# ARTICLES

## Ultrasonic Absorption Spectra in Aqueous Solutions of Alkylamines. Effect of Isotopic Solvents on Kinetics of Hydrolysis and Aggregation Reactions

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At 25 °C ultrasonic absorption coefficients for aqueous solutions of 1-pentylamine in heavy water (0.0434−2.5093 mol $dm^{-3}$) and in light water (0.0242−0.3071 mol $dm^{-3}$) have been measured as functions of frequency in the range of 0.8−220 MHz and solute concentration. The sound velocity and density have also been investigated in these solutions. The measured spectra have been analyzed in terms of a Debye-type relaxational equation, and two kinds of relaxational acoustic absorptions have been found. The causes of the relaxations have been attributed to a proton/deuteron transfer and an association−dissociation process. The forward and backward reaction rates, the equilibrium constants, the standard volume change of the reactions, and the adiabatic compressibility have been determined from the ultrasonic parameters, and the isotope effects have been evaluated. The results are discussed with those of the previous investigations for other amines, i.e., 1-butylamine, 1-propylamine, and ethylamine.

### Introduction

Recently, successive interest in the fast kinetic isotope effects on the hydrolysis and aggregation reactions of alkylamines has developed in this group.[1−6] In these studies, we have systematically varied the alkyl chain length of the amine. This paper reviews the series investigations for ethylamine, 1-propylamine, and 1-butylamine along with the latest results obtained in aqueous solutions of 1-pentylamine by means of ultrasonic relaxation methods and proton nuclear magnetic resonance ($^1$H NMR) spectroscopy. It is desired to reveal the detailed reaction mechanism in these solutions, the structure of the intermediate during the hydrolysis of amines, and how the difference from the isotopic solvents, $H_2O$ and $D_2O$, influences the reaction processes subtly. It has been found that for 1-propylamine and 1-butylamine, the proton-transfer rate constants are greater in $D_2O$ than those in $H_2O$, and they are opposite for the backward process. These results were interpreted by the structure of the intermediate, which was deduced from the reaction radii calculated by Debye rate theory. For ethylamine, on the other hand, the faster proton-transfer process was observed in $H_2O$ solvent. This was also interpreted in terms of the structure of the intermediate, in addition to the solvent viscosity and ion mobility. The goal of present study is that the experimental result in 1-pentylamine solution might provide further understanding of the relation between the kinetic isotope effects and the amine structures.

### Experimental Section

**Chemicals**. 1-Pentylamine (98%) was purchased from Wako Pure Chemicals Co. Ltd. and was distilled once under the dry nitrogen gas protection. Heavy water which was from the same company, was guaranteed to be more than 99.75%, and light water was purified by a Milli-Q SP-TOC filter System from Japan Millipore Ltd. (TOC, below 10 ppb; specific resistance, above 18.3 MΩ cm). The aqueous solutions of 1-pentylamine were made by weighing 1 day before the measurements and stored under $N_2$ atmosphere.

**Measurements.** Measurements of ultrasonic attenuation were performed at the odd harmonics of 0.5, 5, 20 MHz fundamental x-cut quartz crystals using a pulse technique in the frequency range from 6.5 to 220 MHz. To measure the absorption coefficient in the low-frequency range, 0.8−7 MHz, a resonance method was employed. The details of both apparatus can be found in our previous papers.[7,8] The sound velocity was measured accurately by a 5 MHz resonator and was calculated from the frequency difference between two resonance peaks.[9] The densities of the solutions were achieved through Anton Paar vibrating density meter (DMA 60/62) with a reproducibility of ±0.01 kg $m^{-3}$. Pure water was used to check the accuracy before the measurements of the sound velocity and density for the sample solutions. The temperature for all measurements was kept at 25 °C with the aid of a water bath (Eyela Uni Ace Bath NCB-2200 for the pulse apparatus) and circulating water (Lauda, RM 20 for the resonance and density apparatus).

