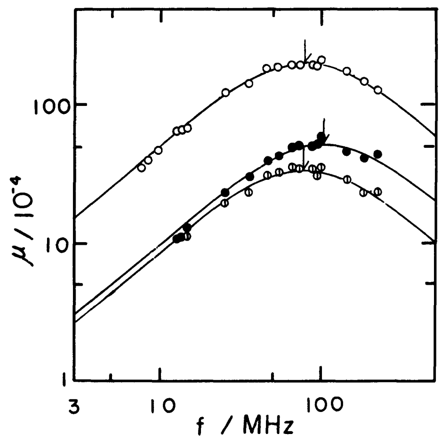

Fig. 1. The representative ultasonic absorption spectra in aqueous solution of *s*-butylamine at 25 °C. ○: 1.67 mol dm^{-3}, ●: 0.500 mol dm^{-3}, ⌽: 0.144 mol dm^{-3}.

Results and Discussion

Typical ultrasonic spectra for an aqueous solution of *s*-butylamine are shown in Fig. 1. In general, the frequency dependence of the absorption coefficient, α, due to a single process with a relaxation frequency, f_r, can be expressed as

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

or

$$\mu = Afc/\{1+(f/f_r)^2\}, \tag{2}$$

were μ is the excess absorption per wave length, f the frequency, A the amplitude of the excess absorption,

Table 1. Thermodynamic and Ultrasonic Parameters in Aqueous Solution of *s*-Butylamine at 25 °C

Concd	ρ	c	A	B	f_r	pH
mol dm^{-3}	g cm^{-3}	m s^{-1}	10^{-17} s^2 cm^{-1}		MHz	
0.0115	0.9970	1494.7	49	22	22	11.19
0.0225	0.9970	1497.9	48	20	39	11.28
0.0478	0.9967	1500.2	55	21	44	11.54
0.0510	0.9966	1499.2	55	21	46	11.40
0.0904	0.9965	1502.6	55	19	63	11.75
0.144	0.9956	1506.4	58	19	78	11.85
0.185	0.9949	1509.6	63	19	80	11.91
0.222	0.9946	1512.6	63	20	85	11.95
0.316	0.9940	1515.0	65	19	93	12.03
0.411	0.9923	1524.0	60	23	105	12.09
0.500	0.9910	1530.6	66	21	104	12.13
0.739	0.9875	1545.8	63	26	109	12.22
0.966	0.9844	1560.5	66	28	115	12.29

B the background absorption, and c the sound velocity. The solid curves in Fig. 1 were calculated using ultrasonic parameters determined by a nonlinear least-mean-square method. The agreement between experimental and calculated values was very good. The obtained ultrasonic parameters are listed in Table 1 along with the measured solution density, ρ. Figure 2 shows the dependence of the ultrasonic parameters on the concentration. In the concentration range less than 1 mol dm^{-3}, both A and B maintain a plateau. However, in a range greater than 1 mol dm^{-3}, A increases dramatically and shows a peak at about 2.4 mol dm^{-3} while B increases monotonously with the concentration. This indicates that the cause of the absorption in the high-concentration range is different from that observed in the low-concentration range.

In this paper, the relaxation phenomenon observed at less than 1 mol dm^{-3} is mainly considered. There have been many reports concerning ultrasonic absorption in aqueous solutions of various amines.[4,10,11,13–15] A process associated with an unimolecular reaction, such as rotational isomerization, might be ruled out since the relaxation frequency strongly depends on the concentration. In such a relatively dilute aqueous solution, the most feasible absorption mechanism is related to a hydrolysis of an amine. This can be expressed by

$$\text{R-NH}_3^+ + \text{OH}^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{R-NH}_2 + \text{H}_2\text{O}, \tag{3}$$

where k_f and k_b are the forward and backward rate constants, respectively. The relationship between the relaxation time, τ, and the reactant concentrations is given by

$$2\pi f_r = \tau^{-1} = \gamma^2 k_f\{[\text{R-NH}_3^+] + [\text{OH}^-]\} + k_b, \tag{4}$$

where γ is an activity coefficient calculated using Davies equation,[16] $-\log\gamma = 0.5[I^{1/2}/(I^{1/2}+1) - 0.3I]$. I is the ionic strength. The ion concentrations were obtained from pH measurements in the solution. Plots of f_r vs. $\gamma^2[\text{OH}^-]$ which are shown in Fig. 3 provide us

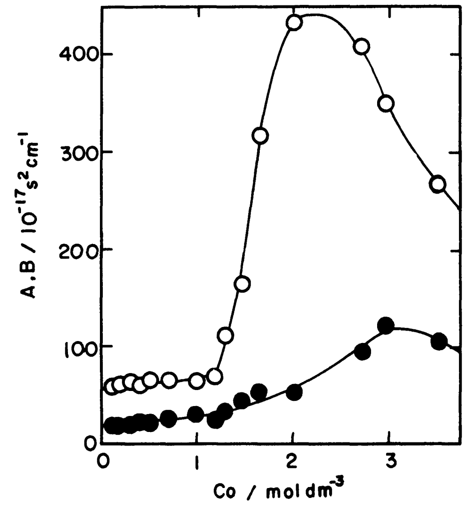

Fig. 2. Concentration dependences of the amplitude of the excess absorption (○), the background absorption (●) for aqueous solution of *s*-butylamine.

