Ultrasonic Relaxations in Aqueous Solutions of Piperidine and Pyrrolidine

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In order to examine ultrasonic absorption mechanisms and dynamical properties in aqueous solutions of heterocyclic amines, the absorption coefficients in a frequency range from 3.0 to 220 MHz were measured in solutions of pyrrolidine and piperidine at 25 °C. In the solution of pyrrolidine, a single relaxational absorption associated with a proton transfer reaction was observed, and the rate and thermodynamic parameters were determined from the concentration dependence of the relaxation frequency and the maximum absorption per wavelength. In the solution of piperidine, another relaxational absorption in addition to that due to the proton transfer reaction was observed in the relatively concentrated solution. It was attributed to a perturbation of an equilibrium associated with an aggregation reaction of nonionized molecules. The mean aggregation number and the rate parameters were estimated from the solute concentration dependence of the relaxation parameters. The results were compared with those observed in aliphatic amine solutions.

It is well known that heterocyclic amines play important roles in biological systems. A proton transfer reaction as a diffusion controlled reaction in aqueous media is one of the most important reactions occurring in living systems. This reaction can be directly observed by an ultrasonic method. Ultrasonic waves have been usefully applied to investigations of various solution characteristics.[1,2] Present authors have been also using the ultrasonic method to study reaction mechanisms occurring in aqueous solutions of amines. Based on the series of our experimental studies, it has been shown that ultrasonic relaxational absorptions in the MHz frequency range for aqueous solutions of aliphatic amines are characterized by two relaxations processes.[3—6] One is associated with the proton transfer reaction, which is observed in most solutions of amines; the other is the relaxational process observed in solutions the solute of which consists of a relatively large hydrophobic group. It has been predicted that the cause of the latter relaxational absorption is due to a molecular aggregation reaction. If this relaxation is related to the balance between the hydrophobicity and the hydrophilicity of a molecule, it is expected that a similar phenomenon may be found in solutions of heterocyclic amines. The ultrasonic absorption data in a morpholine aqueous solution indicate the clear existence of relaxational absorption due to the proton transfer reaction, and that of a small relaxational absorption due to an aggregation reaction; it has been found that the absorptions in the solution of piperidine clearly show both of the relaxation processes.[6] However, an analysis of the relaxational absorption observed in the concentrated solutions of piperidine has not yet clarified the details of the mechanism. It is desired to study more precisely the ultrasonic relaxation mechanisms in aqueous solutions of heterocyclic amines, because of the importance of their participation in biological systems. Especially, clarifying the ultrasonic absorption mechanisms in relatively concentrated aqueous solutions may provide variable information for practical applications of ultrasonic waves. For these situations, piperidine and pyrrolidine have been chosen as solutes and the relations between the molecular structure and the ultrasonic relaxation mechanisms are to be considered in this report.

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Experimental

Piperidine and pyrrolidine of reagent grade were purchased from Wako Pure Chemical Co., Ltd., and from Tokyo Kasei Co., Ltd., respectively. Piperidine was distilled once under a normal pressure and pyrrolidine was used without further purification. The desired sample solutions were prepared by using distilled and filtered water through a MilliQ SP-TOC system from Japan Millipore Ltd. The other chemicals used were of the purest grade obtainable. The aqueous solutions of piperidine were prepared by weighting, because the relatively concentrated solutions were desired. The pyrrolidine solutions were obtained by diluting the concentrated stock solution in concentrations less than 1 mol dm^{-3}; more concentrated solutions were made by weighting.

The ultrasonic absorption coefficients were measured by a pulse method in the frequency range from 7.5 to 220 MHz, and by a resonance method from 3.0 to 6.2 MHz. The sound velocity was measured by a sing-around velocity meter at 1.92 MHz, and the density was obtained by a vibrating density meter in the same bath with the sing-around meter at the same time. The more detailed procedures and apparatuses for these measurements are described elsewhere.[7,8] The solution pH was measured by a Toa Denpa HM-60S pH meter in the ultrasonic absorption cell during measurements of the absorption coefficients. The concentration range of the absorption measurement was from 1.51 to 7.00 mol dm^{-3} for piperidine solutions and from 0.005 to 4.00 mol dm^{-3} for pyrrolidine ones. All of the measurements were always performed in

dry N_2 gas atmosphere in order to avoid as much as possible any contamination of carbon dioxide during the measurements. All of the measurement cells were immersed in a water bath maintained at 25 °C. The temperature fluctuation of the bath was controlled to within ±0.002 °C. An NEC 9800 microcomputer was used to calculate the rate and thermodynamic parameters for which the software were all homemade. They are available on request to one of the authors (S.N.) along with the original data for the ultrasonic absorption and velocity.