### Results and Discussion

Plots of acoustic absorption as a function of frequency for 1-pentylamine in $D_2O$ and in $H_2O$ are displayed in Figure 1. The curves going through the data represent the best fits of the conventional Debye-type relaxational equation

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

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**TABLE 1: Ultrasonic Parameters for 1-Pentylamine in $D_2O$ and in $H_2O$ at 25 °C**

| $C_o$, mol dm$^{-3}$ | pH | $f_{r1}$, MHz | $f_{r2}$, MHz | $A_1$, $10^{-15}$ s$^2$ m$^{-1}$ | $A_2$, $10^{-15}$ s$^2$ m$^{-1}$ | $B$, $10^{-15}$ s$^2$ m$^{-1}$ | $\nu$, m s$^{-1}$ | $\rho$, kg dm$^{-3}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | In $D_2O$ | | | | |
| 2.5093 | 12.88 | | 58 ± 2 | | 465 ± 14 | 62 ± 3 | 1400.4 ± 0.4 | 1.0204 |
| | | [83.6][a] | (52 ± 4)[b] | [184] | (270 ± 17) | (54 ± 1) | | |
| 2.3000 | 12.82 | | 50 ± 1 | | 507 ± 9 | 73 ± 2 | 1401.7 ± 0.2 | 1.0284 |
| | | [75.7] | (39 ± 1) | [173] | (364 ± 9) | (67 ± 1) | | |
| 2.0586 | 12.78 | | 43 ± 1 | | 665 ± 13 | 65 ± 2 | 1406.6 ± 0.1 | 1.0389 |
| | | [71.0] | (34 ± 1) | [165] | (543 ± 10) | (59 ± 1) | | |
| 1.5472 | 12.74 | | 32 ± 1 | | 970 ± 29 | 57 ± 3 | 1415.3 ± 0.1 | 1.0546 |
| | | [66.7] | (31 ± 1) | [157] | (796 ± 34) | (42 ± 1) | | |
| 0.9154 | 12.68 | 59 ± 6 | 12 ± 3 | 178 ± 34 | 1990 ± 40 | 36 ± 2 | 1431.7 ± 0.3 | 1.0775 |
| | | [60.7] | (14 ± 1) | [146] | (1850 ± 33) | (27 ± 3) | | |
| 0.5364 | 12.67 | 54 ± 38 | 4 ± 16 | 175 ± 83 | 5439 ± 739 | 27 ± 15 | 1435.4 ± 0.3 | 1.0911 |
| 0.4500 | 12.65 | 50 ± 34 | 3.5 ± 18 | 154 ± 72 | 4024 ± 763 | 29 ± 12 | 1427.9 ± 0.3 | 1.0934 |
| 0.4004 | 12.64 | 53 ± 2 | | 129 ± 4 | | 28 ± 1 | 1426.0 ± 0.1 | 1.0936 |
| 0.3200 | 12.62 | 51 ± 2 | | 125 ± 5 | | 29 ± 1 | 1420.3 ± 0.1 | 1.0959 |
| 0.2084 | 12.41 | 42 ± 1 | | 104 ± 2 | | 28.7 ± 0.3 | 1410.7 ± 0.1 | 1.1001 |
| 0.1086 | 12.29 | 34 ± 1 | | 113 ± 3 | | 27.1 ± 0.3 | 1407.4 ± 0.1 | 1.1018 |
| 0.0434 | 11.70 | 19 ± 1 | | 106 ± 5 | | 27.9 ± 0.2 | 1403.1 ± 0.1 | 1.1028 |
| | | | | In $H_2O$ | | | | |
| 0.3071 | 12.22 | 97 ± 7 | | 66 ± 2 | | 22 ± 2 | 1517.5 ± 0.1 | 0.9928 |
| 0.2015 | 12.10 | 101 ± 9 | | 51 ± 2 | | 21 ± 1 | 1509.4 ± 0.1 | 0.9944 |
| 0.1228 | 11.85 | 72 ± 3 | | 56 ± 2 | | 19 ± 1 | 1502.5 ± 0.1 | 0.9958 |
| 0.0725 | 11.76 | 56 ± 4 | | 54 ± 3 | | 21 ± 1 | 1499.6 ± 0.1 | 0.9964 |
| 0.0242 | 11.52 | 43 ± 2 | | 39 ± 2 | | 20.2 ± 0.2 | 1497.0 ± 0.1 | 0.9969 |

[a] [Values] are estimated from the relation between the relaxation frequency and the reactant concentrations and those from eqs 3 and 6. [b] (Values) are recalculated ones after subtraction of the absorption due to proton-transfer reaction.

