Effect of Ether Oxygen on Proton Transfer and Aggregation Reactions of Amines in Water by Ultrasonic Absorption Method

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Ultrasonic absorption coefficients in the frequency range from 6.5 to 220 MHz have been measured in aqueous solutions of 3-ethoxy- and 3-butoxypropylamine as functions of their concentrations along with the sound velocity at 2.5 MHz and the density. In a 3-ethoxypropylamine solution, only one relaxational absorption has been observed up to 3.0 mol dm^{-3}. The cause has been clarified to be due to a proton-transfer reaction of the amine from the concentration dependences of the relaxation frequency and the relaxational amplitude. The rate and thermodynamic parameters have been determined and reasonable values have been obtained as a diffusion-controlled reaction. In the solution of 3-butoxypropylamine, another relaxation process in addition to that due to the proton-transfer reaction has been observed in the concentrations of more than 0.5 mol dm^{-3}. This relaxation process has been attributed to a perturbation associated with an aggregation reaction, $4A \longleftrightarrow A_4$, from the concentration dependences of the relaxation frequency and the relaxational amplitude of the absorption. The rate and thermodynamic constants for the proton-transfer and aggregation reactions have been determined. It has been found from a comparison of the results for the two solutions and others reported previously that the introduction of ether oxygen into amine molecules has little influence on the proton-transfer reaction, but prevents the formation of aggregates due to the hydrophobic interaction. It has also been seen from the results of 3-butoxypropylamine solutions that the butoxyl group has a fairly high ability of hydrophobic interaction and that nonionized molecules form aggregates in the aqueous solution.

The dynamic properties of aqueous solutions of various alkylamines have been clarified so far by measurements of the ultrasonic absorption coefficients in a pulse frequency range from 6.5 to 220 MHz.[1-4] One of the characteristic properties regarding absorption is the observation of a relaxation process due to a proton-transfer reaction. This process has been found in many aqueous and nonaqueous solutions of amines, phenols and benzoic acids in a similar frequency range.[5-9] It is generally expressed for amine solutions as $R\text{-}NH_3^+ + OH^- \leftrightarrow R\text{-}NH_3^+ \cdots OH^- \leftrightarrow R\text{-}NH_2 + H_2O$. In addition, we have proposed from a detailed analysis of the absorption data[3] that the cause of the relaxational absorption observed in the pulse frequency range is only due to the first step though the intermediate of the above mentioned reaction is important. The effect of the second step on absorption is negligibly small. The importance of the proton-transfer reaction mechanisms in biological systems is stressed,[10] and a detailed dynamical interpretation for the process is desired in relation to both the solute structure and kinetics.

When the hydrophobicity of amine molecule increases, such as butyl-[1] and pentylamine,[2,4] another relaxational absorption appears in a slightly lower frequency range, although the position of the relaxation frequency depends on the structure of the solutes. We have predicted that the relaxation process is related to the molecular aggregation of the nonionized amine molecules, and that such aggregates have a relatively small aggregation number. This phenomenon begins remarkably with the solution of butylamines for monoalkylamines, and it is characterized by the so-called Peak Sound Absorption Concentration. This was originally discussed by Barfield and Schneider[11] regarding an aqueous solution of diethylamine in relation to the solute and solvent interaction. However, it is very dependent of the hydrophobicity of solute molecules. If an ether oxygen is introduced to the alkyl group of an amine molecule, it is expected that the hydrophobicity would decrease and that the dynamic characters of the solutions might be changed. It is desired to dynamically elucidate how the ether oxygen affects the balance of the hydrophobicity and hydrophilicity of amine molecules. In order to observe the above speculation, we chose the two solutes, 3-butoxypropylamine and 3-ethoxypropylamine, and the ultrasonic absorption coefficients were measured as functions of both the frequency and concentration. The results are reported in this paper.

Experimental

Chemical: 3-Butoxypropylamine and 3-ethoxypropylamine were purchased from Wako Pure Chemicals. The former was distilled at normal pressure. The latter was used without further purification, since the gas-chromatographic data indicated the purity to be more than 99%. The solvent water was distilled twice and highly pure N_2 gas was passed for about 10 min with boiling. The desired aqueous solutions were made by weight and by dilution for the dilute solutions.

Apparatus: The ultrasonic absorption coefficient was measured by a pulse method in the frequency range from 6.5 to 220 MHz. Detail of the measurement procedure are described elsewhere.[12] The frequency dependence of the absorption coefficient has been analyzed by a Debye-type relaxational equation as

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

and

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

where α is the absorption coefficient, f the frequency, A_i the relaxational absorption amplitude for the i-th process, f_{ri} the relaxation frequency, μ the absorption per wave length, c the sound velocity and B includes the residual and classical absorptions. The ultrasonic parameters were determined by a nonlinear least mean-squares computer program, which is also described elsewhere.[12] The sound velocity was measured by an interferometer at 2.5 MHz. These ultrasonic cells were immersed in a water bath maintained at a constant temperature within ±0.002 °C. All the solutions were isolated from the air by circulating dry N_2 gas onto the solutions in the cells in order to maintain a constant hydroxide concentration. The solution density was measured using a conventional Ostwald-type pycnometer, of which the volume was about 5 cm^3. The solution pH's were determined by Hitachi-Horiba pH meter and the Towa Denpa HM-60S pH meter. All measurements were carried out at 25 °C.

