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The Kinetics of Association-Dissociation Reaction in an Aqueous Solution of *n*-Butylamine by Means of Ultrasonic Absorption

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The ultrasonic absorptions of *n*-butylamine in aqueous solutions were measured at 25°C in the range of frequency from 15 to 220 MHz and of concentration from 0.698 to 3.00 M. The peak sound absorption was found. The mechanism of the observed peak sound absorption was attributed to the $4A \rightleftarrows A_4$ reaction where A and A_4 are the monomer and tetramer of the solute respectively. The rate constants of the forward and backward reaction were determined to be 2.2×10^6 M^{-3} sec^{-1} and 9.0×10^7 sec^{-1} respectively, and the standard volume change between the initial and final state in the reaction was calculated to be 14 ml mol^{-1}.

The method of ultrasonic absorption has been successfully applied to the investigation of reaction kinetics which occurs 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 liquid mixtures exhibit a maximum in their excess absorption at an intermediate concentration. Andreae and his coworkers[1] have summarized the data for these systems and developed a theory which is associated with the solute-solvent interactions. 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.

It has reported that some amines also show the peak sound absorption phenomena at intermediate concentrations of their aqueous solutions.[1] The purpose of the present investigation is to report the ultrasonic absorption data on aqueous solutions of *n*-butylamine and to clarify the mechanism of the peak sound absorption using the relaxation theory.

Experimental

The *n*-butylamine was of a guaranteed reagent grade and was purified by distillation once. The purity was verified to be higher than 99.9% by the gas-chromatographic method. Deionized and distilled water was used as the solvent. The measurements of the ultrasonic absorption were made at the odd harmonic frequencies of 5 and 20 MHz X-cut quartz transducers by means of the pulse technique.[2] The frequency range of the measurement was from 15 to 220 MHz. The sing-around method was employed at 1.92 MHz to measure the sound velocity. The densities were measured by the standard pycnometer. The pH values of the solutions were measured by a Hitachi-Horiba type F-5 pH meter. All the measurements were made at 25°C.

Results

In Fig. 1 the plots of α/f^2 *vs.* the concentration are shown, where α is the sound absorption coefficient and f is 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 absorption 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:

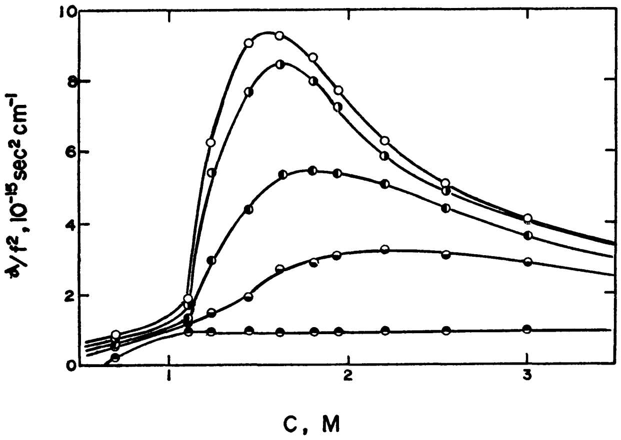

Fig. 1. The plots of α/f^2 *vs.* concentration in aqueous solutions of *n*-butylamine at 25 °C. ○: $f \to 0$, ◑: $f=15$ MHz, ◐: $f=45$ MHz, ◒: $f=100$ MHz, ◓: $f \to \infty$.

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

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

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

where f_{ri} is the relaxation frequency for the i-th process and A_i and B are constants. In particular, for single and double relaxation processes Eq. (1) can be rewritten as:

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

and:

$$\alpha/f^2 = \frac{A_1}{1+(f/f_{r1})^2} + \frac{A_2}{1+(f/f_{r2})^2} + B \qquad (3)$$

