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# The Kinetics of Proton-transfer Reaction in an Aqueous Solution of *n*-Butylamine by Means of Ultrasonic Absorption

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Various mechanisms associated with the ultrasonic absorptions in aqueous solutions of amines have previously been proposed.[1-4] Some problems relating to the elucidation of the mechanisms seem, however, to be still in question. On the other hand, the clarification of the dynamic properties of aqueous solutions of amines may provide useful and fundamental information on the kinetics and mechanisms associated with the conformational changes of the protein molecules.

The purpose of the present investigation is to confirm the mechanism of the excess absorption in a dilute aqueous solution of *n*-butylamine in detail by measuring the ultrasonic absorption.

## Experimental

The chemical used in the present experiment were of a guaranteed reagent grade. The *n*-butylamine was purified by distillation, and its purity was confirmed by the gas-chromatographic method to be higher than 99.9%. The pH of the solution was adjusted to the desired values using either NaOH or $HClO_4$. The ultrasonic absorptions were measured at the odd harmonic frequencies of 5 MHz and 20 MHz X-cut quartz crystals by the pulse technique.[5] The frequency range of the measurement was from 15 to 220 MHz. Since the aqueous solution of amine is highly basic, the cell was made air-tight, and nitrogen gas was passed over the solution to prevent the contamination of specimens by the oxidation with air. The sing-around method was employed at 1.92 MHz to measure the sound velocity. The pH values of the solutions were measured by a Hitachi-Horiba F-5 type pH meter. All the measurements were made at 20°C.

## Results and Discussion

Figure 1 shows an example of the ultrasonic absorption spectra of aqueous solutions of *n*-butylamine. These

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Table 1. Ultrasonic parameters and densities for the solution of *n*-butylamine at 20°C

| M | pH | $\rho$ g cm$^{-3}$ | $c$ m sec$^{-1}$ | $A$ $10^{-16}$ dB | $B$ sec$^2$ cm$^{-1}$ | $f_r$ MHz | $(\alpha\lambda)_{\max}$ $10^{-3}$ neper |
|---|---|---|---|---|---|---|---|
| 0.0322 | 11.39 | 0.9966 | 1484.0 | 44.5 | 21.0 | 36±10 | 1.3 |
| 0.0978 | 11.73 | 0.9953 | 1489.2 | 65.0 | 22.0 | 55±5 | 2.9 |
| 0.217 | 11.94 | 0.9936 | 1499.0 | 62.0 | 24.0 | 82±7 | 3.8 |
| 0.283 | 12.05 | 0.9928 | 1504.6 | 57.5 | 25.0 | 90±7 | 3.9 |
| 0.401 | 12.13 | 0.9917 | 1516.5 | 59.0 | 23.5 | 105±10 | 4.7 |
| 0.505 | 12.17 | 0.9909 | 1521.6 | 59.5 | 25.0 | 115±10 | 5.2 |
| 0.537 | 12.25 | 0.9901 | 1524.3 | 63.0 | 23.0 | 130±15 | 5.4 |

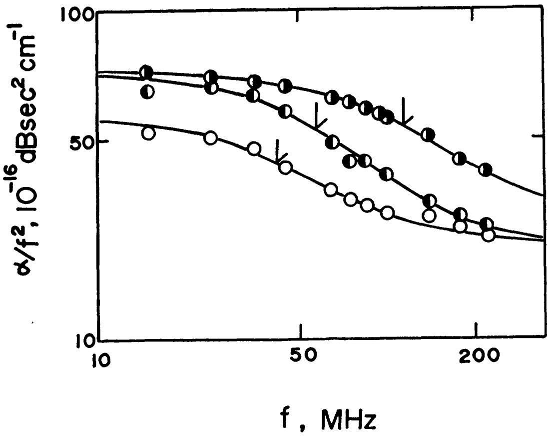

Fig. 1. Ultrasonic absorption spectra in aqueous solutions of *n*-butylamine at 20°C. The arrows show the relaxation frequencies:

◑: 0.505M, ◐: 0.0978M, ○: 0.0322M.