Results

Figures 1 and 2 show the representative ultrasonic absorption spectra in aqueous solutions of 3-butoxypropylamine and 3-ethoxypropylamine at various concentrations, respectively. The solid curves in the figures indicate the calculated values by Eqs. 1 and 1′ when i=1. The detailed procedure for judging if the spectrum is due to a single relaxational process or not is described elsewhere.[13] The fitnesses between the experimental and theoretical values might look as if a single relaxational process was observed. However, small deviations at a lower frequency range were found at concentrations at around 0.6—1.2 mol dm^{-3} of 3-butoxypropylamine. The concentration

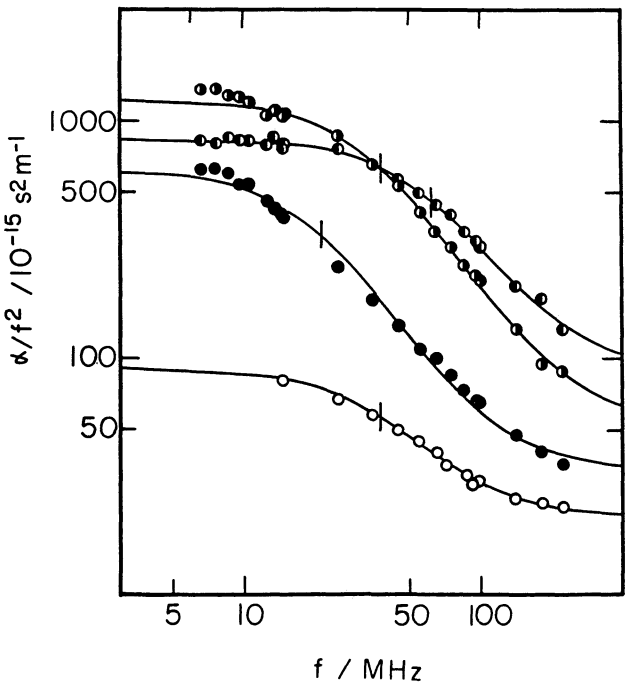

Fig. 1. The representative ultrasonic absorption spectra in aqueous solution of 3-butoxypropylamine at 25 °C.
○: 0.148 mol dm^{-3}, ●: 0.606 mol dm^{-3}, ◑: 1.212 mol dm^{-3}, ◐: 1.798 mol dm^{-3}.

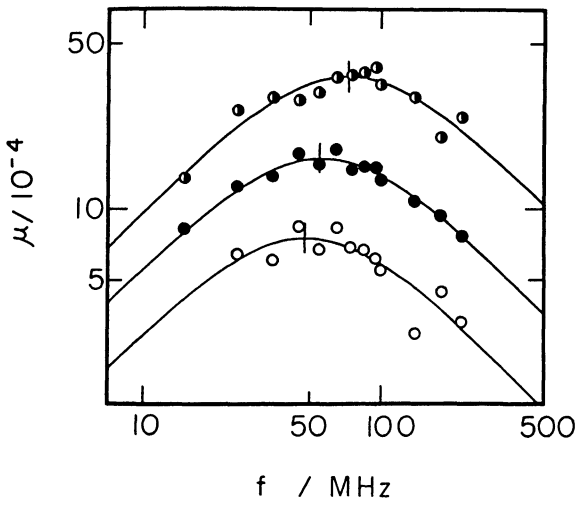

Fig. 2. The representative ultrasonic absorption spectra in aqueous solution of 3-ethoxypropylamine at 25 °C.
○: 0.0489 mol dm^{-3}, ●: 0.127 mol dm^{-3}, ◑: 3.028 mol dm^{-3}.

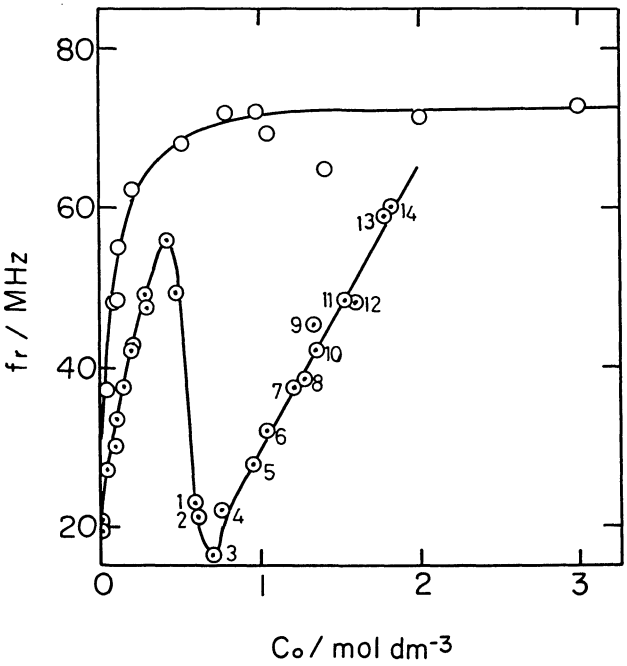

Fig. 3. Concentration dependence of the apparent relaxation frequency for aqueous solutions of 3-ethoxypropylamine (○) and 3-butoxypropylamine (◉).