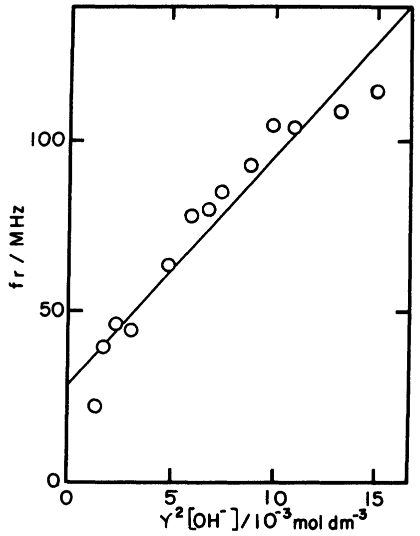

Fig. 3. The plots of f_r vs. $\gamma^2[\text{OH}^-]$ for aqueous solution of *s*-butylamine at 25 °C.

Table 2. The Proton-Transfer Reaction Rate Constants for Four Butylamines

Solute	Temp	$k_{12}(k_f)$	k_{f0}	$k_{21}(k_b)$	k_{b0}	K_{32}	K_b [a)]	ΔV	Ref.
	°C	10^{10} mol^{-1} dm^3 s^{-1}		10^8 s^{-1}		10^{-2}	10^{-4} mol dm^{-3}	cm^3 mol^{-1}	
Normal	20	3.6±0.1	0.22±0.01	1.2±0.1	1.4±0.4	5.4±2.0	1.7±0.5	30	10)
	25	2.4±0.2	0.13±0.01	3.1±0.3	2.9±1.9	2.0±1.0	2.5±1.5	28	This work
Iso	20	1.3±0.1	0.052±0.002	3.1±0.2	2.9±0.3	0.93±0.5	2.2±1.2	31	20)
Tertiary	20	1.9±0.1	0.11±0.01	2.0±0.2	2.7±0.4	3.9±3.0	4.2±2.7	25	20)
Secondary	25	2.1±0.1	0.048±0.004	1.8±0.2	3.4±0.5	3.5±2.7	2.9±2.2	26	This work

a) The dissociation constants have been calculated by Eq. 12.

the rate constants from the slope and the intercept. The results are shown in Table 2. Though the equilibrium constant, which might be calculated from the ratio of the two rate constants, should be the same as that determined by a static methods,17) they are different from each other by at least a factor of ten. Equation 4 can be expressed in terms of the analytical concentration, C_0, by

$$(2\pi f_r)^2 = \tau^{-2} = 4\gamma^2 k_f k_b C_0 + k_b^2. \tag{5}$$

Then, the forward and backward rate constants can also be obtained from the plots of f_r^2 vs. $\gamma^2 C_0$. They are also listed in Table 2 and are indicated as k_{f0} and k_{b0}. However, the rate constants, especially the forward rate constants, obtained by the above two procedures are very different as can be seen in Table 2. In order to test the accuracy of the ion concentrations in the solutions, we have estimated the dissociation constant using

$$K_b = \gamma^2[\mathrm{OH}^-]^2/(C_0-[\mathrm{OH}^-]). \tag{6}$$

The calculated dissociation constant is $(2.8\pm1.6)\times10^{-4}$ mol. This is close to the literature value.17) This means that the ion concentrations are not incorrect. These dynamic and static results indicate that the hydrolysis of amine proceeds through more complicate steps. The more detailed proton-transfer reaction mechanism has been originally proposed by Eigen,9) which is expressed by Eq. 7 and it seems to have been successfully applied to the ultrasonic analysis for many aqueous solutions of amines and amino acids.3,4)

$$\mathrm{R\text{-}NH_3^+ + OH^-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{R\text{-}NH_3^+\cdots OH^-} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}}$$
$$\mathrm{R\text{-}NH_2 + H_2O} \tag{7}$$

where k_{ij} represents the rate constant at each step. According to the procedure of the analysis used so far,3,4,18) the rate constants of k_f and k_b in Eq. 3 are connected by the next equation on the assumption that the first step is much slower than the second.

