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Proton Transfer and Aggregation Reactions in Aqueous Solutions of Isobutylamine and Isopentylamine Studied by Ultrasonic Methods

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Ultrasonic absorption and velocity measurements have been performed in aqueous solutions of isobutylamine and isopentylamine at 25 °C. Two different relaxation phenomena are observed in these sample solutions. One of them, observed at a high frequency range, has been attributed to a proton transfer reaction of amines from the concentration dependence of the relaxation frequency and the maximum excess absorption per wavelength. The rate and thermodynamic constants have been determined for ion-pair formation and dissociation. The other, observed at a low frequency range becomes more striking as the hydrophobicity of the solute increases; it has been considered that the cause of the relaxation may be associated with a hydrophobic interaction. The formation of small aggregates has been speculated in both solutions. The rate and thermodynamic constants for the association and dissociation reactions of nonionized amine molecules have been estimated from the concentration dependences of the relaxation frequency and the maximum excess absorption per wavelength. Furthermore, the coupling effect of the two relaxation processes has been discussed briefly.

In a previous study[1] concerning the ultrasonic absorption mechanisms in aqueous solutions of isomeric butylamines, we have shown the existence of two different relaxational processes in the frequency range from 6.5 to 220 MHz from the measurements of the absorption coefficients as a function of the frequency. One of these processes has been attributed to a perturbation of the $R\text{-}NH_3^+ + OH^- \leftrightarrow R\text{-}NH_3^+ \cdots OH^-$ equilibrium. We have predicted from some experimental facts that the other may be due to the aggregation reaction of a nonionized solute.[2] The ultrasonic property due to this reaction is very dependent on the size of the hydrophobic groups. Atkinson et al.,[3] on the other hand, have analyzed the ultrasonic absorption results in an aqueous solution of *t*-butylamine on the basis of the hydrolysis and fluctuation model proposed by Romanov et at.[4] In order to clarify the justification of the interpretation of the ultrasonic absorption results in aqueous solutions of various amines over a wide concentration range and in order to substantiate the effect of the size of the hydrophobic groups on the ultrasonic absorption properties, the accumulation of many ultrasonic absorption results has been earnestly desired. The purpose of the present investigation is to report the ultrasonic absorption and velocity results for aqueous solutions of isobutylamine and isopentylamine as a function of their concentrations and to provide information about the dynamics of their solutions. Further, the analytical procedure of the relaxation times for the studies of fast reactions in solutions is examined for a system where two relaxation processes are observed in an equivalent time region.

Experimental

The isobutylamine and isopentylamine were purchased from Wako Pure Chemicals and then distilled. The desired concentrations of the aqueous solutions were prepared with doubly distilled water by weight.

The ultrasonic measurements were performed over the frequency range from 3.5 to 220 MHz by the use of semiautomatic pulse equipment connected with an 8 bit microcomputer. The computer programs had been developed so as to obtain the absorption spectrum elegantly. It is necessary to see the linearity of the attenuation vs. the moving distance of the transducer in order to obtain the absorption coefficient accurately. Such plots are seen on a display just after the measurements; when the error of the plots is less than 2%, the absorption coefficient is stored. Once the measurements at the available frequencies are performed, the computer program goes to the determination of the ultrasonic parameters. The details of the calculation procedure have been described elsewhere.[5]

The sound velocity was measured by a sing around method at 1.92 MHz and by use of an interferometer at 2.5 MHz. The accuracies are within 1 m s^{-1}. The densities of the solutions were determined by the use of a pycnometer, volume of which was about 4 cm^3. The pH's of the solutions were measured by means of a Hitachi-Horiba pH meter with a glass electrode. All the ultrasonic and pH measurements were carried out under a dry nitrogen gas in order to prevent the contamination of the solutions with carbon dioxide.