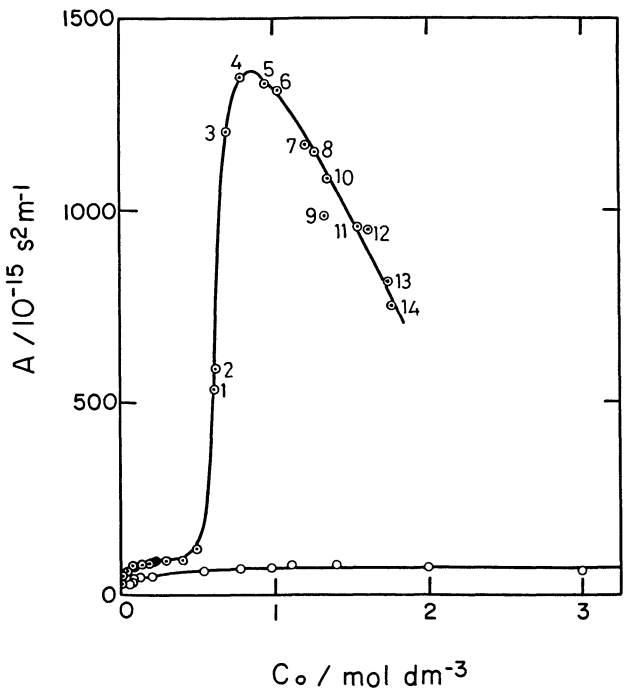

Fig. 4. Concentration dependence of the apparent amplitude of the relaxational absorption for aqueous solutions of 3-ethoxypropylamine (○) and 3-butoxypropylamine (◉).

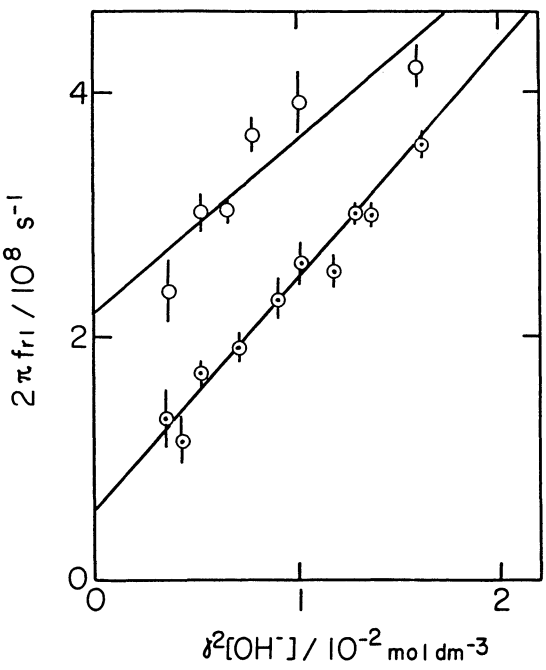

Fig. 5. The plots of the relaxation frequency, f_{r1} $\gamma^2[OH^-]$ for aqueous solutions of 3-ethoxypropylamine (○) and 3-butoxypropylamine (◉).

dependences of the relaxation frequency and the relaxational amplitude, thus calculated, are presented in Figs. 3 and 4 for both solutions. The obtained ultrasonic absorption coefficients as a function of the frequency (12 concentrations for 3-ethoxypropylamine solution and 26 concentrations for 3-butoxypropylamine) and the ultrasonic parameters including the probable errors as a function of concentration are available upon request to one of the authors, S. N. As can be seen in Fig. 3, the relaxation frequency for the solutions of 3-ethoxypropylamine increases monotonously with the analytical concentration, C_o, and tends to reach a plateau at more than 1 mol dm^{-3}. The relaxational amplitude also increases and shows a plateau at more than 0.5 mol dm^{-3} (Fig. 4). On the other hand, in the solutions of 3-butoxypropylamine, the relaxation frequency indicates a discontinuous trend regarding the concentration. The relaxational amplitude shows a similar dependence at less than 0.4 mol dm^{-3}, as that for 3-ethoxypropylamine, and increases dramatically at more than 0.4 mol dm^{-3}. It then goes through a maximum at 0.8 mol dm^{-3}. The smooth changes of the relaxation frequency and the relaxation amplitude for 3-ethoxypropylamine seem to suggest that a perturbation of only one equilibrium is the cause of relaxational absorption. On the other hand, the curious dependences of the ultrasonic parameters in 3-butoxypropylamine may indicate that another cause of the absorption also exists in concentrations of more than 0.5 mol dm^{-3}. However, the dependences of the ultrasonic parameters on the analytical concentration at a low concentration range of less than 0.6 mol dm^{-3} for the 3-ethoxypropylamine solution and 0.4 mol dm^{-3} for the 3-butoxypropylamine solution are similar. We therefore first tried to analyze the results at these concentration ranges.

Such dependences of the ultrasonic parameters are characteristic of a perturbation of an equilibrium associated with the proton-transfer reaction of amine. It is generally described by

$$R\text{-}NH_3^+ + OH^- \underset{k_{21}}{\overset{k_{12}}{\longleftrightarrow}} R\text{-}NH_3^+\cdots OH^- \underset{k_{32}}{\overset{k_{23}}{\longleftrightarrow}} R\text{-}NH_2 + H_2O, \quad (2)$$

where k_{ij} is the rate constant for each step. The relation between the relaxation frequency and the concentrations of the reactants is given by the following equation on the assumption that the effect of the second step on the first one is either small or negligible:

$$2\pi f_{r1} = 2k_{12}\gamma^2[OH^-] + k_{21}, \quad (3)$$

where γ is the activity coefficient, which can be estimated by the Davis equations,[14] subscript 1 for the relaxation frequency is indicated in order to distinguish the other process shown next. Figure 5 shows plots of $2\pi f_{r1}$ vs. $\gamma^2[OH^-]$ for the two solutions, the slope and intercept of which provide the forward and backward rate constants. It should be noticed that the intercept is not close to zero. The rate constants, thus obtained, are listed in Table 1.