Results

Figure 1 represents the concentration dependence of α/f^2 at 25 MHz for aqueous solutions of piperidine and pyrrolidine, where α is the absorption coefficient and f the measurement frequency. For concentration of up to 1 mol dm^{-3} for the piperidine solution, it increases monotonously, and then increases dramatically. Further, it goes through a maximum value at around 2.5 mol dm^{-3}, though the position of the peak depends on the frequency. On the other hand, for the aqueous solution of pyrrolidine, the profile is very different from that observed in the piperidine solution, and it increases continuously. These results imply that the ultrasonic absorption mechanism in the concentrated solutions depends on the solute structures.

The absorption mechanism in the dilute solution of piperidine has been confirmed to be due to a perturbation of an equilibrium associated with the proton transfer reaction;[6,9] also the rate and thermodynamic constants have been already reported. Figure 2 shows the representative ultrasonic absorption spectra for the relatively concentrated solutions of piperidine. They were analyzed by a Debye-type single relaxational equation,

$$\alpha/f^2 = A/[1+(f/f_r)^2]+B, \quad (1)$$

where A is the amplitude of the relaxational absorption, f_r the relaxation frequency and B the background absorption. The solid curves in the figure represent the calculated values. As can be seen, these absorption spectra appear to be well fitted to a single relaxational curve. Figure 3 represents the concentration dependence of the calculated relaxation frequency, and Fig. 4 that of the amplitude of the relaxation and the background absorption, where the results concerning the relatively dilute solutions of piperidine were taken from previous work.[6] The data in the concentration range less than 3.5

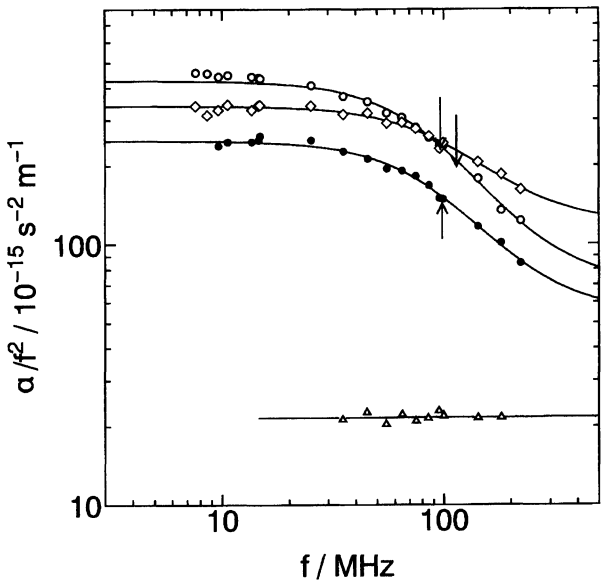

Fig. 2. Representative ultrasonic absorption spectra in aqueous solutions of piperidine. ●: 1.50 mol dm^{-3}, ○: 2.01 mol dm^{-3}, ◇: 3.50 mol dm^{-3}, △: 2.00 mol dm^{-3}, the solution of which was controlled by addition of HCl to be pH = 8.90.

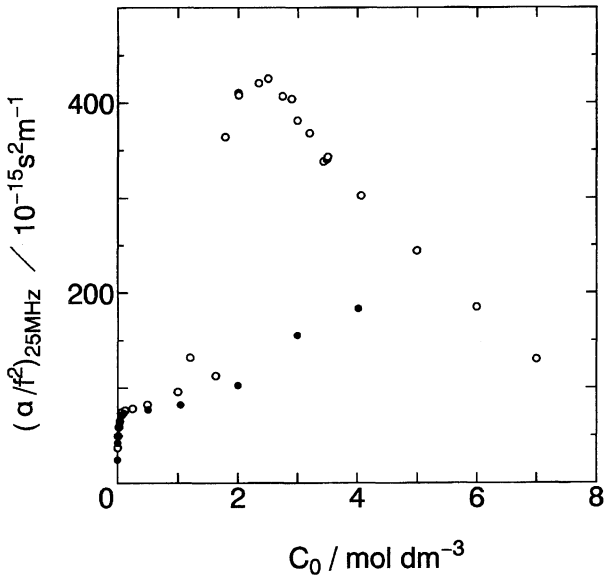

Fig. 1. Concentration dependence of ultrasonic absorption at 25 MHz for aqueous solutions of piperidine (○) and pyrrolidine (●) at 25 °C.