Results and Discussion

In order to interpret the ultrasonic absorption mechanisms, there are several procedures. The most effective one is to see how the absorption coefficient, α, depends on the measurement frequency, f.[6] When the absorption is related to the fluctuation in solutions attributable to the critical mixtures, as is occasionally seen in various amine aqueous solutions, the absorption would show unusual tendencies, e.g., an abnormal increase in the absorption coefficient when the system is close to the critical point. However, in the amine solutions studied here, the absorption did not show such trends in our frequency range and the values of α/f^2 tend to show a plateau at a low frequency range. Therefore, the absorption coefficients, as a function of the frequency in the aqueous solutions of the two amines, have been tested by the equation associated with the usual relaxation process.[6]

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

or

$$\mu=\sum_i A_i fc/[1+(f/f_{ri})^2], \qquad (2)$$

where f_{ri} is the relaxation frequency for the i-th process. μ the excess absorption per wavelength, c the sound velocity, and A_i and B the constants. Some typical ultrasonic spectra for isopentylamine and isobutylamine are shown in Figs. 1 and 2 respectively.

For the isopentylamine aqueous solution, a double relaxational equation (i=2 for Eq. 1 or 2) has been found to fit the experimental data well in the concentration range from 0.4 to 1.77 mol dm^{-3}. In the range less than 0.4 mol dm^{-3}, the ultrasonic spectra are well-expressed by a single relaxational equation, i.e. i=1 in Eq. 1 or 2. The ultrasonic parameters, f_{ri}, A_i, and B have been determined by means of a nonlinear least-mean-square method; the solid curves indicate the calculated values. The parameters obtained are listed in Table 1.

For the isobutylamine solution, the spectra in the concentrations below 0.719 mol dm^{-3} are well fitted to the single relaxational equation. Further, with increase in the concentration the spectra still look like those associated with a single relaxation process. Figures 3 and 4 show the amplitude of the excess absorption, A, and the relaxation frequency, f_r which have been determined by a single relaxational equa-

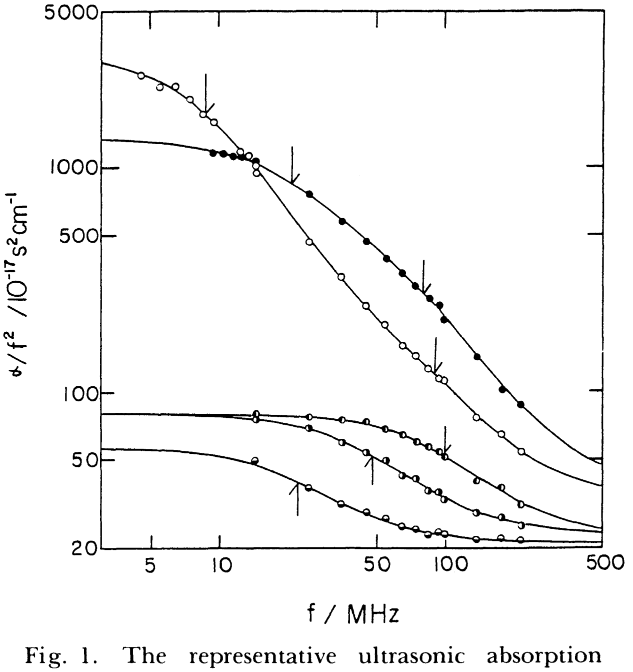


Fig. 1. The representative ultrasonic absorption spectra in aqueous solution of isopentylamine at 25 °C. ●: 1.50 mol dm^{-3}, ○: 0.700 mol dm^{-3}, ◐: 0.221 mol dm^{-3}, ◑: 0.050 mol dm^{-3}, ◒: 0.0070 mol dm^{-3}. The arrows show the positions of the relaxation frequency.