Table 1. The Kinetic and Thermodynamic Constants for the Proton-Transfer Reaction in Aqueous Solutions of 3-Ethoxypropylamine and 3-Butoxypropylamine at 25 °C

Solute	$10^{-10}\,k_{12}$	$10^{-8}\,k_{21}$	K_{23}	$10^{4}\,K_b$	$10^{6}\,\Delta V_1$
	$mol^{-1}\,dm^3\,s^{-1}$	s^{-1}		$mol\,dm^{-3}$	$m^3\,mol^{-1}$
3-Ethoxypropylamine	1.2±0.2	2.3±0.2	0.0068	1.3±0.4[a] (1.4±0.6)[b]	30
3-Butoxypropylamine	1.8±0.1	0.57±0.08	0.066	2.0±0.5[a] (2.0±0.5)[b]	21

a) Estimated values from the relation, $K_b=\gamma^2[OH^-]^2/(C_o-[OH^-])$. b) The equilibrium constant was determined by the relation between the analytical concentration and the relaxation frequency (Eq. 12 given in Ref. 3). c) All of the rate and thermodynamic constants in this table were determined in the concentration range less than 0.5 mol dm^{-3}.

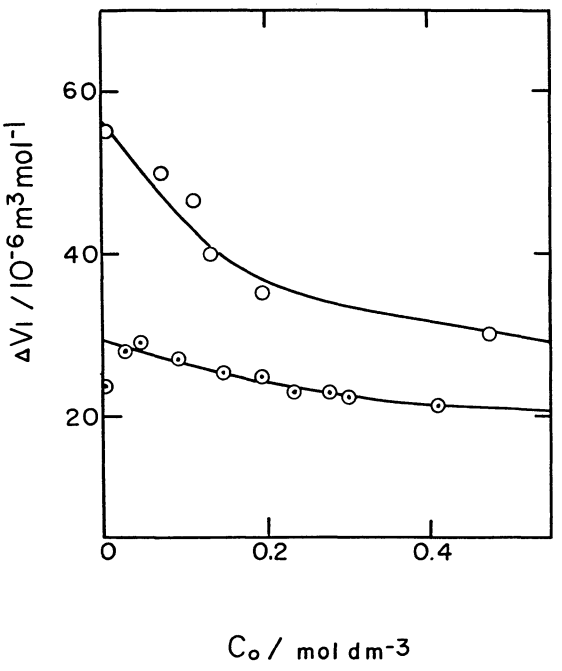

Fig. 6. The concentration dependence of the standard volume change of the proton-transfer reaction for 3-ethoxypropylamine (○) and 3-butoxypropylamine (◉).

For the proton-transfer reaction it is possible to estimate the concentration dependence of the maximum excess absorption per wave length, μ_{m1}, by

$$\mu_{m1}=0.5\,A_1 f_{r1} c=\pi\rho c^2\Gamma_1\,(\Delta V_1)^2/2RT, \quad (4)$$

where ρ is the solution density, ΔV_1 the standard volume change of the reaction and $\Gamma_1=\{2/[OH^-]+1/[R\text{-}NH_3^+\cdots OH^-]+2\partial \ln \gamma/\partial[OH^{-1}]\}^{-1}$. Using the above relation, the volume change has been determined and the results are shown in Fig. 6. Usually, the standard volume change of the reaction has been considered to be concentration independent. However, as can be seen in this figure, it seems to be dependent on the concentration for both solutions. This trend has also been found by Atkinson et al.[16] for an aqueous solution of *t*-butylamine. A detailed analysis by the present authors[15] also shows that the dependence is quite large in relatively dilute solutions, and that it reaches a constant value with increasing concentration. The values which seem to have become constant are listed in Table 1. In these analyses, the ultrasonic absorption results in relatively concentrated solutions were not used, and those in the concentration range of less than 0.5 mol dm^{-3} were taken. The reason will be considered in the discussion section. The equilibrium constant, K_b, for hydrolysis may provide useful information concerning a clarification of the proton-transfer reaction mechanisms. Unfortunately, it has not been previously reported for these aqueous solutions. It has therefore been estimated by the relation $K_b=\gamma^2[OH^-]^2/(C_o-[OH^-])$, where $C_o=[R\text{-}NH_3^+]+[R\text{-}NH_2]+[R\text{-}NH_3^+\cdots OH^-]$. They are also listed in Table 1. It is seen that the equilibrium constants, K_b, are far apart from the ratio of the forward and backward rate constant, k_{21}/k_{12}.

Secondly, we analyze the absorption mechanism observed in the relatively concentrated solution of 3-butoxypropylamine. A different relaxation process is considered to be observed in the solution from the profile of the ultrasonic parameters, as can be seen in Figs. 3 and 4. The relaxational amplitude goes through a maximum, the so-called Peak Sound Absorption Concentration. Similar dependences of the relaxation frequency and the relaxational amplitude on the concentration were observed in the solutions of various butylamines and pentylamines.[1,2,4] Therefore, we have considered that the same reaction may proceed in solution of 3-butoxypropylamine. However, the proton-transfer reaction is also expected to proceed in the solution; then, the values of α/f^2 due to the proton-transfer reaction should be subtracted from the experimental values. In order to carry out this procedure correctly it is appropriate to express the concentration dependences of the pH, the sound velocity and the solution density by proper functions of the analytical concentration. These experimental values were fitted to appropriate polynomials in order to minimize the standard deviations by a least-mean