$$k_f = k_{12} \text{ and } k_b = k_{21}k_{32}/k_{23} \tag{8}$$

If the above procedure is correct, the ratio k_b/k_f should be close to the dissociation constant, K_b, because $K_b \cong k_b/k_f = (k_{21}/k_{12})(k_{32}/k_{23})$. However, this did not hold since these values were calculated using the rate constants in Table 2. An agreement can not be produced, even if the error of the intercept is taken into account. In the analysis procedure previously used, the rate constant, k_f, was determined using Eq. 5 with the help of a dissociation constant in the literature. The backward rate constant was then calculated and the results appear to be consistent. However, the intercept of plots of the experimental relaxation frequency vs. the ion or analytical concentration seems to be an actual high value although it should have been very close to the origin of the coordinate axes. Also, there is no kinetic experimental evidence concerning the dissociation rate constant. Only an estimation using the theoretical equation proposed by Eigen has been performed. Dickson et al.18) have analyzed the proton-transfer reaction for aqueous solutions of some diamines in terms of a strong coupling two-step reaction scheme. They seem to have considered the intermediate to consist of a hydrogen-bonded complex, although they have not touched upon the intermediate exactly. If the elementary step of the proton-transfer is taken into account, there should be an ion-pair formation process before the making of a hydrogen bond. Then, it should be necessary to assume another step between the reactants, $\mathrm{R\text{-}NH_3^+\cdots OH^-}$ and $\mathrm{R\text{-}NH_2}$, in Eq. 7. Such a step has been also proposed by Eigen.1) Even if such a complicated reaction mechanismis considered, the reactants, $\mathrm{R\text{-}NH_3^+\cdots OH^-}$ and $\mathrm{R\text{-}NH_2\cdots OH_2}$, are not distinguishable because the intramolecular proton-transfer reaction is expected to be too fast to be detected. Then, the reaction scheme of Eq. 7 is the same as that being taken into account such another intermediate, $\mathrm{R\text{-}NH_2\cdots OH_2}$. Under these circumstances, we have simply considered that the observed relaxation in the concentration range of 0.0115 to 1 mol dm^{-3} is assumed to be only due to the first step and the influence of the other steps is approximately negligible within the experimental error even if such process exists in a higher or lower frequency range. Then, the rate constants obtained from the plots of the relaxation frequency vs. $\gamma^2[\mathrm{OH}^-]$ in Fig. 3 may be those of the first step, k_{12} and k_{21}. From this hypothesis, it is possible to estimate the equilibrium constants, K_{32} and K_b, as follows. The equilibrium constants of the first and second steps are expressed as

$$K_{21} = k_{21}/k_{12} = \gamma^2[\text{R-NH}_3^+][\text{OH}^-]/[\text{R-NH}_3^+\cdots\text{OH}^-] \quad (9)$$

and

$$K_{32} = k_{32}/k_{23} = [\text{R-NH}_3^+\cdots\text{OH}^-]/[\text{R-NH}_2],$$

respectively. The dissociation constant or the equilibrium constant, K_b, can be precisely expressed by the next equation when the intermediates are taken into account.

$$K_b = K_{21}/(1+K_{32}^{-1}) \quad (10)$$

When the concentration of the R-NH$_3^+\cdots$OH$^-$ is small, K_b is approximately equal to $(k_{21}/k_{12})(k_{32}/k_{23})$. It is possible to calculate the equilibrium constant, K_{32}, with the help of Eq. 10 since K_{21} is obtained from k_{12} and k_{21}. The result is shown in Table 2. The small value of K_{32} indicates that the intermediate of the amine hydrolysis does not exist to a great extent. Using Eqs. 9 and 10, and the analytical concentration, Eq. 4 is transformed to

$$2\pi f_r = \tau^{-1} = k_{12}\{-K_b+(K_b^2+4\gamma^2C_0K_b)^{1/2}\} + k_{21}. \quad (11)$$

Consequently, solving for K_b, we obtain

$$K_b = [(\tau^{-1})^2 + k_{21}^2 - 2\tau^{-1}k_{21}]/ [k_{12}(4\gamma^2C_0k_{12} + 2k_{21} - 2\tau^{-1})] \quad (12)$$

Fig. 4 indicates the calculated K_b against C_0, where k_{12} and k_{21} obtained from the slope and the intercept in Fig. 3 are used. The obtained K_b listed in Table 2 is very close to that found in the literature.[17] The above analysis of the amine hydrolysis makes us believe that the observed relaxation is approximately due to a perturbation of the first step. In a determination of the rate constants, k_{12} and k_{21}, according to the analytical concentration, it is no wonder that the same rate constants, k_{12} and k_{21}, as those obtained by Eq. 4 are availabel if Eq. 11 is used in order to determine them. The rate constant, k_{12}, is consistent with the diffusion-controlled reaction predicted by Debye's equation.[9] However, the backward rate constant, k_{21} is small when compared to that predicted by the theoretical equation using the ordinary parameters such as the reaction radius, diffusion coefficient and dielectric constant. It should be of the order of 10^{10} s^{-1} according to the theory while the experimental value of k_{21} is of that of 10^8 s^{-1}. However, there is no direct observation that dissociation rate constant, k_{21}, is of the order predicted by theory. Applegate et al.[19] have also reported that in their proton-transfer reaction study, the decomposition of the reaction into two steps was arbitrary.