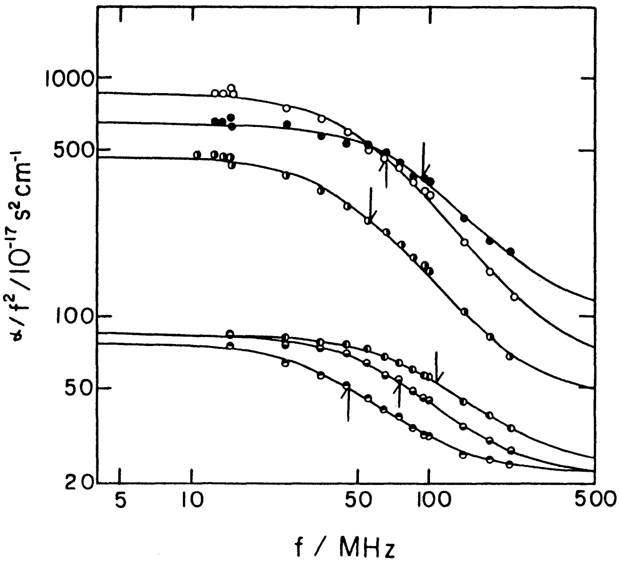


Fig. 2. The representative ultrasonic absorption spectra in aqueous solution of isobutylamine at 25 °C. ●: 2.75 mol dm^{-3}, ○: 1.75 mol dm^{-3}, ◑: 1.29 mol dm^{-3}, ◐: 0.566 mol dm^{-3}, ◒: 0.243 mol dm^{-3}, ◓: 0.0784 mol dm^{-3}.

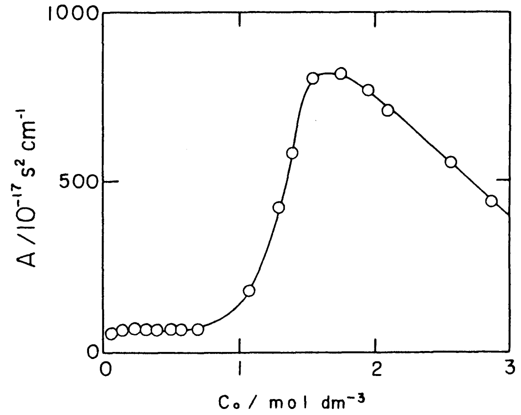


Fig. 3. Concentration dependence of the amplitude excess absorption, A, for aqueous solution of isobutylamine. They are those determined by a single relaxational equation.

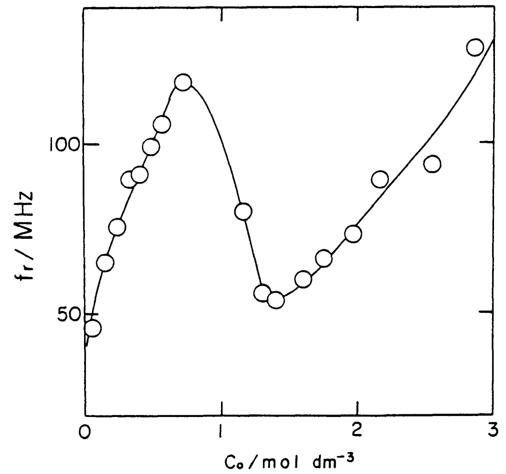


Fig. 4. Concentration dependence of the relaxation frequency f_r, for aqueous solution of isobutylamine.

Table 1. Ultrasonic and Thermodynamc Parameters for Aqueous Solutions of Isopentylamine and Isobutylamine at 25 °C