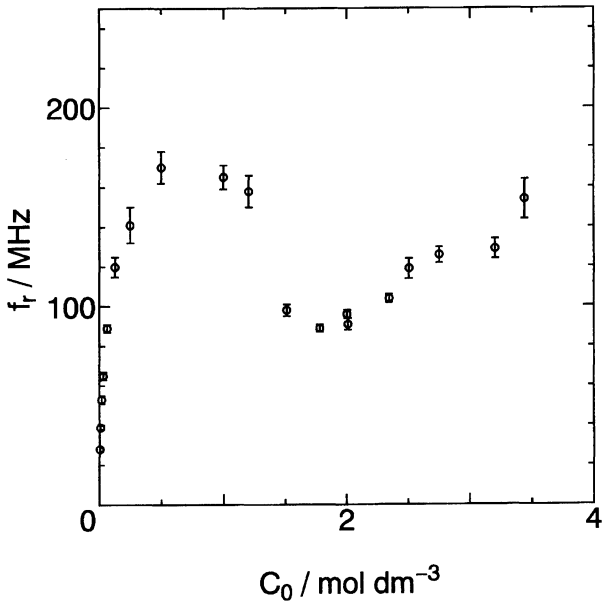

Fig. 3. Concentration dependence of the primarily determine relaxation frequency for aqueous solution of piperidine at 25 °C.

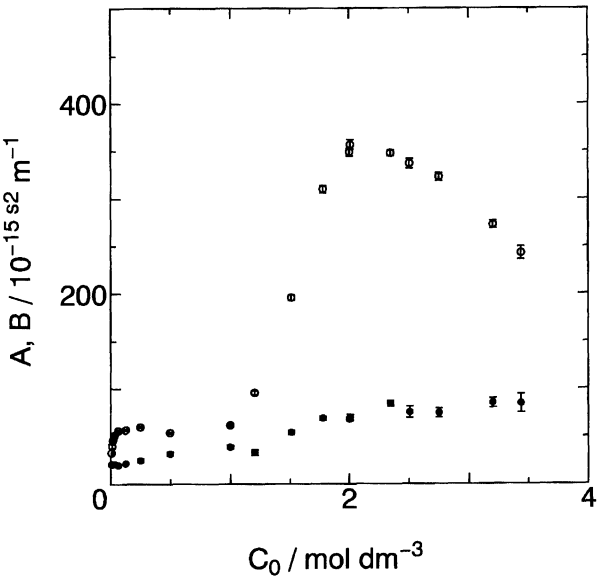

Fig. 4. Concentration dependence of the amplitude of the ultrasonic relaxation (○) and the background absorption (●) for aqueous solution of piperidine, which were calculated primarily.

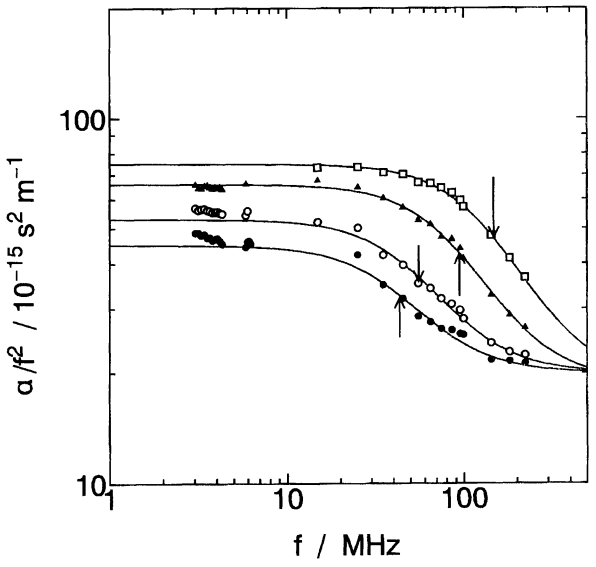

Fig. 5. Representative ultrasonic absorption spectra for relatively dilute solutions of pyrrolidine at 25 °C. ●: 0.0050 mol dm^{-3}, ○: 0.011 mol dm^{-3}, ▲: 0.050 mol dm^{-3}, □: 0.105 mol dm^{-3}.

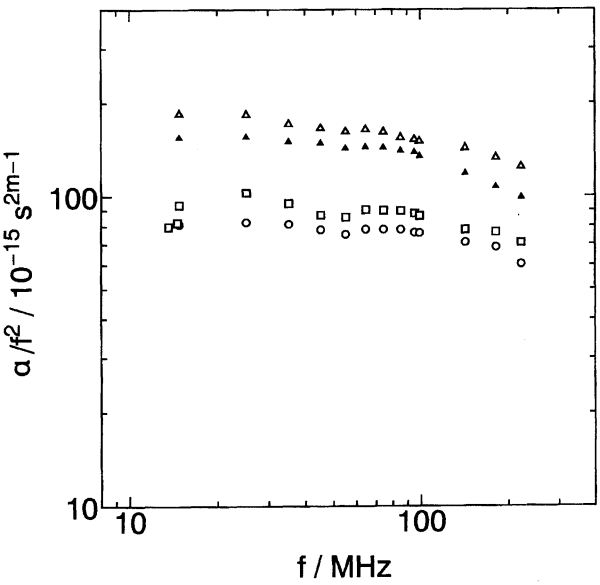

Fig. 6. Ultrasonic absorption spectra for relatively concentrated aqueous solution of pyrrolidine at 25 °C. ○: 1.05 mol dm^{-3}, □: 2.00 mol dm^{-3}, ▲: 3.00 mol dm^{-3}, △: 4.02 mol dm^{-3}.