squares method. They are as follows:

$$pH = 0.28248C_o^{1/2} + 12.037 \quad (0.596—1.902\ \text{mol dm}^{-3}),$$

$$c = 1495.12 + 139.557C_o - 110.401C_o^2 + 24.8807C_o^3 \quad (0—1.8\ \text{mol dm}^{-3}),$$

and

$$\rho = 0.99727 - 3.6015\times10^{-2}\,C_o + 2.5046\times10^{-2}\,C_o^2 - 8.5832\times10^{-3}\,C_o^3 \quad (0—1.8\ \text{mol dm}^{-3}),$$

where the values indicated in the parentheses are the concentration ranges within which the above equations are applicable. Also, the relaxation frequency and the relaxational amplitude at any concentration can be speculated by Eqs. 3 and 4 for the proton-transfer reaction. It is then possible to calculate $(\alpha/f^2)_{\text{residual}}$ which is the residual absorption subtracted those due to the proton-transfer reaction from the experimental values. The residual absorptions were again analyzed by the single relaxational equation; and it was found that they could be reasonably fit to the theoretical curves. The calculated ultrasonic absorption parameters are shown in Figs. 7 and 8; the numbers which correspond to the data are shown in Figs. 3 and 4. As can be seen, the relaxational amplitude are close to those values given in Fig. 4, but are slightly larger, and the increment at a concentration around 0.6 mol dm^{-3} becomes steeper. The relaxation frequencies shift to a slightly lower frequency and tend to increase monotonously, as can be seen in Fig. 7. These results indicate that the absorption is much larger than that due to the proton-transfer reaction. The cause of the residual relaxational absorption is considered to be due to an aggregation reaction associated with the hydrophobicity of the nonionized amine molecules since the relaxation process disappears when the solution pH decreases, it is not found in 3-ethoxypropylamine aqueous solution, and it is not observed when organic solvents are used. In general, although the aggregation reaction may proceed through a stepwise process,[19] we simply assume that it is given by the following formula for a reaction with a small aggregation number:

$$n\,\mathrm{A} \underset{k_{43}}{\overset{k_{34}}{\longleftrightarrow}} \mathrm{A}_n. \tag{5}$$

The relation between the relaxation frequency, f_{r2}, and the reactant concentration is derived as[1]

$$2\pi f_{r2} = n^2 k_{34}[\mathrm{A}]^{n-1} + k_{43} \tag{6}$$

where subscript 2 for the relaxation frequency is used in order to distinguish that for the proton-transfer reaction and n, the aggregation number. In order to analyze the concentration dependence of the ultrasonic parameters, the concentration of the nonionized monomer molecules is necessary. It may be a good approximation that the equilibrium constant of the hydrolysis, defined as $K_b = \gamma^2[\mathrm{OH}^-][\mathrm{R\text{-}NH_3}^+]/([\mathrm{R\text{-}}$

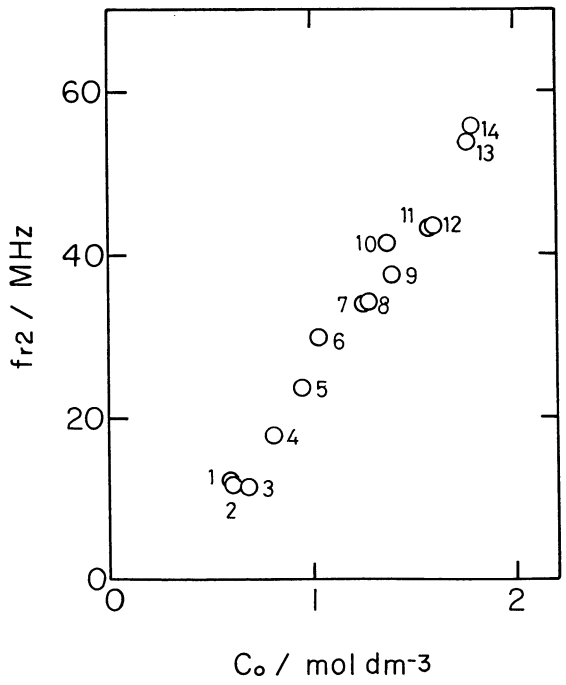

Fig. 7. The concentration dependence of the relaxation frequency, f_{r2}, calculated from the residual absorption for aqueous solution of 3-butoxypropylamine.

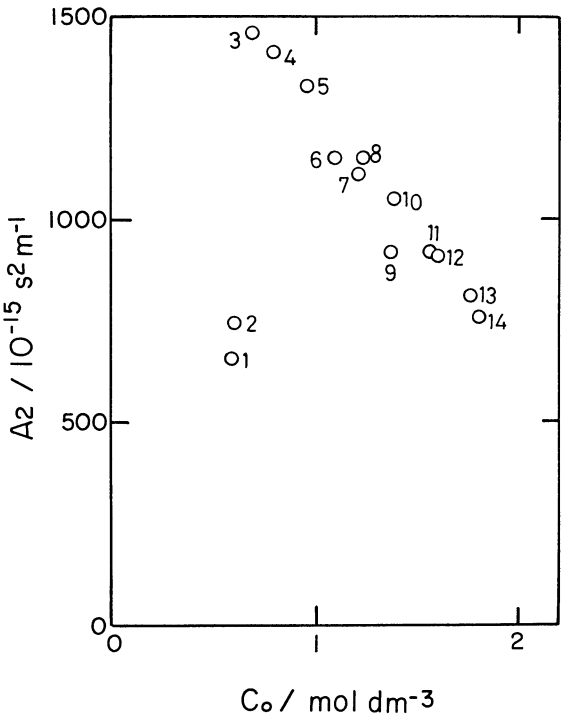

Fig. 8. The concentration dependence of the amplitude of the relaxational absorption, A_2, calculated from the residual absorption for aqueous solution of 3-butoxypropylamine.