Concn	pH	ρ	c	f_{r1}	f_{r2}	A_1	A_2	B
mol dm^{-3}		g cm^{-3}	m s^{-1}	MHz		10^{-17} s^2 cm^{-1}		
			(Isopentylamine)					
0.0070	11.17	0.9970	1497	22		36		21
0.0097	11.25	0.9970	1496	25		40		22
0.0170	11.39	0.9969	1497	36		46		21
0.0283	11.51	0.9965	1498	38		52		22
0.0500	11.64	0.9964	1499	48		56		23
0.0997	11.80	0.9960	1503	64		60		21
0.119	11.84	0.9952	1503	78		60		21
0.150	11.89	0.9950	1508	83		64		19
0.221	11.98	0.9939	1509	100		58		22
0.350	12.09	0.9915	1524	124		68		18
0.601	12.31	0.9878	1498	109	6.4	84	3815	26
0.652	12.32	0.9858	1495	96	7.9	113	3957	26
0.700	12.33	0.9857	1492	90	8.8	114	3154	33
0.751	12.35	0.9849	1490	62	9.2	225	3502	41
0.800	12.36	0.9836	1489	73	12	184	2738	35
1.282	12.38	0.9700	1488	43	13	687	865	55
1.500	12.38	0.9660	1487	80	21	347	965	37
1.770	12.39	0.9600	1486	79	26	325	548	57
			(Isobutylamine)					
0.0784	11.60	0.9965	1501	46		56		22
0.158	11.78	0.9954	1505	65		63		21
0.243	11.90	0.9942	1513	75		64		21
0.322	11.97	0.9932	1515	90		61		22
0.403	12.04	0.9921	1522	91		61		23
0.482	12.08	0.9912	1529	99		64		22
0.566	12.16	0.9900	1534	106		61		23
0.719	12.22	0.9878	1543	118		68		21
1.13	12.32	0.9812	1560	142*	54	84*	118	21
				(80)		(181)		(32)
1.29	12.36	0.9811	1566	152*	44	87*	384	27
				(56)		(425)		(45)
1.40	12.38	0.9775	1569	157*	44	89*	546	30
				(54)		(580)		(51)
1.59	12.41	0.9744	1568	165*	54	91*	754	26
				(60)		(807)		(50)
1.75	12.42	0.9710	1564	168*	60	91*	764	38
				(66)		(815)		(62)
1.97	12.44	0.9672	1558	174*	66	91*	718	47
				(73)		(769)		(69)
2.16	12.45	0.9629	1549	177*	72	92*	640	64
				(79)		(705)		(81)
2.57	12.47	0.9562	1536	183*	83	92*	487	83
				(93)		(554)		(99)
2.87	12.48	0.9465	1522	186*	117	94*	355	63
				(127)		(439)		(71)

The ultrasonic parameters indicated in parentheses for the solution of isobutylamine are those calculated by a single relaxational equation. Those indicated by the super asterisk are calculated using Eqs. 4 and 7.

tion as a function of the analytical concentration, C_o, for the isobutylamine solution. As may be seen in these figures, the excess absorption amplitude, A, increases suddenly around 1 mol dm^{-3} and goes through a maximum. Further, the relaxation frequency also indicates an unusual trend at around 1 mol dm^{-3}. Therefore, it is considered that the cause of the absorption in the high concentration range differs from that in the low concentration range. Therefore, it may be necessary to distinguish the multiple relaxation processes, which we will describe later.

Firstly, in order to analyze the excess absorption mechanisms in the two solutions, the absorptions in a relatively low concentration range (less than 0.4 mol dm^{-3} for isopentylamine and less than 1 mol dm^{-3} for isobutylamine) are considered. The characteristic properties of the ultrasonic absorption are that the relaxation frequencies increase monotonously with the analytical concentration and that the amplitudes of the excess absorption indicate a plateau, as may be seen in Table 1. Such dependences have been observed in various amine solutions, and the absorptions have been well analyzed by the reaction kinetics of the hydrolysis.[1,2,7-9] As has been pointed out in a previous report,[1] the amine hydrolysis in aqueous media proceeds through an intermediate, which is expressed by the next equilibria:

$$\text{R-NH}_3{}^+ + \text{OH}^- \xleftrightarrow[k_{21}]{k_{12}} \text{R-NH}_3{}^+\cdots\text{OH}^- \xleftrightarrow[k_{32}]{k_{23}} \text{R-NH}_2 + \text{H}_2\text{O} \qquad (3)$$

This reaction mechanism was originally proposed by Eigen.[8] When the relaxation frequencies associated with the above two steps are close to each other, the coupling effects on the relaxation frequencies and the amplitudes of the relaxations should be taken into account. However, the observed ultrasonic absorption spectra is clearly expressed by a single relaxational equation. When the coupling effect is considered, an unreasonable dissociation constant, K_b, is obtained, which has been described in detail in Ref. 1. Therefore, we have assumed that the observed relaxation phenomena are due only to a perturbation of the equilibrium of the first step in Eq. 3. The relation between the relaxation frequency and the reactant concentration is simply expressed as:

$$2\pi f_{r1} = \gamma^2([\text{R-NH}_3{}^+]+[\text{OH}^-])k_{12}+k_{21}, \qquad (4)$$