Figure 2 shows the representative ultrasonic absorption spectra of aqueous solutions of *n*-butylamine. All these spectra except the one at 1.10 M show the characteristic behavior due to the single relaxation process which is represented by Eq. (2). The spectrum at 1.10 M is represented by Eq. (3). The relaxation parameters were determined so as to obtain the best fit of the data of Eq. (2) or (3). As may be seen in this figure, the excess absorptions observed in more than 1.10 M are different from those in less than 1.10 M. The latter was attributed to hydrolysis, which was reported in a previous paper by the present authors.[3] In the concentrated solution, the experimental values of α/f^2 at high frequencies tend to be lower than the theoretical ones, as is shown in Fig. 2. This is because the excess absorptions associated with hydrolysis exist in a higher frequency range than that investigated here and the effect due to this relaxation process appears in the experimental values at high frequencies. However, the excess absorption in the concentrated solutions could be treated approximately as a single relaxation process. The concentration dependences of the sound velocity, c, and of the excess absorption, A, are shown in Fig. 3. The concentration at which the sound velocity shows its maximum is lower than that of the excess absorption. This kind of phenomenon has also been observed in binary mixtures.[1,4] The relaxation parameters and the sound velocity obtained are listed in Table 1, together with the density, the pH and the activity coefficient of ions, the last of which was calculated by Davis equation,

$$-\log \gamma = 0.5[\{\sqrt{I}/(1+\sqrt{I})\} - 0.3I].$$

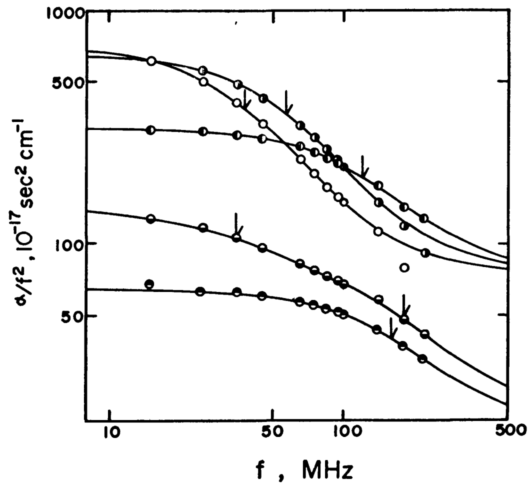

Fig. 2. Ultrasonic absorption spectra in aqueous solutions of *n*-butylamine at 25°C. ◒: 0.698 M, ◓: 1.10 M, ◑: 1.44 M, ○: 1.80 M, ◐: 3.00 M.

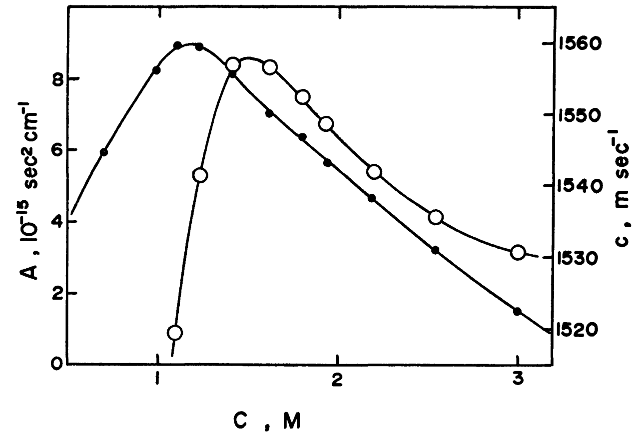

Fig. 3. Concentration dependence of the excess absorption and of the sound velocity. ○: A, ●: c.

TABLE 1. RELAXATION PARAMETERS, SOUND VELOCITY AND DENSITY IN THE AQUEOUS SOLUTION OF *n*-BUTYLAMINE AT 25°C

C M	pH	γ	ρ g ml^{-1}	c m sec^{-1}	f_r MHz	A 10^{-17} sec^2 cm^{-1}	B 10^{-17} sec^2 cm^{-1}
3.00	12.63	0.794	0.9460	1524.8	120	312	97.9
2.54	12.62	0.795	0.9534	1531.1	100	411	97.9
2.19	12.61	0.797	0.9604	1538.3	82	532	97.9
1.94	12.58	0.800	0.9653	1543.1	67	670	95.6
1.80	12.57	0.802	0.9718	1549.0	57	748	97.9
1.61	12.56	0.803	0.9721	1550.1	50	829	89.2
1.41	12.53	0.808	0.9757	1554.9	40	839	95.0
1.23	12.49	0.812	0.9796	1559.4	35	524	97.9
1.10	12.44	0.816	0.9834	1559.5	35, 180	86.3, 74.8	20.7
0.698	12.30	0.837	0.9884	1544.5	160	62.7	20.7