mol dm^{-3} were analyzed because the relaxation frequency tends to locate in the high frequency range, the background absorption is large, and therefore accurate ultrasonic parameters are too difficult to determine. The relaxation frequency goes through a peak at around 0.5 mol dm^{-3}, and then decreases. After that, it increases smoothly. The amplitude of the relaxational absorption increases up to 0.1 mol dm^{-3}, remains at a plateau until around 1 mol dm^{-3}, and then goes through a maximum. The background absorption increases monotonously.

Figures 5 and 6 show some absorption spectra in the aqueous solutions of pyrrolidine. In the concentration range less than 0.1 mol dm^{-3}, the spectra are well fitted to Eq. 1. Along with an increase in the concentration, the ultrasonic absorption still gradually increases, as can be seen in Fig. 6. However, the ultrasonic parameters in the concentrated solutions are too difficult to determine precisely, because high relaxation frequency might exist in a higher frequency range of more than 220 MHz.

Based on the above experimental facts, it is considered that the relaxational absorption observed in the concentrated solutions of piperidine is different from that observed at the lower concentrations, and that the absorption due to the proton transfer reaction may be superimposed on the absorption observed at the concentrated solution.

We first present an analysis of the results in the relatively dilute solutions of pyrrolidine. The trends concerning the ultrasonic parameters are very similar to those for the relatively dilute solutions of piperidine[6] and other aliphatic amines.[3–5]

Therefore, a similar relaxation process is expected to exist in the pyrrolidine solution. It is associated with a perturbation of the equilibria related to the proton transfer reaction, as follows:

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

where k_{ij} are the rate constants for the individual steps. As described in a previous paper,[3–6] the observed relaxational phenomenon in aqueous solutions of various amines is well interpreted based on the assumption that the perturbation of the first equilibrium is a cause of the relaxation. We have therefore tried to analyze the results in the pyrrolidine solution, in the same manner. The rate constants can be determined from the hydroxide concentration dependence of the observed relaxation frequency using the following

equation (hereafter, we define the relaxation frequency as f_{r1} when used in the dilute solution):

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

where γ is the activity coefficient calculated by Davis's equation. The data for concentrations less than 0.1 mol dm^{-3} were used because of the uncertain values of the high relaxation frequency in the concentrated solutions. Figure 7 shows plots of f_{r1} vs. $\gamma^2[OH^-]$, the good linearity of which confirms that the cause of the relaxation is due to the proton transfer reaction. The intercept and slope give the rate constants with a least mean-squares method; they are listed in Table 1 along with those in aqueous solutions of the other heterocyclic amines in order to make comparison.

The dissociation constant, K_b, is obtainable from the hydroxide concentration dependence on the analytical concentration by the relation, $K_b=\gamma^2[OH^-]^2/(C_0-[OH^-])$. It is listed in Table 1. The dissociation constant can also be estimated using the relation among the rate constants, the relaxation frequency and the analytical concentration, as follows;

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

The determined values are listed in Table 1. The values derived by the two different equations are almost the same, and are close to the literature values.[10]

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

$$\mu_{m1} = 0.5Af_{r1}c = \pi\rho c^2\Gamma(\Delta V_1)^2/2RT, \quad (5)$$

where ρ is the solution density and c the sound velocity. ΔV_1 in Eq. 5 is a term containing the standard volume change, $\Delta V_1'$, and the standard enthalpy change, ΔH, associated with the reaction as $\Delta V_1=\Delta V_1'-\alpha_p\Delta H/\rho C_{p'}$, where α_p is the thermal expansion coefficient and C_p the specific heat at constant pressure. Also, the Γ is the concentration term derived as $\Gamma=(2/[OH^-]+1/[\phi\text{-}NH_2^+\cdots OH^-])^{-1}$. Since the term containing the enthalpy change is small in an aqueous solution, it is approximately neglected. As a result, the concentration dependence of μ_{m1} provides the standard volume change of the reaction, $\Delta V_1'$. The results are given in Fig. 8 as a function of the analytical concentration along with those of a piperidine solution. It can be seen that the obtained volume changes are very close to those for other amine hydrolysis.[3—6]