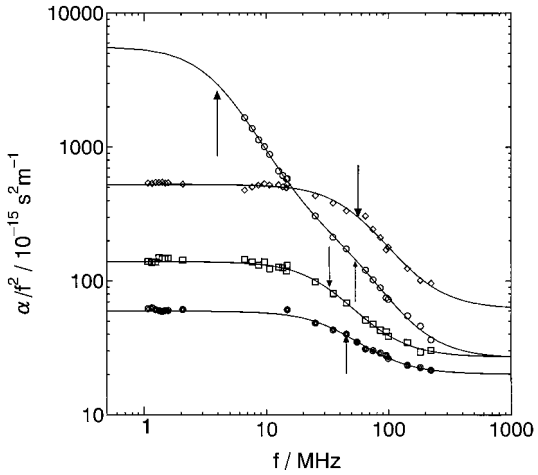


**Figure 1.** Representative ultrasonic relaxation absorption spectra in aqueous solutions of 1-pentylamine in $D_2O$ and in $H_2O$; (◎) 0.0242 mol dm$^{-3}$ in $H_2O$; (□) 0.1086 mol dm$^{-3}$ in $D_2O$; (◇) 2.5093 mol dm$^{-3}$ in $D_2O$; (○) 0.5364 mol dm$^{-3}$ in $D_2O$. Double relaxations have been observed in the concentration range of 0.45−0.92 mol dm$^{-3}$ in $D_2O$. The position of the relaxation frequency is indicated by the arrow.

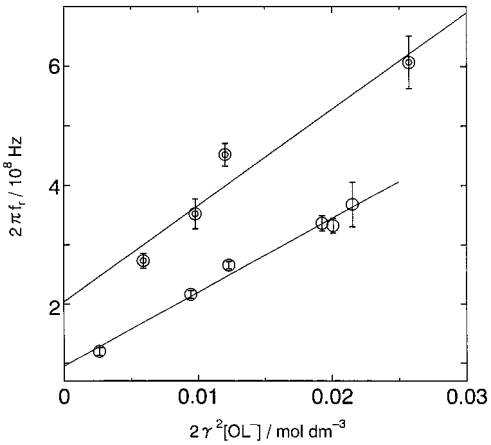


**Figure 2.** Rate constants determination of the deuteron/proton-transfer reaction for 1-pentylamine in $D_2O$ (○) and in $H_2O$ (◎) through the linear relationship between the relaxation frequency and the concentration term $2\gamma^2[OL^-]$, where L denotes H or D.

In eq 1, α is the absorption coefficient, $A_i$ is the amplitude of the ultrasonic absorption for the $i$th process, $f_{ri}$ is the relaxation frequency, and $B$ represents the attenuation associated with the viscosity and the thermal conductivity of the medium as well as that due to any very rapid chemical or structural relaxations. Generally, $B$ is a constant close to the value of $\alpha/f^2$ of the solvent. A nonlinear least-mean-squares procedure was employed to determine the best fitted $f_{ri}$, $A_i$, and $B$, and these ultrasonic parameters are tabulated in Table 1. The spectra for 1-pentylamine in $D_2O$ clearly show two relaxation absorptions in the concentration range between 0.45 and 0.92 mol dm$^{-3}$ but only one out of this range. This kind of spectra was also observed for other aqueous solutions of amines, i.e., 1-pentylamine in $H_2O$[1] and 1-butylamine in $H_2O$[2] and in $D_2O$.[3]

First, on the basis of previous results for other amines[1−6] and amino acids,[10] in dilute 1-pentylamine solutions (below 0.45 mol dm$^{-3}$) in $D_2O$ and in $H_2O$, the absorption mechanism is also considered to be related to a hydrolysis of amine proposed originally by Eigen[11] where L denotes H or D and $k_{ij}$ is the rate

$$R{-}NL_3^+ + OL^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} R{-}NL_3^+ \cdots OL^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} R{-}NL_2 + L_2O \quad (2)$$

constant at individual steps. It is considered that the amino hydrogen atoms of amine molecules are replaced by deuterium when $D_2O$ is used as solvent.[12] For this reaction, the rate constants, $k_{12}$ and $k_{21}$, can be determined from the slope and the intercept of the plots of $2\pi f_{r1}$ vs $\gamma^2[OL^-]$ (Figure 2) according to the relationship $\tau_1^{-1} = 2\pi f_{r1} = k_{12}\gamma^2([R{-}NL_3^+] + [OL^-]) + k_{21} = 2k_{12}\gamma^2[OL^-] + k_{21}$, in which $\tau_1$ is the relaxation time and $\gamma$ is the activity coefficient, which is calculated by Davis's equation. The deuterioxide concentration is available by a pH meter reading using the following relation:[13−16] $pD_{\text{in } D_2O} =$