$NH_3^+\cdots OH^-]+[R\text{-}NH_2]$), is still held in a slightly concentrated solution. The equilibrium constants for the first and second step in Eq. 2, $K_{12}=k_{21}/k_{12}=\gamma^2[OH^-]^2/[R\text{-}NH_3^+\cdots OH^-]$ and $K_{23}=k_{32}/k_{23}=[R\text{-}NH_3^+\cdots OH^-]/[R\text{-}NH_2]$ may be also defined. Then, Eq. 6 can be arranged as

$$2\pi f_{r2}=n^2(\gamma^2[OH^-]^2)^{n-1}\,k_{34}(1/K_b-1/K_{12})^{n-1}+k_{43}. \quad (7)$$

The aggregation number, n, was changed so as to obtain a least error of plots of $2\pi f_{r2}$ vs. $(\gamma^2[OH^-]^2)^{n-1}$. When $n=3$ the intercept of the plots gave a negative value. By giving more than 4 for the aggregation number, the error is increased. We thus took the aggregation number to be four. Figure 9 shows plots of $2\pi f_{r2}$ vs. $(\gamma^2[OH^-]^2)^3$, which give the backward rate constant, k_{43}, from the intercept to be $(5.7\pm0.8)\times10^7\ s^{-1}$ and the product of the rate and equilibrium constants from the slope. Equation 6 is also arranged using the total concentration of the reactants under consideration, C_o', as

$$2\pi f_{r2}=k_{43}\,nC_o'(\gamma^2[OH^-]^2)^{-1}\,(1/K_b-1/K_{12})^{-1}+(1-n)k_{43}, \quad (8)$$

where

$$C_o'=C_o-[R\text{-}NH_3^+]-[R\text{-}NH_3^+\cdots OH^-]$$
$$=[R\text{-}NH_2]+n[(R\text{-}NH_2)_n].$$

Figure 10 shows plots using Eq. 8 when $n=4$. The obtained backward rate constant, k_{43}, was $(12\pm1)\times10^7\ s^{-1}$ from the intercept, the plots of which gave a better linearity with smaller probable errors. It is therefore shown in Table 2. It seems to be close to that value obtained by Eq. 7. The equilibrium constant, K_b, was thus estimated to be $(3.8\pm0.2)\times10^{-4}$ mol dm^{-3} using the slope and intercept values of linear plots of Eq. 8, since the equilibrium constant, K_{12}, is obtained from the results concerning the proton-transfer reaction. As a result, going back to Eq. 7, it is possible to obtain the forward rate constant, k_{34}, from the slope of the linear plots; it is also shown in Table 2.

The maximum excess absorption per wave length for this process is derived as[1]

$$\mu_{m2}=\pi\,\rho c^2\,k_{34}[A]^n\,\tau\,(\Delta V_2)^2/2RT, \quad (9)$$

where the volume relaxation has been assumed for the above process and $\tau=(2\pi f_{r2})^{-1}$. Once the rate con-

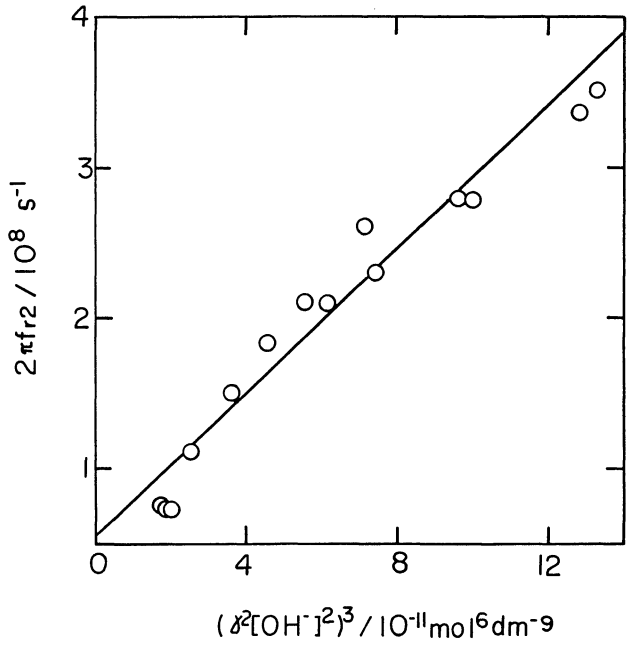

Fig. 9. The plots of $2\pi f_{r2}$ vs. $(\gamma^2[OH^-]^2)^3$ for aqueous solution of 3-butoxypropylamine.