We now analyze the absorption mechanism in the concentrated solutions of pyrrolidine and piperidine. A large relaxational absorption has been observed in the concentrated solutions of piperidine, and a peak sound absorption concentration phenomenon is seen. On the other hand, the absorption in the solution of pyrrolidine increases monotonously with the concentration as shown in Figs. 1 and 6. These facts mean that an additional relaxational absorption may exist in the piperidine solution. Therefore, we have tried to analyze the absorption mechanism observed in the piperidine solution. Although the absorption due to the proton transfer reaction observed in the dilute solution is smaller than that observed in the concentrated solution, it should also be taken account into. Thus, we have used the next equation,

$$(\alpha/f^2)_{cal} = (\alpha/f^2)_{exp} - \Delta(\alpha/f^2)_{hydrolysis}, \quad (6)$$

where $\Delta(\alpha/f^2)_{hydrolysis}$ is the absorption due to the proton transfer reaction, which can be calculated at the concentrations under consideration using Eqs. 3 and 5. We applied $(\alpha/f^2)_{cal}$ to the single relaxation equation, which is the same as to Eq. 1. As the result, $(\alpha/f^2)_{cal}$'s show a smooth frequency

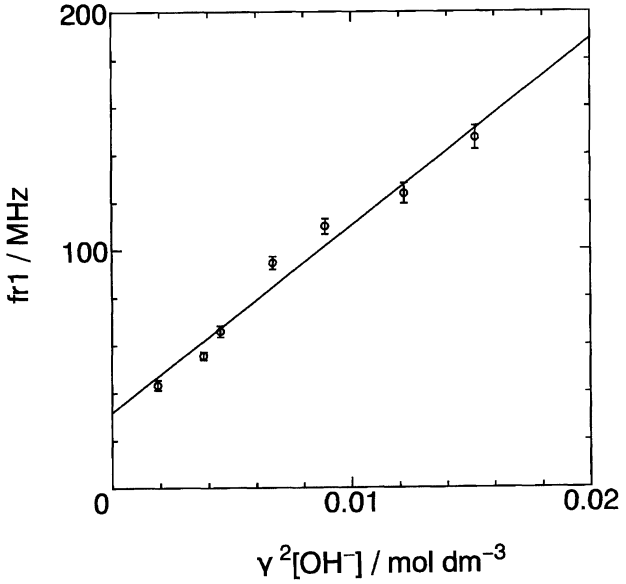

Fig. 7. The plots of f_{r1} vs. $\gamma^2[OH^-]$ for aqueous solution of pyrrolidine at 25 °C.

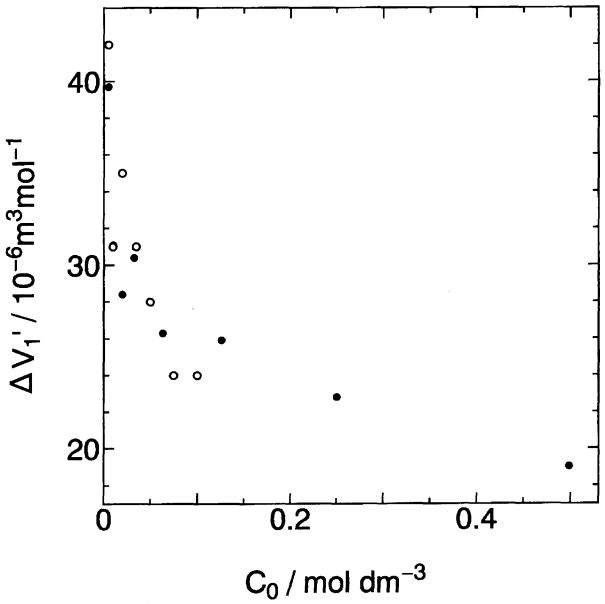

Fig. 8. Concentration dependence of the standard volume change for the proton transfer reaction. ○: pyrrolidine solution, ●: piperidine solution.

Table 1. Rate and Equilibrium Constants for Proton Transfer Reaction in Aqueous Solutions of Some Cyclic Amines

Solute	Pyrrolidine	Morpholine	Piperidine
k_{12}($mol^{-1}dm^3s^{-1}$)	$(2.6\pm0.1)\times10^{10}$	$(2.9\pm0.3)\times10^{10}$	$(2.3\pm0.2)\times10^{10}$
k_{21}(s^{-1})	$(1.8\pm0.1)\times10^{8}$	$(3.7\pm0.2)\times10^{7}$	$(1.5\pm0.3)\times10^{8}$
K_b[a]	$(2.4\pm0.6)\times10^{-3}$	$(1.1\pm0.6)\times10^{-6}$	$(1.3\pm0.2)\times10^{-3}$
K_b[b]($mol\,dm^{-3}$)	$(2.5\pm0.5)\times10^{-3}$	$(1.2\pm0.6)\times10^{-6}$	$(1.2\pm0.2)\times10^{-3}$
K_b[c]	1.3×10^{-3}	3.1×10^{-6}	1.3×10^{-3}
Reference	This work	(7)	(7)

a) From the relation, $K_b=\gamma^2[OH^-]^2/(C_0-[OH^-])$. b) From Eq. 4. c) From the Ref. 10.