where f_{r1} is the relaxation frequency observed in the higher frequency range and γ the ion activity coefficient which is calculated by the use of the Davies equation.[10] Figure 5 shows the plots of f_{r1} vs. $\gamma^2[\text{OH}^-]$, the intercept and slope of which provide the rate constants. These good linearities confirm that the cause of the excess absorption is the hydrolysis of the amines. The rate constants obtained are tabulated in Table 2. The dissociation constant, K_b, is related to each equilibrium constant as

$$K_b = K_{12}/(1+K_{32}{}^{-1}) \qquad (5)$$

where $K_{12}=k_{21}/k_{12}$ and $K_{32}=k_{32}/k_{23}$. Therefore, K_{32} may be calculated; it is also shown in Table 2. The relation between the relaxation frequency and the analytical concentration is derived, under the same assumption, as:[1]

$$2\pi f_{r1} = k_{12}[-K_b+(-K_b{}^2+4\gamma^2 C_0 K_b)^{1/2}]+k_{21}. \qquad (6)$$

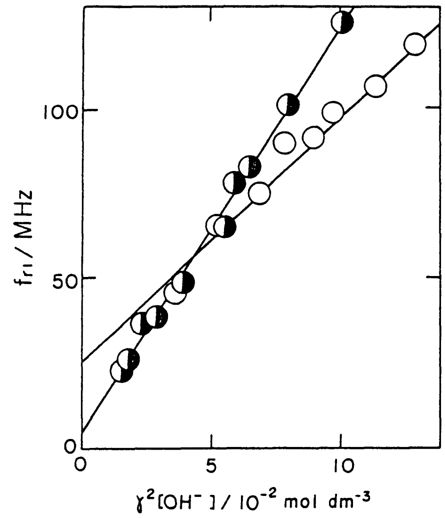


Fig. 5. The plots of f_{r1} vs. $\gamma^2[\text{OH}^-]$ for the analysis of the proton transfer reaction. ◑: isopentylamine, ○: isobutylamine.

Using this equation, it is possible to estimate whether or not the above interpretation is reasonable. The dissociation constants, K_b, have been calculated; they are close to those in the literature.[11]

Another important parameter obtained by the ultrasonic absorption and velocity measurements is the maximum excess absorption per wavelength, μ_{m1};[6]

$$\mu_{m1} = 0.5A_1 f_{r1} c = \pi\rho c^2 \Gamma(\Delta V_1 - \alpha_p \Delta H/\rho C_p)^2/2RT, \qquad (7)$$

where ρ is the solution density, ΔV_1 the standard volume change of the reaction, ΔH the standard enthalpy change of the reaction, α_p the thermal expansion coefficient at the high frequency limit, C_p the specific heat, and Γ the concentration term, which is expressed for the reaction under consideration as:

$$\Gamma = \{1/[\text{R-NH}_3{}^+]+1/[\text{OH}^-] + 1/[\text{R-NH}_3{}^+\cdots\text{OH}^-]\}^{-1}. \qquad (8)$$

Since the enthalpy term can be quite small compared with the volume term for proton transfer reactions in general, the enthalpy term is neglected. As a result, the plots of μ_{m1} vs. $\rho c^2\Gamma$, which are shown in Fig. 6, provide the standard volume change of the reaction. The results are also given in Table 2. The volume changes thus obtained are very close to those for other amine hydrolysis obtained by use of the ultrasonic method.[8]

Table 2. The Rate and Thermodynamic Constants for Proton Transfer Reaction in Aqueous Solutions of Isopentylamine and Isobutylamine at 25 °C

Solute	$10^{-10}\,k_{12}$	$10^{-8}\,k_{21}$	K_{32}	$10^4\,K_b$[a)]	ΔV_1
	mol^{-1} dm^3 s^{-1}	s^{-1}		mol dm^{-3}	cm^3 mol^{-1}
Isobutylamine	2.3	1.7	0.035	2.5 (3.3)	27
Isopentylamine	3.7	0.39	0.51	3.7 (4.4)	26

a) The dissociation constants have been determined from the ultrasonic absorption measurements using Eq. 6. The values in parentheses are those in the literature.[11]