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

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

Interpretation of Results

Theoretical. The molecules which consist of hydrophilic and hydrophobic groups have a tendency to associate in an aqueous solution as in the case of surfactants.[5] Therefore, let us consider the reaction expressed by the next formula:

$$\mathrm{nA} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{A}_n \tag{4}$$

where A is the monomer, A_n is the aggregate, n is the aggregation number, and k_f and k_b are the forward and backward rate constants respectively. If one denotes the molar concentrations of the components, A and A_n, by C_1 and C_2, the rate of return of the system to equilibrium is governed by the rate law:

$$\frac{dC_2}{dt} = k_f(C_1)^n - k_bC_2 \tag{5}$$

Provided that very small periodic perturbations are applied to the system, it may be assumed that the perturbed rate constants and the concentrations differ only slightly from their equilibrium values. One can write for the perturbed variables a series of relations such as:

$$\left.\begin{aligned} C_1 &= \bar{C}_1 + \delta C_1\cdot\exp(i\omega t), & C_2 &= \bar{C}_2 + \delta C_2\cdot\exp(i\omega t), \\ k_f &= \bar{k}_f + \delta k_f\cdot\exp(i\omega t), & k_b &= \bar{k}_b + \delta k_b\cdot\exp(i\omega t), \end{aligned}\right\} \tag{6}$$

where the equilibrium values of the rate constants and the concentrations are indicated by a bar over each symbol and the quantities δC_i and δk_i represent the amplitudes of the small variations associated with the sound wave. As the relation between δC_1 and δC_2 is $\delta C_1 = -n\delta C_2$, one obtains the next equation:

$$\delta C_2 = \frac{(\bar{C}_1)^n\delta k_f - \bar{C}_2\delta k_b}{i\omega + \bar{k}_f n^2(\bar{C}_1)^{n-1} + \bar{k}_b} \tag{7}$$

The relaxation time, τ, can be defined as:

$$\tau^{-1} = 2\pi f_r = \bar{k}_f n^2(\bar{C}_1)^{n-1} + \bar{k}_b \tag{8}$$

Since the equilibrium constant is $K = k_b/k_f = (C_1)^n/C_2$,

$$\delta K = \frac{\bar{k}_f\delta k_b - \bar{k}_b\delta k_f}{(\bar{k}_f)^2} \tag{9}$$

The thermodynamic dependence of the equilibrium constant on the pressure is given by the equation:

$$\left(\frac{\partial K}{\partial P}\right)_T \frac{1}{K} = -\frac{\Delta V^\circ}{RT} \tag{10}$$

where ΔV° is the standard volume change, R is the gas constant and T is the absolute temperature. The standard volume change, ΔV°, is defined by $\Delta V^\circ = \bar{V}_2 - n\bar{V}_1$ where $\bar{V}_1$ and $\bar{V}_2$ are the partial molar volumes of A and A_n respectively. The complex compressibility, defined as $\beta' = (-1/V)(\delta V/\delta P)_T$, is related to the relaxational compressibility, β_r:

$$\beta' = \frac{\beta_r}{1+i\omega\tau} = -\frac{1}{V}\left(\frac{\partial V}{\partial C_2}\right)_T\left(\frac{\partial C_2}{\partial P}\right)_T \tag{11}$$

The relaxational compressibility in a reacting system close to the equilibrium is given by:

$$\beta_r = \frac{2\mu_{max}}{\pi\rho c^2} \tag{12}$$

where ρ is the density and μ_{max} is the maximum excess absorption per wavelength. Therefore, one obtains the next equation:

$$\mu_{max} = \frac{\pi\rho c^2}{2}\cdot\frac{(\Delta V^\circ)^2}{RT}\bar{k}_f(\bar{C}_1)^n\tau \tag{13}$$

Comparison with Experiment. In aqueous solutions of *n*-butylamine, there exists the following equilibrium in addition to that of Eq. (4):

$$\mathrm{R\text{-}NH_3^+ + OH^- \rightleftharpoons R\text{-}NH_2 + H_2O} \tag{14}$$