dependence as seen in Fig. 9 and give an excellent agreement with the theoretical curves. Thus the recalculated relaxation frequency, f_{r2}, and the amplitude of the ultrasonic relaxation, A_2, are given in Fig. 10. Since calculations at concentration range less than 1.2 $mol\,dm^{-3}$ are not appropriate, because of the too small amplitude of the relaxational absorption, and also because of large errors, we reluctantly determined the relaxation parameters from 1.2 to 3.5 $mol\,dm^{-3}$ for the analysis.

When the solution pH decreased, this large absorption suddenly disappeared as shown in Fig. 2. This means that the nonionized molecules participate in the observed relaxation process. It is certain that the relaxational absorption is very sensitive to the hydrophobic parts of the solute, since the absorption is not found in the pyrrolidine solution. We have therefore considered that the cause of the relaxation may have been related to an aggregation reaction associated with hydrophobic interactions, as has been observed in aliphatic amine solutions,[3,5] as follows:

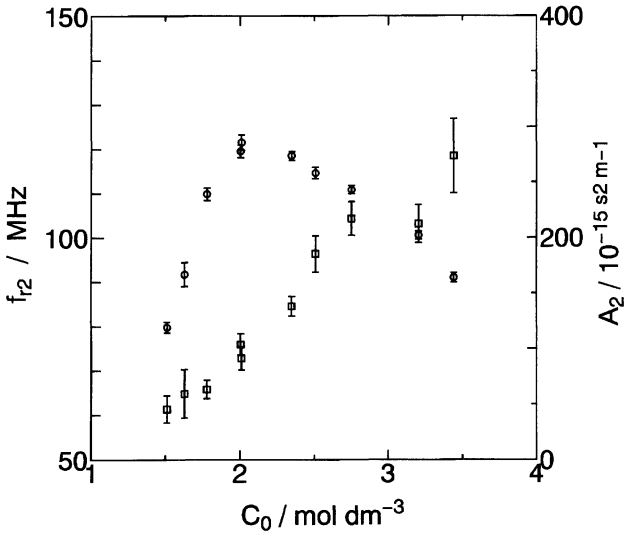

Fig. 10. Recalculated ultrasonic relaxation amplitude (○) and relaxation frequency (□) for the relatively concentrated aqueous solution of piperidine.

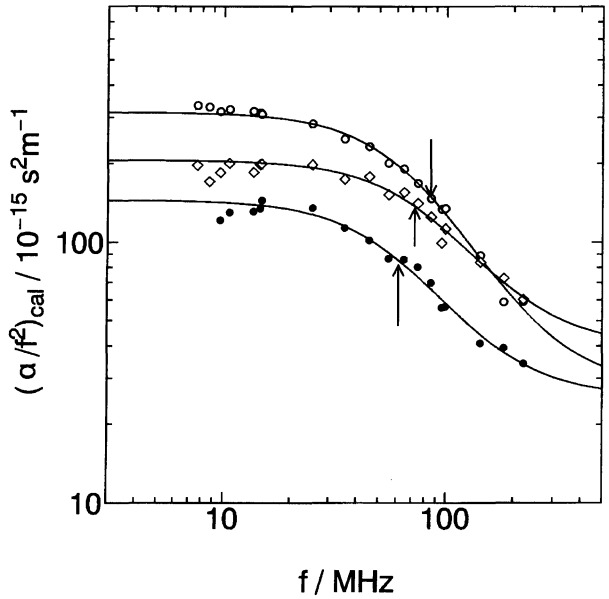

Fig. 9. Representative ultrasonic absorption spectra subtracted the absorption due to the proton transfer reaction for aqueous solution of piperidine. ●: 1.50 $mol\,dm^{-3}$, ○: 2.01 $mol\,dm^{-3}$, ◇: 3.50 $mol\,dm^{-3}$.