**TABLE 2: Rate and Thermodynamic Constants of Proton/Deuteron-Transfer Reaction for 1-Pentylamine in $H_2O$ and in $D_2O$ at 25 °C**

| reactants | $k_{12}$, $10^{10}$ mol$^{-1}$ dm$^3$ s$^{-1}$ | $k_{21}$, $10^7$ s$^{-1}$ | $\Delta V_1$, $10^{-6}$ m$^3$ mol$^{-1}$ | $K_{21}$, $10^{-3}$ mol dm$^{-3}$ | $K_{32}$ | $K_b$, $10^{-4}$ mol dm$^{-3}$ |
|---|---|---|---|---|---|---|
| pentylamine in $H_2O$ | $1.6 \pm 0.2$ | $20 \pm 3$ | $25 \pm 7$ | 12.5 | 0.05 | $5.4 \pm 1.0$ |
| pentylamine in $D_2O$ | $1.3 \pm 0.1$ | $10 \pm 1$ | $30 \pm 6$ | 7.7 | 0.03 | $2.5 \pm 1.0$ |

**TABLE 3: Isotope Effects on Proton/Deuteron Transfer-Reaction for 1-Pentylamine, 1-Butylamine, 1-Propylamine, and Ethylamine in $H_2O$ and in $D_2O$ at 25 °C**

| reactants | $k_{12}^H/k_{12}^D$ | $k_{21}^H/k_{21}^D$ | $\Delta V_1^H/\Delta V_1^D$ |
|---|---|---|---|
| pentylamine | 1.2 | 2.0 | 0.8 |
| butylamine | 0.9 | 1.7 | 0.8 |
| propylamine | 0.8 | 1.8 | 0.8 |
| ethylamine | 1.3 | 1.0 | 0.7 |

$pH_{\text{meter reading in } D_2O} + 0.41$. The rate constants are determined using a least-mean-squares method, and the results are tabulated in Table 2. Therefore, the isotope effects, defined as the ratio of the quantity in $H_2O$ over that in $D_2O$, are obtained for the forward and reverse rate constants (Table 3). For aqueous solutions of 1-pentylamine, the dissociation constant, $K_b$, is obtainable as $K_b = \gamma^2[OL^-]^2/([R{-}NL_3^+\cdots OL^-]+[R{-}NL_2]) = \gamma^2[OL^-]^2/(C_o - [OL^-])$. Such an estimated $K_b$ value in $H_2O$ is very close to the literature values.[17,18] The equilibrium constant for step II in eq 2, $K_{32}$, was calculated from the relationship $1/K_b = 1/K_{21} + 1/(K_{21}K_{32})$.[3,4,6,19]

The standard volume change of the reaction $\Delta V$ is related to the maximum absorption per wavelength, $\mu_{max}$, by the relationship $(\mu_{max})_i = 0.5A_i f_{ri}\nu = 0.5\pi\rho\nu^2\Gamma_i(\Delta V_i - \alpha_A\Delta H_i/\rho C_{PA})^2$ where $\rho$ is the solution density, $\nu$ is the sound velocity, $\alpha_A$ is the coefficient of thermal expansion, $C_{PA}$ is the isobaric specific heat, and $\Delta H_i$ is the standard enthalpy change of the reaction. $\Gamma_i$ is a concentration term that is described below. The contribution from the enthalpy change of the reaction to $\mu_{max}$ is generally negligible in aqueous solution. Thus, $\mu_{max}$ can be described as

$$(\mu_{max})_i = 0.5A_i f_{ri}\nu = 0.5\pi\rho\nu^2\Gamma_i\Delta V_i^{\,2} \qquad (3)$$

For a reaction

$$\lambda_1 P_1 + \lambda_2 P_2 + \cdots \rightleftharpoons \lambda_m P_m + \lambda_{m+1} P_{m+1} + \cdots \qquad (4)$$

the concentration term $\Gamma$ is defined as

$$\Gamma = -(1/V)(\partial A/\partial\xi)_{TP}^{\,-1} = (1/RT)\{\sum(\lambda_j^2/C_j) - (\sum\lambda_j)^2/\sum C_j\}^{-1} \qquad (5)$$

where affinity $A$ is expressed as $-\sum\lambda_j\mu_j$, $C_j$ is the concentration of species $P_j$, and $\xi$ is the extent of the reaction, with $R$ and $T$ having their normal meaning.