The equilibrium constant, $\bar{K}_b$, is defined by:

$$K_b = \frac{\gamma^2[\mathrm{OH^-}]^2}{[\mathrm{R\text{-}NH_2}]} \tag{15}$$

where γ is the activity coefficient. Therefore, Eq. (8) may be rewritten as:

$$\tau^{-1} = 2\pi f_r = \bar{k}_f n^2\left(\frac{\gamma^2[\mathrm{OH^-}]^2}{\bar{K}_b}\right)^{n-1} + \bar{k}_b \tag{16}$$

The value of n was determined so as to obtain the straight line of the plots of $2\pi f_r$ *vs.* $(\gamma^2[\mathrm{OH^-}]^2)^{n-1}$; the result was $n=4$. Figure 4 shows the plots of $2\pi f_r$ *vs.* $(\gamma^2[\mathrm{OH^-}]^2)^3$. The forward and backward rate

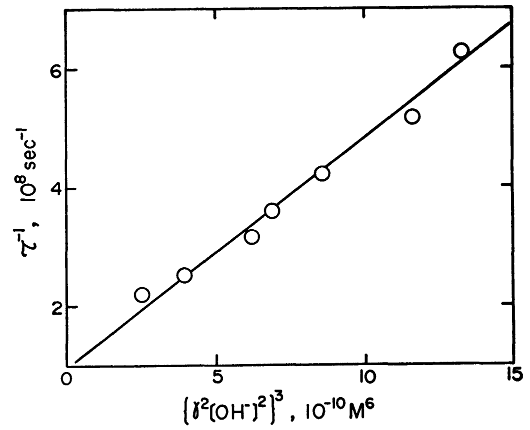

Fig. 4. The plots of τ^{-1} vs. $\{\gamma^2[\mathrm{OH^-}]^2\}^3$.

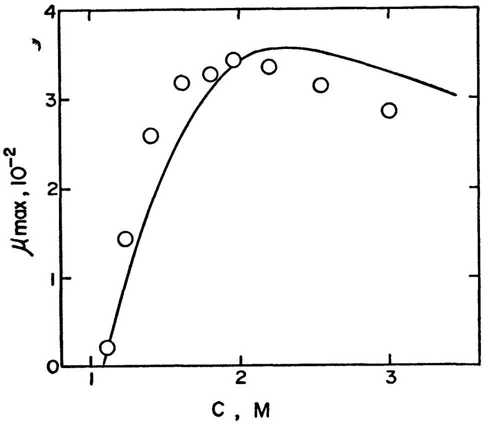

Fig. 5. Comparison of experimental values of μ_{max} with the theoretical ones.

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[5] K. Shinoda and T. Nakagawa, "Colloidal Surfactants," Academic Press, New York (1963).

constants were determined from the slope and the intercept of this line, using the equilibrium constant, $\bar{K}_b = 4.44 \times 10^{-4}$ M, in the literature.[6]

On the other hand, the maximum excess absorption per wavelength, μ_{max}, was calculated from Eq. (13). The result of the theoretical calculation of μ_{max} at $n=4$ is shown in Fig. 5, together with the experimental values. A considerably good agreement between the experimental and theoretical values was obtained, as is seen in this figure. The value of ΔV° was calculated from Eq. (13) by using the experimental value for μ_{max} at the concentration of 1.94 M. The rate constantes and the standard volume change obtained in the present investigation are $\bar{k}_f = 2.2 \times 10^6$ M^{-3} sec^{-1}, $\bar{k}_b = 9.0 \times 10^7$ sec^{-1} and $\Delta V^\circ = 14$ ml mol^{-1}.

Discussion

The phenomena that the excess absorption and velocity of ultrasonic wave exhibit the maximum in the intermediate concentration have previously been reported in many binary mixtures. The excess absorption mechanism has been explained in terms of the solute-solvent interaction.[1,4] The models are:

$$AA + BB \rightleftharpoons 2AB, \qquad (17)$$

$$A + B_m \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}} AB_m \qquad (18)$$