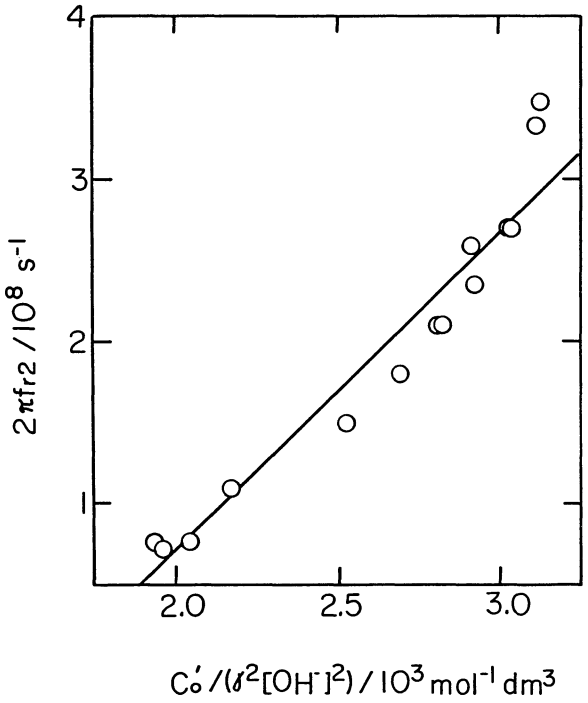

Fig. 10. The plots of $2\pi f_{r2}$ vs. $C_o'/(\gamma^2[OH^-]^2)$ for aqueous solution of 3-butoxypropylamine.

Table 2. Rate and Thermodynamic Parameters for the Aggregation Reactions at 25 °C

Solute	n	$10^{-6}\,k_{34}$	$10^{-7}\,k_{43}$	$10^6\,\Delta V_2$	Reference
		$(mol^{-1}\,dm^3)^{n-1}\,s^{-1}$	s^{-1}	$m^3\,mol^{-1}$	
Butylamine	4	2.2	9.0	14	(1)
3-Butoxypropylamine	4	12	12	21	This work
Pentylamine	5	4.7	3.0	17	(2)

stants, k_{34} and k_{43}, are obtained, the monomer concentration is available. Using the experimental τ values, then, the volume change of the reaction has been estimated, and is given in Table 2.

Discussion

The results of the proton-transfer reaction are first discussed. The forward rate constants, k_{12}, for both solutions are reasonable as a diffusion-controlled reaction.[17] However, the ratio of the forward and backward rate constants, k_{21}/k_{12}, is far apart from the equilibrium constant, K_b, for the hydrolysis, as can be seen in Table 1. Similar results have been obtained in other amine solutions.[3,4,14] The coupling effect of the faster process on the slower one is usually taken into account in order to interpret such phenomena. However, as has been reported in a previous paper,[3] it is rather reasonable that the perturbation of the first step in Eq. 2 is the cause of the observed relaxation and the second step is too fast to affect on the first step. Furthermore, our analytical procedure[3] using the relation between the relaxation frequency and the analytical concentration (Eq. 12 in Ref. 3) has given the reasonable equilibrium constants, K_b, as is shown in Table 1. Another equilibrium constant, K_{23}, was estimated to be less than unity from the relation, $K_b=K_{12}/(1+K_{23}^{-1})$ where the K_b value estimated by the static procedure (listed in Table 1) was used. These results show that the concentration of the intermediate is very small compared with that of R-NH_2. This means that the second step may correspond to a intramolecular proton-transfer and that the intermediate is not very stable. It is expected that this process is too fast to be observed by the time range under study. As can be seen in Table 1, the forward rate constant, k_{12}, is not much affected, even if the structures of amine molecules are different. This means that the most effective term in the reaction includes the diffusion of hyrdoxyl ions in aqueous media. Although only data for relatively dilute solutions of both solutions are used to obtain the proton-transfer reaction rate constants, the same ultrasonic relaxational absorption due to the reaction can be observed in concentrated solutions of 3-ethoxypropylamine (Fig. 3). The relaxation frequencies obtained (more than 0.6 mol dm^{-3}) are lower than those expected from the calculated values (around 100 MHz) using Eq. 2. This might be because a solute-solute interaction, such as the interaction due to hydrogen bonding, interrupts the proton-transfer reaction. However, the aggregates associated with the hydrophobicity of the solute (discussed next) may not exist in solution of 3-ethoxypropylamine. Another possibility may be due to an alternation of the solvent water structure by the addition of an amine at the high-concentration range.

It is not very clear why the volume change of the reaction is dependent on the concentrations of both solutions. One of the reasons might be that the approximation of the volume relaxation for the proton-transfer reaction is not appropriate. If it includes a thermal-relaxation term, the volume change, ΔV_1, should be expressed as $\Delta V_1=\Delta V_{real}-\alpha_p\Delta H/\rho C_p$, were α_p is the thermal expansion coefficient, ΔH the standard enthalpy change of the reaction, and C_p the specific heat at constant pressure. However, without this experimental information concerning α_p and C_p, no definite conclusion can be given at this stage.

Next, the absorption mechanism observed in a relatively concentrated solution of 3-butoxypropylamine is discussed. The difference in the absorption characters from those in solution of 3-ethoxypropylamine can clearly be seen in the profiles given in Figs. 3 and 4; that is, the relaxational amplitude increases steeply and goes through a maximum. Although the original ultrasonic absorption spectra look like those due to single relaxational absorption, as was analyzed in a previous section, the spectra associated with two relaxation processes are considered to be superimposed since the relaxational amplitude due to the proton-transfer reaction is much smaller than that newly observed in the relatively concentrated solution, and the respective relaxation frequencies are not very far apart. Ideally, two relaxation processes should be distinguished by the double relaxational equation (i=2 in Eq. 1) using the observed values of the absorp-