Therefore, for the deuteron/proton-transfer reaction of eq 2, we have

$$\Gamma_1 = (1/RT)\{1/[R{-}NL_3^+] + 1/[OL^-] + 1/[R{-}NL_3^+\cdots OL^-] - [1/([R{-}NL_3^+] + [OL^-] + [R{-}NL_3^+\cdots OL^-])]\}^{-1} \qquad (6)$$

Combining eqs 3 and 6, the mean values of $\Delta V_1$ for the deuteron/proton-transfer reaction are determined from the data in Table 1, and the results are listed in Table 2. The isotope effects of the volume change of the reaction as eq 2 for four amines, $\Delta V_1^H/\Delta V_1^D$, are shown in Table 3 for a comparison. Although the rate and thermodynamic constants in $H_2O$ for the reaction under consideration have been reported by the present authors,[1] the present results are more available because the absorption data in the lower frequency range are obtained by the resonance method and these have provided more accurate ultrasonic relaxation parameters.

In the previous investigations of the isotope effects on the proton-transfer process of 1-butylamine, 1-propylamine, and ethylamine, the results were interpreted by the effective reaction radii deduced from Debye rate equation, which describes the diffusion-controlled rate constant determination.[3,4,6,11] When the same steric factor is used ($\sigma = 0.58$)[4] for 1-pentylamine solutions, we obtain the reaction radius as $r = 1.6 \times 10^{-10}$ m in $H_2O$ and $2.9 \times 10^{-10}$ m in $D_2O$, which are too small. This means that the steric factor is overestimated because the 1-pentylamine molecule has a considerably large alkyl chain group. Thus it is not prudent to discuss the reaction radius for the proton-transfer reaction of 1-pentylamine as is done for the above three amines. However, the smaller value of $k_{12}$ for 1-pentylamine than those of others may arise from the smaller steric factor of the reaction. The result of the isotope effect for the forward rate constant to be more than unity may be interpreted by the compensation of two factors, i.e., the lowering of the zero-point energy level of the reactants and the lowering of the activation energy owing to the deuteration for the forward process. The former factor for the proton-transfer reaction is considered to be similar for all amines, but the latter one depends on the structure of the activated complex, which seems to have a structure similar to that of the intermediate. The intermediate still holds several solvent molecules. The higher the number of solvent molecules in the activated complex, the lower the zero-point energy level of the activated complex gets. That is, the activated complex for 1-pentylamine is considered to involve fewer solvent molecules. This is also reflected by the $\Delta V_1$ values for these amines,[6] i.e., $\Delta V_1$ values decrease monotonically with increasing hydrophobicity of amines. The isotope effect of the reverse process is simply recognized by the lowering of the activation energy owing to deuteration of the intermediate, $R{-}NL_3^+\cdots OL^-$.

Next, the ultrasonic absorption results in the concentrated solutions of 1-pentylamine in $D_2O$ are interpreted. In the concentration range from 0.45 to 0.92 mol dm$^{-3}$, double-relaxational processes appear ($i = 2$ in eq 1), and the absorption data above 0.92 mol dm$^{-3}$ are well fitted to the single-relaxational equation ($i = 1$ in eq 1). These results indicate that above 0.45 mol dm$^{-3}$ another relaxation process exists along with that caused by the proton/deuteron-transfer reaction. Although the experimental absorption data above 0.92 mol dm$^{-3}$ look to fit to the single relaxational equation, the relaxational absorption due to the deuteron-transfer reaction is considered to superimpose on the observed spectra. It is possible to estimate the relaxation frequency, $f_{r1}$, and the amplitude of the absorption, $A_1$, in the concentrated solutions of 1-pentylamine using the rate and thermodynamic parameters listed in Table 2 on the assumption that the deuteron-transfer reaction is still proceeding in a similar fashion in the concentrated solutions. The estimated ultrasonic relaxation parameters are indicated in the brackets in Table 1. Then, the absorption due to the deuteron-transfer reaction is subtracted from the experimental data as $(\alpha/f^2)' = \alpha/f^2 - A_1/[1+(f/fr_1)^2]$. The residual values, $(\alpha/f^2)'$, have been analyzed by the single-relaxational equation by which it is found