where A is the solute molecule, B is the water molecule, B_m is the aggregate of water molecules and the AB or AB_m complex is formed by hydrogen bonding. First, if the mechanism of the excess absorption in the aqueous solution of *n*-butylamine is due to the perturbation of the equilibrium expressed by Eq. (17), P. S. A. C should be 0.5 mole fraction of the solute. However, the observed value of P. S. A. C is 0.04 mole fraction of amine for the aqueous solution of *n*-butylamine. Secondary, if the mechanism is associated with the model of Eq. (18), the relation between the relaxation time and the concentration is derived to be $\tau^{-1} = 2\pi f_r = \bar{k}_f' \sqrt{\{\bar{K}' + \bar{C}_a - (\bar{C}_b/m)\}^2 + (4\bar{C}_b/m)\bar{K}'}$ where $\bar{K}' = \bar{k}_b/\bar{k}_f'$ and $\bar{C}_a$ and $\bar{C}_b$ are the total concentrations of the solute and the solvent respectively. However, the concentration dependence of the relaxation time cannot be interpreted by this equation, since the reasonable parameters, $\bar{k}_f'$ and $\bar{K}'$ have not been determined unitarily. Therefore, these two mechanisms must be ruled out as the cause of the excess absorption in the aqueous solution of *n*-butylamine.

The *n*-butylamine, which consists of hydrophilic and hydrophobic groups, is one of the surface active agent.[7,8] Therefore, the molecule has a tendency to aggregate in an aqueous solution. The aggregate is formed by hydrophobic bonding. Expressing Eq. (8) in terms of $C_0 = [\text{R–NH}_2] + n[(\text{R–NH}_2)_n]$ yields:

$$\tau^{-1} = 2\pi f_r = n\bar{k}_b\bar{K}_b \frac{C_0}{y^2[OH^-]^2} + (1-n)\bar{k}_b \qquad (19)$$

One can estimate the equilibrium constant, $\bar{K}_b$, from this equation. The value is $\bar{K}_b = (8 \pm 3) \times 10^{-4}$ M which is very close to the value in the literature.[6] This information also confirms that the cause of the excess absorption in the aqueous solution of *n*-butylamine is attributable to the perturbation of the equilibrium expressed by Eq. (4).

As there exist two types of equilibria in the solution, it may be necessary to consider precisely the two-step mechanism, that is, the reaction which is coupled by Eqs. (4) and (14). Therefore, the following formula may be considered:

$$A^+ + B^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \frac{1}{n}A_n \qquad (20)$$

The relaxation times are derived from the next determinant:[9]

$$\begin{vmatrix} a_{11} - \tau^{-1} & a_{12} \\ a_{21} & a_{22} - \tau^{-1} \end{vmatrix} = 0 \qquad (21)$$

where $a_{11} = \bar{k}_{12}(\bar{C}_{A^+} + \bar{C}_{B^-}) + \bar{k}_{21}$, $a_{12} = n\bar{k}_{21}$, $a_{21} = \bar{k}_{23} \times (\bar{C}_A)^{n-1}$, and $a_{22} = \bar{k}_{32} + \bar{k}_{23}(\bar{C}_A)^{n-1}n^2$. If one denotes the relaxation time for the faster process by τ_1, and that for the slower process by τ_2, one obtains the next equation under the condition $\tau_1 \ll \tau_2$:

$$\tau_2^{-1} = \bar{k}_{23}(\bar{C}_A)^{n-1}\left\{\frac{n^2(\bar{C}_{A^+} + \bar{C}_{B^-})}{\bar{C}_{A^+} + \bar{C}_{B^-} + \bar{K}_b}\right\} + \bar{k}_{32} \qquad (22)$$

Therefore, the contribution from the faster process to the slower one is expressed in terms of $(\bar{C}_{A^+} + \bar{C}_{B^-})/(\bar{C}_{A^+} + \bar{C}_{B^-} + \bar{K}_b)$ comparing with Eq. (8). The neglect of this term alters the calculated values of $\bar{k}_f$ and $\bar{k}_b$ in Eq. (4) by less than 2%.

Similar investigations for aqueous solutions of other amines will give an insight into the more detailed clarification of the cause of the phenomena associated with the peak sound absorption.

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[6] M. C. Cox, D. H. Everett, D. A. Landsman, and R. J. Munn, *J. Chem. Soc., B*, **1968** 1373.

[7] S. K. Sharma, *Kolloid-Z. Z. Polym.*, **233**, 962 (1969).

[8] R. Wolff, *Kollid-Z.*, **138**, 181 (1954).

[9] G. H. Czerlinski, "Chemical Relaxation," Marcel Dekker Inc., New York (1966).