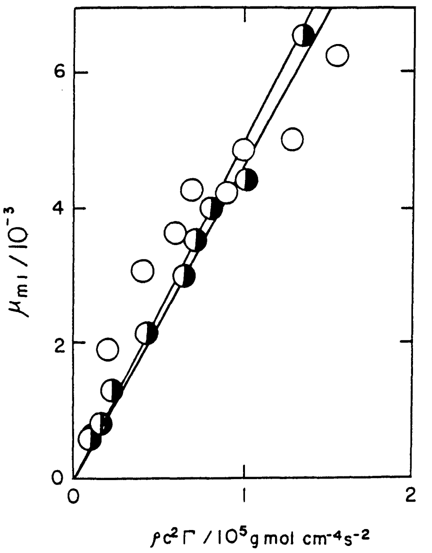


Fig. 6. The plots of μ_{mi} vs. $\rho c^2\Gamma$ for the determination of the standard volume change of the reaction. ◑: isopentylamine, ○: isobutylamine.

However, they seem to be slightly larger than those obtained by the static method.[12] This might be because the latter are the over all results for the hydrolysis reaction, while the former are those for only the first step of the ion-pair formation process. The forward rate constants are reasonable for diffusion controlled reactions in the aqueous media. The equilibrium constant, K_{32}, which is smaller than unity, indicates that the intermediate concentration is small.

Secondly, the excess absorption mechanism in the concentrated solutions will now be considered. This phenomenon is observed in the lower frequency range. In the analysis of the absorption spectra, it is now necessary to distinguish the multiple relaxations. When two relaxation frequencies are far apart in a measured frequency range, it might be suitable to analyze the experimental results using eigher Eq. 1 or 2, as i=2. This may be appropriate in the case of the isopentylamine aqueous solution. The calculated ultrasonic parameters are listed in Table 1 in the concentration range above 0.6 mol dm^{-3}. However, for aqueous solutions of isobutylamine, the spectra look like a single relaxation one, so the above procedure for the determination of the ultrasonic parameters is not adequate. The parameters calculated using the single relaxational equation are indicated in the parentheses in Table 1 for the concentration range above 1 mol dm^{-3}. Fortunately, the excess absorption associated with the hydrolysis, which is observed in the higher frequency range and in the dilute solutions, may be expected to take place also in the concentrated solutions. Therefore, once the concentrations of the reactants for the hydrolysis are determined, the amplitude of the excess absorption and the relaxation frequency can be predicted by the use of Eqs. 4, 7, and 8. We have, then, assumed that the ultrasonic absorption due to the hydrolysis should be subtracted from the experimental data. As a result, it is possible to see if the residual absorptions fit Eq. 1 or 2. It is found that they have been well-analyzed by the single relaxational equation. The ultrasonic parameters obtained in this way are listed in Table 1 for the isobutylamine solutions in the concentration range above 1.13 mol dm^{-3}. Figure 7 shows an example of an absorption in which the two relaxation processes in the solution are distinguished. The experimental values all fit the calculated curves perfectly. There is some experimental evidence[2] concerning the excess absorption under consideration. (1) Such excess absorption is not observed in the aqueous solutions of propylamine and ethylamine. (2) The amplitude of the excess absorption increases and then decreases with the concentration; this is the so called "PSAC" (peak sound absorption concentration). This phenomenon becomes more striking with an increase in the hydrophobicity of the solute and is also observed in aqueous solutions of alcohols and ethers. (3) In an orgaic solvent, however, it is not found. (4) When the solute is ionized, the excess absorption disappears. These facts lead us to predict that the excess absorption may be associated with the hydrophobic effect of the nonionized solute molecules. The most plausible mechanism seems to be a molecular aggregation reaction by means of the hydrophobic interaction, which might be close to the micelle formation of surface active agents. However, such big micelles may not be formed because the hydrophobic groups of isobutylamine and isopentylamine are not very large. Actually, there have been several theories[13,14] to interpret the micelle formation