Another important parameter obtained by ultrasonic absorption and velocity measurements is the maximum absorption per wavelength, $\mu_{\max}$, expressed as

$$\mu_{\max} = \pi\rho c^2\Gamma(\Delta V-\alpha_p\Delta H/\rho C_p)^2/2RT, \quad (13)$$

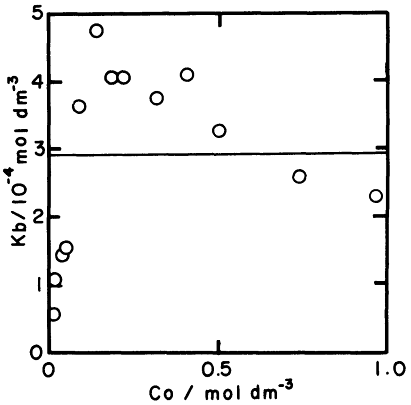

Fig. 4. The dissociation constants in aqueous solutions of *s*-butylamine calculated by Eq. 12 at 25 °C.

where ΔV is the standard volume change of the reaction, ΔH the standard enthalpy change of the reaction, α_p the thermal expansibility, C_p the specific heat, and Γ the concentration term which is expressed for the reaction under consideration as

$$\Gamma = \{1/[\text{R-NH}_3^+] + 1/[\text{OH}^-] + 1/[\text{R-NH}_3^+\cdots\text{OH}^-]\}^{-1}. \quad (14)$$

In the proton-transfer reaction, the enthalpy term can be quite small compared with the volume term in Eq. 13. Then, plots of $\mu_{\max}$ vs. $\rho c^2\Gamma$ provide the standard volume change of the reaction. The result is given in Table 2.

A similar experiment and the analysis for an aqueous solution of butylamine have been performed at 25 °C. The kinetic results are also shown in Table 2. Also, the analyses of other butylamine solutions for which ultrasonic experimental results have been reported so far[10,21] have been performed. The calculated rate and thermodynamic constants are listed in Table 2. Inconsistent values are also obtained when it is assumed that the second step influences the first step. However, an analysis based on the assumption that the ultrasonic absorption is only due to the perturbation of the equilibrium associated with the first step has been shown to be reasonable.

In conclusion, the ultrasonic relaxation observed in the MHz frequency range in relatively dilute aqueous solutions of butylamines can be attributed to the hydrolysis which proceeds in an intermediate state. The first process of ion-pair formation is associated with the observed relaxation. However, it seems to be hard to distinguish the difference in the kinetic parameters of the four isomeric butylamines. This means that the association process is a diffusion-controlled reaction which depends mainly on the coefficients of the hydroxide ions in the solutions. However, it is hard to say whether the dissociation process is also the diffusion-controlled reaction as predicted by Eigen.

Next, we briefly discuss an excess absorption mechanism which was observed in a concentration range greater than 1 mol dm^{-3}. As can be seen in Fig. 2, the amplitude of the relaxational absorption has a maximum. The sound velocity also has a maximum. Such dependences on the concentration have been found in some aqueous solutions of amines with relatively large hydrophobic groups, such as in the solution of pentylamine.[20] On the other hand, such phenomena are not observed in solutions in which solutes consist of a small hydrophobic group.[11,20] From these experimental facts, we conclude that the aggregate associated with a hydrophobic interaction might be created in butylamine aqueous solutions. Unfortunately, it has not been possible to distinguish two relaxation processes at greater than 1 mol dm^{-3}. All measured spectra can be approximately expressed by a single relaxational equation, though the relaxation frequency shows a discontinuous dependence on the concentration at around 1 mol dm^{-3}. This means that the coupling between the hydrolysis and the aggregation reaction is quite strong in butylamine solutions. In the case of a pentylamine aqueous solution,[20] two such distinguishable relaxations have been clearly observed.

We are considering that the relaxation observed in the concentrated aqueous solutions of amines with relatively large hydrophobic groups might be closely related to those observed in aqueous solutions of some alcohols or ethers since both aqueous solutions may indicate quite similar ultrasonic characters. In order to determine the correlations between them, it is required to accumulate more ultrasonic data for aqueous solutions of various nonelectrolytes as functions of the concentration and frequency.

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