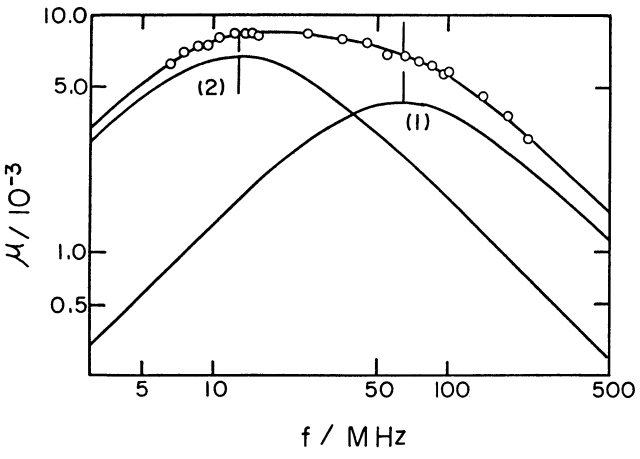

Fig. 11. The spectrum analyzed by the double relaxational equation for 3-butoxypropylamine at 0.605 mol dm^{-3}. The calculated parameters are f_{r1}=(64.4±5.5) MHz, A_1=(88.5±10.5)×10^{-15} s^2m^{-1}, f_{r2}=(12.7±0.6) MHz, A_2=(690.8±16.1)×10^{-15} s^2m^{-1} and B=(27.2±0.8)×10^{-15} s^2m^{-1}. The parameters obtained by the extrapolation by Eqs. 3 and 4 are f_{r1}=79.8 MHz and A_1=90.3×10^{-15} s^2m^{-1} and those calculated by the procedure shown in result section are f_{r2}=11.7 MHz, A_2=745.5×10^{-15} s^2m^{-1} and B=22.3×10^{-15} s^2m^{-1}.
(1): The absorption due to the proton transfer reaction and (2): That due to the aggregation reaction.

tion coefficients. Then, applying the double relaxational equation to the data at more than 0.5 mol dm^{-3}, unrealistic ultrasonic parameters were obtained (e.g. negative ultrasonic parameters and the larger probable errors than the most probable values), except those at 0.596 and 0.605 mol dm^{-3} These data correspond to those indicated by the number, 1 and 2, in Figs. 3 and 4. At these limited concentrations, the relaxation amplitudes are not very much larger and the relaxation frequencies are still quite far apart from that due to the proton transfer. Also, the deviations from the calculated values in the original spectra have been found, as can be seen in Fig. 1. Figure 11 shows one of the spectra calculated by the double relaxational equation at such intermediate concentrations. Thus, the calculated ultrasonic parameters at these two concentrations are very close to those determined in the previous section. These calculations indicate that the superimposed spectra are observed at more than 0.65 mol dm^{-3}. The subtraction procedure used to obtain the ultrasonic parameters given in the previous section seems to be appropriate.

Even if the ether oxygen, which produces hydrophilic activity, is introduced to the molecule, the butyl group seems to play fairly the rule as the hydrophobic interaction. Thus, a small aggregate exists in aqueous media. It should be noticed that the equilibrium constant, K_b, estimated from the aggregation reaction given by Eq. 8, (K_b=3.8×10^{-4} mol dm^{-3}) seems to be close to that obtained in the lower concentration range listed in Table 1. This also supports the idea that the cause of the relaxational absorption is due to reaction associated with aggregates of the nonionized amine molecules. The slightly larger value may be due to a solute-solute interaction, such as a hydrogen-bonding interaction in the relatively concentrated solutions. The aggregation number is close to that in a solution of pentyl or butylamine. This might mean that the activity of the hydrophobicity is close to that of the alkylamines, which have five or four carbon atoms. We speculate that the propyl group has a border activity regarding hydrophobicity to form the aggregate. This is also considered to be true from the fact that the relaxation associated with the aggregation reaction is observed in an aqueous solution of propyl alcohol,[18] although it is not found in a aqueous solution of propylamine. The hydroxyl group may be considered to be less hydrophilic than the amino group. This is also recognized from the solubility difference between the butyl alcohol and butylamine in water. It is interesting to compare the ultrasonic results with those in solutions of pentylamine and butylamine,[1,2] which have previously been reported and are also shown in Table 2. The position of the peak sound absorption concentration in the present solution is lower than that of butylamine. The relaxational amplitude is larger than that of butylamine. These differences seem to indicate that the hydrophobicity of 3-butoxypropylamine is slightly larger than butylamine. This comparison may indicate that the propyl group bonded with the ether oxygen has a slightly the hydrophobic character, which increases the hydrophobicity of the entire molecule. A similar comparison between 3-butoxypropylamine and pentylamine shows that the former is less hydrophobic than the latter. It can then be easily understood why such aggregate is not formed in solution of 3-ethoxypropylamine. Either the ethyl group is too small to form an aggregate through a hydrophobic interaction, or the ether oxygen acts as the hydrophilicity, thus preventing the formation of an aggregate by the hydrophobic interaction.

Finally, it may be meaningful to indicate that the concentration dependence of the relaxation frequency for the aggregation reaction (Eq. 8 used in this study) is very similar to that proposed theoretically by Teubner[19] and widely used.[20,21] That is, the relaxation frequency is proportional to $C_0'/[A]$ in both treatments, even though the former corresponds to a variance of the size distribution of unity and $k_{43}n$ is k^-/m when k^- is the mean of the dissociation rate constant and m is the mean aggregation number.

Although the two relaxation processes due to both proton-transfer and aggregation reactions were observed in the same ultrasonic frequency range in the present study, the coupling effect of the two reactions may be ignored since a very fast intramolecular reaction proceeds between the above-two reactions under consideration.

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