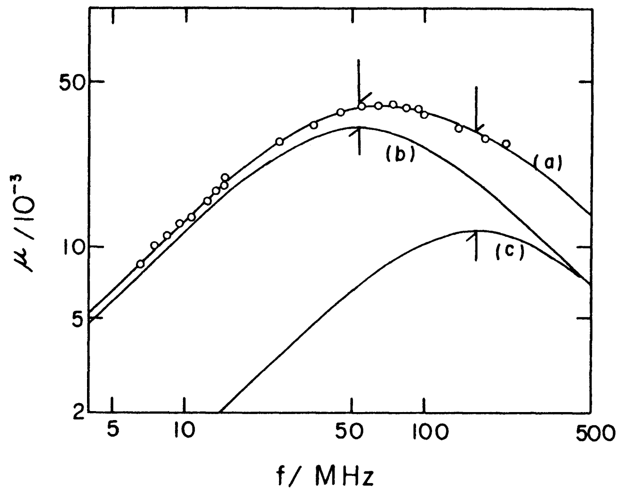


Fig. 7. The frequency dependence of the excess absorption per wavelength for 1.59 mol dm^{-3} isobutylamine aqueous solution. ○'s are the experimental values. The curve (c) is the calculated excess absorptions per wavelength associated with the proton transfer reaction and the curve (b) is those associated with the aggregation reaction. The solid curve (a) is the sum of the two relaxational curves, (b) and (c).

and breakage kinetics. However, they all assume the distribution of the aggregates, which is only applicable when the aggregation number is quite large. Therefore, we will simply consider the perturbation of the following equilibrium by the sound wave:

$$nA \underset{k_{43}}{\overset{k_{34}}{\longleftrightarrow}} A_n, \tag{9}$$

when n is the aggregation number. The relation between the relaxation frequency and the reactant concentration is given by the next equation:[15,16]

$$2\pi f_{r2} = 1/\tau = k_{34}n^2[A]^{(n-1)} + k_{43}, \tag{10}$$

where τ is the relaxation time and [A] the equilibrium concentration of the free nonionized solute. If the equilibrium constant (dissociation constant), K_b, in the concentration range is still satisfactorily expressed by $K_b=\gamma^2[R\text{-}NH_3^+][OH^-]/[R\text{-}NH_2]$, it is possible to determine the monomer concentration, [A], from the pH measurement, because the two equilibrium constants in Eq. 3 have been determined. Then, it may be possible to estimate the rate constants using an appropriate aggregation number, n. The plots of f_{r2} vs. $[A]^{(n-1)}$ are shown in Fig. 8. The best straight lines have been obtained for the aqueous solution of isobutylamine when n=4 and for that of isopentylamine when n=5. For the isobutylamine solution, the forward and backward rate constants have been determined from the slope and the intercept. They are listed in Table 3. However, the intercept of the plots for the isopentylamine solution is very close to zero. Therefore, it is not suitable for determining the backward rate constant. Equation 10 is also expressed in a different form with the analytical concentration as follows:[16]

$$2\pi f_{r2} = k_{43}n^2C_o/[A] + (1-n)k_{43}. \tag{11}$$

If the above procedure is correct, the same rate constant may be determined by the use of Eq. 11. For the isobutylamine solution, the values of k_{43} have been determined to be 2.7×10^8 s^{-1} from the slope and 3.0×10^8 s^{-1} from the intercept; these values are very close to that in Table 3. For the isopentylamine solution, the values have been determined to be 1.5×10^7 s^{-1} and 1.4×10^7 s^{-1} from the slope and the intercept respectively; the mean values are listed in Table 3.

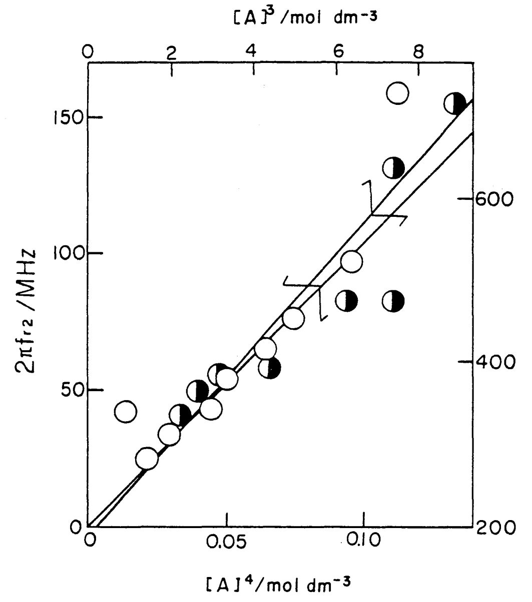


Fig. 8. The plots of $2\pi f_{r2}$ vs. $[A]^{(n-1)}$ for the two aqueous solutions. ◑: isopentylamine, ○: isobutylamine.