spectra can be represented by the formula of a single relaxation as follows:

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

where $\alpha$ is the absorption coefficient; $f$, the frequency; $f_r$, the relaxation frequency, and $A$ and $B$, constants. The values of these constants were determined so as to obtain the best fit of the data to Eq. (1). The ultrasonic parameters and densities thus obtained are listed in Table 1. If these excess absorptions are due to hydrolysis, the reaction scheme is given by the following equation:

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

The reciprocal relaxation time is related to the rate constants and concentrations as follows:

$$1/\tau = 2\pi f_r = k_f[[\text{R-NH}_3^+]+[\text{OH}^-]]\Pi\gamma_i + k_b. \tag{3}$$

where $\tau$ is the relaxation time, $k_f$ and $k_b$ are the forward and backward rate constants respectively, and $\gamma_i$ is the activity coefficient. If the activity coefficients and concentrations of the R–NH$_3^+$ ion are equal to those of the OH$^-$ ion at each concentration, Eq. (3) can be rewritten as:

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

The relationship between the ionic strengths and the activity coefficients of monoamine and OH$^-$ ions has been given by almost the same curve.[6] Assuming that the relationship also holds for *n*-butylamine, the appropriate activity coefficients can be obtained graphically.

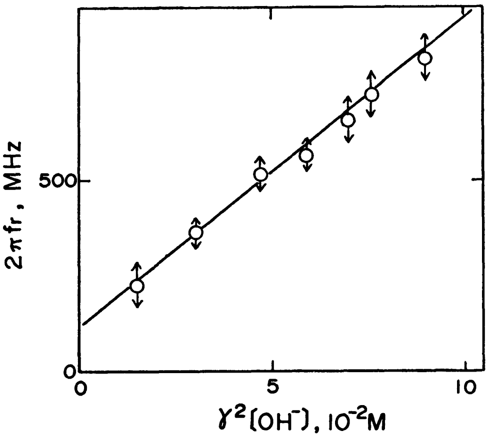

Fig. 2. The plots of $2\pi f_r$ *vs.* $\gamma^2$[OH$^-$] for aqueous solutions of *n*-butylamine at 20°C.

Figure 2 shows the plot of $2\pi f_r$ *vs.* $\gamma^2$[OH$^-$]. The linearity of the plot confirms that the mechanism of excess absorption is associated with hydrolysis. The forward and backward rate constants were calculated from the slope and intercept respectively of the plots. The standard volume change, $\Delta V$, of the reaction can be determined in the following manner. The excess absorption per wavelength shows a maximum at the $f=f_r$ frequency and can be written as:

$$(\alpha\lambda)_{\max} = \frac{1}{2}Af_rc \tag{5}$$

where $(\alpha\lambda)_{\max}$ is the maximum excess absorption per wavelength, and $c$, the velocity of sound. For a chemical process of the type represented by Eq. (2), the maximum excess absorption per wavelength can be represented by:

$$(\alpha\lambda)_{\max} = \frac{1}{2}\pi\rho c^2\frac{(\Delta V)^2}{RT}\Gamma_c \tag{6}$$

where $\rho$ is the density and where $\Gamma_c=[1/[\text{OH}^-]+1/[\text{R-NH}_3^+]+1/[\text{R-NH}_2]]^{-1}$. In Table 2 the rate constants and the mean standard volume change associated with the hydrolysis of *n*-butylamine are tabulated, together with the results for other amines obtained by Eigen and his co-workers.[4,7,8]