$$n\phi\text{-NH} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} (\phi\text{-NH})_n, \tag{7}$$

where n is the aggregation number, ϕ-NH the nonionized piperidine molecule and $(\phi\text{-NH})_n$ the aggregate. Such an aggregation reaction may proceed through a stepwise process, like that observed in surfactant solutions.[11,12] However, the aggregation number is considered to be not very large. It is therefore expected that the reaction in Eq. 7 may be taken as a mean process for the aggregation reaction, and that the usual relaxational analytical procedure may be applicable.[13] It is possible to determine the monomer concentration using the equilibrium constants in hydrolysis (Eq. 2). However, the calculated results gave the monomer concentrations to be more than the analytical concentration, which is not probable. Therefore, the following analytical procedures were taken. The relation between the relaxation frequency and the reactant concentration is given by[3]

$$2\pi f_{r2} = k_{34}n^2[\phi\text{-NH}]^{n-1} + k_{43}. \tag{8}$$

It is assumed that: (i) the dissociation constant may not be the same in a concentrated solution as that in a dilute solution, (ii) the equilibrium constant, K_{32}, for the second step in hydrolysis in Eq. 2 is not altered in a concentrated solution,

about which we will discuss in the next section. Thus, the following relations are usable:

$$K_{32} = k_{32}/k_{23} = [\phi\text{-NH}_2{}^+\cdots\text{OH}^-]/[\phi\text{-NH}] = 0.2^{7)}, \quad (9)$$

$$K_{agg} = k_{34}/k_{43} = [(\phi\text{-NH})_n]/[\phi\text{-NH}]^n, \quad (10)$$

$$C_0\text{-}[\text{OH}^-] = 1.2[\phi\text{-NH}] + nK_{agg}[\phi\text{-NH}]^n. \quad (11)$$

At the first stage, the aggregation number, n, is assumed. Then, if the concentration of the aggregate is small, the monomer concentration, $[\phi\text{-NH}]$, is roughly calculated from the relation, $[\phi\text{-NH}]=(C_0\text{-}[\text{OH}^-])/1.2$. The forward and backward rate constants are determined using Eq. 8 and the equilibrium constant, K_{agg}, is estimated. Once K_{agg} is obtained, the monomer concentration, which is more reliable, may be recalculated using Eq. 11; we then use Eq. 8 to recalculate the value of K_{agg}. This calculation is repeated until K_{agg} reaches a constant value, and the error of the plots for Eq. 8 also gives a minimum value. In the next step, another aggregation number is chosen to determine the rate and thermodynamic constants, and a similar calculation is carried out. When the error of the plots for Eq. 8 is the smallest, the aggregation number is accepted as a reasonable value. Figure 11 shows plots of the recalculated relaxation frequency, f_{r2}, vs. the concentration term, $[\phi\text{-NH}]^3$, where the most reasonable straight line has been obtained. The thus-determined results are n=4, $k_{34}=(2.4\pm0.2)\times10^6$, $(\text{mol}^{-1}\,\text{dm}^3)^3\,\text{s}^{-1}$, and $k_{43}=(3.4\pm0.2)\times10^8\ \text{s}^{-1}$.

The standard volume change of the reaction is also estimated by the following equation:[3)]

$$\mu_{m2} = 0.5A_2 f_{r2} c$$
$$= \pi\rho c^2(\Delta V_2)^2 k_f[\phi\text{-NH}]^n/(2\pi f_{r2})(2RT), \quad (12)$$

where μ_{m2} is the maximum absorption per wavelength for the aggregation reaction. The calculated volume change is $(18\pm2)\times10^6\ \text{m}^3\,\text{mol}^{-1}$. Also, the dissociation constant, K_b, in the concentrated solutions was estimated to be $K_b=(3.3\pm0.5)\times10^{-3}\ \text{mol}\,\text{dm}^{-3}$ from the relation, $K_b=\gamma^2[\text{OH}^{-1}]^2/([\phi\text{-NH}_2{}^+\cdots\text{OH}^-]+[\phi\text{-NH}])$.

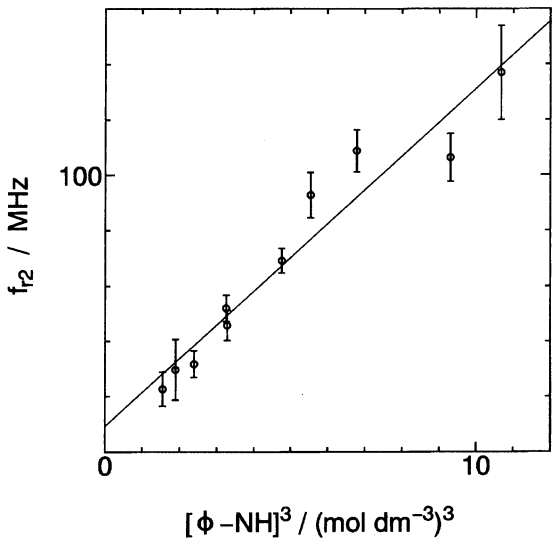

Fig. 11. The plots of f_{r2} vs. $[\phi\text{-NH}]^3$ for aqueous solution of piperidine at 25 °C.