Now, the concentration dependence of the maximum excess absorption per wavelength, μ_{m2}, will be explained. It is derived as follows:[16]

$$\mu_{m2} = \pi\rho c^2(\Delta V_2)^2 k_{34}[A]^n\tau/2RT, \tag{12}$$

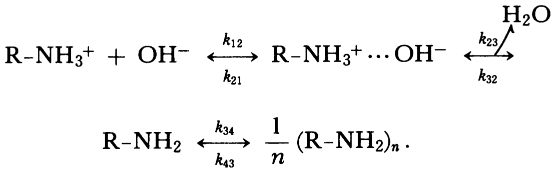
where ΔV_2 is the standard volume change of the aggregation reaction. For simplicity, only the volume relaxation has been assumed. The plots of $\ln(\mu_{m2}/\rho c^2\tau)$ vs. ln[A] provide the aggregation numbers, which have been found to be 3.7±0.2 for the isobutylamine solution and 4.9±1.2 for the isopentylamine solution. These results also confirm that the cause of the excess absorption is the aggregation reaction by the nonionized solute molecules. The standard volume changes of the reaction, ΔV_2 have been calculated with the help of Eq. 12; they are listed in Table 3, along with the results for butylamine[16] and pentylamine[2] solutions. As may be seen in the table, the association rate constant tends to increase with an increase in the hydrophobicity of the solute. On the other hand, the dissociation rate constant seems to decrease with an increase in the carbon number. These results may reflect the stability of the aggregate. Cabani et al.[17] have studied in detail the volumetric properties in aqueous solutions of various nonelectrolytes including amines. They have speculated a presence of the solute-solute interaction of butylamines in aqueous solutions. We consider that such interacting molecules may corre-

Table 3. The Rate Constants for the Aggregation Reaction for Aqueous Solutions of Butylamines and Pentylamines at 25 °C

Solute	n	$10^{-6}\,k_{34}$ / $(\text{mol}^{-1}\,\text{dm}^3)^{n-1}\,\text{s}^{-1}$	$10^{-7}\,k_{43}$ / s^{-1}	ΔV_2 / $\text{cm}^3\,\text{mol}^{-1}$	Reference
Isobutylamine	4	3.7	28	19	This work
Isopentylamine	5	4.1	1.4	22	This work
Butylamine	4	2.2	9.0	14	16
Pentylamine	5	4.7	3.0	17	2

spond to the aggregate under consideration.

As has been described previously, the coupling effect of the two reactions should be taken into account, as the processes of the hydrolysis and the aggregation reaction have been observed experimentally in the equivalent time range. The reaction mechanisms under consideration may be generally expressed as follows when the two reactions shown by Eqs. 3 and 9 are taken into account.



$$\text{R-NH}_3^+ + \text{OH}^- \underset{k_{21}}{\overset{k_{12}}{\longleftrightarrow}} \text{R-NH}_3^+\cdots\text{OH}^- \underset{k_{32}}{\overset{k_{23}}{\longleftrightarrow}} \text{R-NH}_2 \underset{k_{43}}{\overset{k_{34}}{\longleftrightarrow}} \frac{1}{n}(\text{R-NH}_2)_n\,. \qquad (13)$$

with H_2O released in the k_{23} step.

As has been explained, the ultrasonic relaxation process due to the hydrolysis has been well-interpreted on the basis of the fact that the second step in the above reaction scheme may not affect the first step very much. We consider that the second step may be too fast to couple with the first step, as the second step is the intramolecular proton exchange. In our time region, the second step may be estimated to be in the steady state. The third step, associated with the aggregation reaction, is observed in a lower frequency range than the first step. Therefore, the third process may not be so affected by the second step. That is, the independent procedures of absorption analysis may be appropriate for the aqueous solutions of amines investigated in this study.

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