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TABLE 2. RATE CONSTANTS AND STANDARD VOLUME CHANGE

| System | $k_f$<br>$\text{M}^{-1}\,\text{sec}^{-1}$ | $k_b$<br>$\text{sec}^{-1}$ | $\Delta V$<br>$\text{cm}^3\,\text{mol}^{-1}$ |
|---|---|---|---|
| Ammonia | $3.4\times10^{10}$ | $6.0\times10^{5}$ | 26.8 |
| Methylamine | $3.7\times10^{10}$ | $1.6\times10^{7}$ | 26.1 |
| Ethylamine | $3.2\times10^{10}$ | $1.4\times10^{7}$ | 24.3 |
| *n*-Propylamine | $3.0\times10^{10}$ | $1.2\times10^{7}$ | 24.0 |
| *n*-Butylamine[a] | $(4.1\pm0.7)\times10^{10}$ | $(1.1\pm0.7)\times10^{8}$ | 32 |

a) This work

In addition, in order to confirm that the absorption mechanism is due to the perturbation of the equilibrium represented by Eq. (2), the ultrasonic absorptions at a constant concentration of *n*-butylamine were measured at various pH's. The theoretical dependences of $(\alpha\lambda)_{\text{max}}$ and $f_r$ on pH can be calculated from Eqs. (3) and (6) respectively. In Fig. 3, the calculated variation of $\Gamma_c$ with the pH is shown, together with the $(\alpha\lambda)_{\text{max}}$ obtained; the value of the equilibrium constant, $K=k_b/k_f$, in the literature[9] was used to calculate the concentration terms in Eqs. (3) and (6) because large and serious errors usually occur in determining them from ultrasonic data. A reasonable dependence of $f_r$ on pH was observed. This information also provides confirmation that the perturbation of the proton-transfer equilibrium is the origin of the excess absorption.

As a result, the value of the rate constant, $k_f$, for a diffusion-controlled reaction obtained in this study agrees very closely with the results obtained experimentally and theoretically for other compounds.[4,7,8,10,11] The value of $k_f$ obtained is, however, slightly different from those for other amines obtained by Eigen and his co-workers. This difference may be due to the fact that they have employed an equation, $1/\tau=2k_f\sqrt{KC_0}+k_b$, which is derived from Eq. (2) as an approximate form, where $C_0=[\text{R-NH}_2]+[\text{R-NH}_3^+]$.

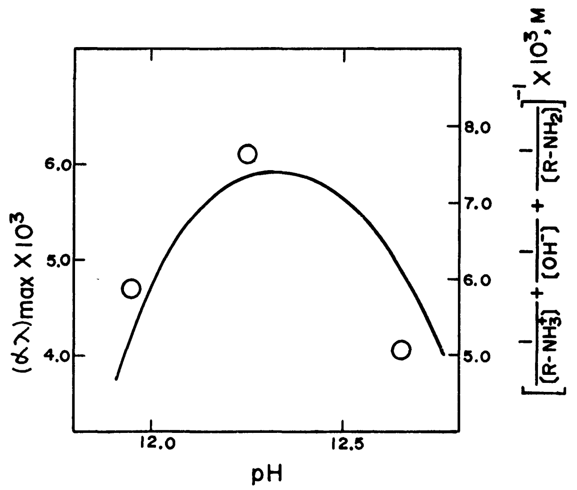

Fig. 3. The variation of $(\alpha\lambda)_{\text{max}}$ and $\Gamma_c$ with pH in 0.537M *n*-butylamine. The solid line represents the predicted behavior of $\Gamma_c$. The circles are the experimental points of of $(\alpha\lambda)_{\text{max}}$.

As has been proposed by Eigen and his co-workers[8] the recombination process of the $\text{OH}^-$ ion with an acid in an aqueous solution might not be as simple as that described in Eq. (3). The process probably proceeds through the complex state expressed by next equations:

$$\text{R-NH}_3^+ + \text{OH}^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \text{R-NH}_3^+ \cdots \text{OH}^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \text{R-NH}_2 + \text{H}_2\text{O} \qquad (8)$$

where the complex state is formed by the hydrogen bond. Therefore, the rate constants obtained should be given by:

$$k_f = k_{12}, \quad k_b = k_{21}\cdot\frac{k_{32}}{k_{23}} \qquad (9)$$

Consequently, the value of $k_f$ depends on the collision frequency of reactant partners, $\text{R-NH}_3^+$ and $\text{OH}^-$. In the case of relatively small molecules, as is shown in Table 2, the values of $k_f$ are probably constant within the limits of experimental error.

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