Discussion

In the aqueous solutions of piperidine and pyrrolidine, the ultrasonic relaxational absorption due to the proton transfer reaction is surely observed; the forward rate constants, k_{12}'s, are reasonable as a diffusion controlled reaction. These values are very close to those estimated by a theoretical equation derived by Debye.[13)] Thus determined forward and backward rate constants can give the equilibrium constant, K_{32}, using $K_b=K_{21}/(1+K_{32}{}^{-1})$, where $K_{21}=k_{21}/k_{12}$ and $K_{32}=k_{32}/k_{23}$. For the pyrrolidine solution, $K_{32}=0.6$ was obtained, and $K_{32}=0.2$ for the piperidine solution, which means that the concentration of the intermediate is still smaller than that of the nonionized molecule. It is considered that the intermediate, $\phi\text{-NH}_2{}^+\cdots\text{OH}^-$, in Eq. 2 may include one or two water molecules,[6)] which might reflect the concentration dependence of the standard volume change of the reaction, as can be seen in Fig. 8. However, the reaction of the second step in Eq. 2 is associated with an interaction of the solute molecule with water molecules which locate very near the amine molecules. Then, the reaction rates are very much fast, and they are expected not to be so influenced, even if the concentration of the solute is relatively high. Therefore, the equilibrium constant, K_{32}, may not be altered in a relatively concentrated solution, speculation of which has been used in an analysis of the absorption mechanism in the relatively concentrated solutions of piperidine.

Next, the results are discussed for the relaxational absorption observed in the concentrated solutions of pyrrolidine and piperidine (more than 1 $\text{mol}\,\text{dm}^{-3}$). Gittins et al.[14)] have reported ultrasonic absorption results in various pure liquid heterocycles with nitrogen in the frequency range from 25 to 100 MHz. Piperidine is one of them. They found a relaxation process, the cause of which has been attributed to nitrogen and ring conversions. The amplitude of the ultrasonic relaxation seems to be large only in the substituted heterocyclic amines, while it is very small, or close to zero, in liquid piperidine. Though we also measured the absorption in liquid piperidine, no clear frequency dependent α/f^2 has been observed. Therefore, the cause of the relaxation process observed in our aqueous solutions is different from that associated with the conversion of the nitrogen or the ring.

In the solution of pyrrolidine, the absorption increases monotonously, and no peak sound absorption concentration phenomenon is observed, as can be seen in Figs. 1 and 6. The slight decrease of α/f^2 at the high frequency range in Fig. 6 may be due to the tail of the relaxational absorption due to the proton transfer reaction. On the other hand, the absorption in the solution of piperidine shows a maximum, i.e., the peak sound absorption concentration phenomenon is found. This kind of behavior has been observed in other nonelectrolyte aqueous solutions, the solutes of which consist of a relatively large hydrophobic group, e.g. in the alcohol

solutions;[15] this is closely related to the balance between the hydrophobicity and the hydrophilicy of molecules. When the piperidine molecule is ionized, the relaxational absorption disappears, as shown in Fig. 2. The hydrophobicity of piperidine is considered to be larger than that of pyrrolidine. A similar relaxational absorption is also observed in aqueous solutions of some aliphatic amines which consist of a relatively large hydrophobic group.[3—5] We have therfore considered that the observed relaxation process in the concentrated solution of piperidine can be attributed to a perturbation of the equilibrium associated with the molecular aggregation reaction expressed by Eq. 7. The aggregate might be formed by hydrophobic interaction, although the aggregation number is small. When the rate constant and the aggregation number are compared with those for aliphatic amine solutions, the profiles for the aggregation reaction of piperidine are close to that of butylamine.[3] Therefore, the hydrophobicity of aliphatic amine is speculated to be larger than that of cyclic amine when the number of carbons is the same in the molecule. This might be because of the surface area which attaches to water molecules. The dissociation constant, K_b, in the concentrated solution of piperidine was obtained to be larger than that in the relatively dilute solution. This might arise from a relative decrease of the nonionized monomer concentration for the sake of the forming the aggregate. The coupling effect between the proton transfer reaction and the aggregation reaction has been discussed in previous reports[4,5] and similar situations are also considered to hold in heterocyclic amine solutions.

In conclusion, the ultrasonic absorption for aqueous solutions of heterocyclic amines are characterized by two relaxation process. One is associated with the proton transfer reaction, and is found in most of amine solutions. The forward rate constant is mostly determined by diffusion of the hydroxide ion. The backward rate reflects the stability of the intermediate for hydrolysis. The other is the relaxation process associated with the molecular aggregation observed in the aqueous solutions, the solutes of which consist of relatively high hydrophobicity.

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