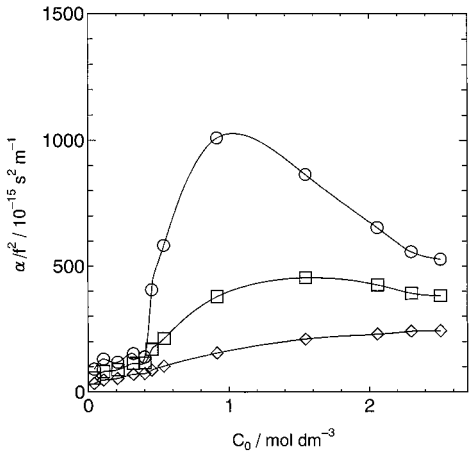


**Figure 3.** Concentration dependence of the absorption at different measuring frequency in 1-pentylamine aqueous solutions in $D_2O$: (○) 15 MHz; (□) 35 MHz; (◇) 75 MHz. It shows a peak sound absorption concentration (PSAC).

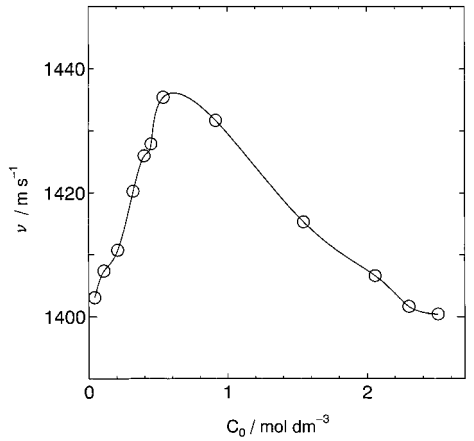


**Figure 4.** Concentration dependence of the sound velocity in 1-pentylamine aqueous solutions in $D_2O$. It shows a peak sound velocity concentration (PSVC).

that they are satisfactorily described. Thus calculated values are shown in parentheses in Table 1.

Figure 3 shows the concentration dependence of $\alpha/f^2$ values at different measuring frequencies, 15, 35, and 75 MHz. A peak sound absorption concentration (PSAC) can be seen for 15 MHz measurements clearly, but it gets obscure with the measuring frequency increased. The concentration dependence of the sound velocity, $v$, which is represented in Figure 4, shows a peak sound velocity concentration (PSVC). Similar phenomena were observed in solutions for 1-butylamine in $H_2O$[2] and in $D_2O$,[3] and in binary mixtures.[20,21] They were well interpreted by the molecular-aggregation reaction and the solute−solvent interaction. 1-Pentylamine molecules consist of amino ends (hydrophilic) and alkyl chains (hydrophobic), and then they trend to associate in aqueous environment. The existence of the 1-pentylamine aggregate has been detected by $^1$H NMR chemical shift (Figure 5).[3] An intersection at about 0.45 mol dm$^{-3}$ for the $\delta$- and $\epsilon$-H's of 1-pentylamine (in $D_2O$) has been observed clearly, while those for the $\gamma$-, $\beta$-, and α-H's gets more and more obscure. This intersection concentration is in very good agreement with the ultrasonic absorption result; i.e., the double-relaxation absorption appears at the same concentration. It is considered that the hydrogen-bond interaction between the hydrophilic amino end of the amines and the bulk heavy water affects the aggregate associated with hydrophobic interaction, and the influence from the hydrogen bond is weakened to the

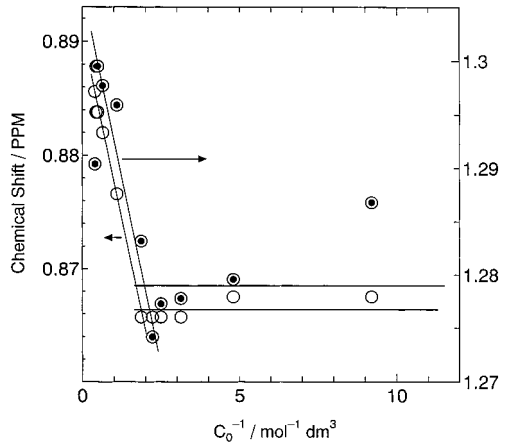


**Figure 5.** The reciprocal concentration dependence of the chemical shift for the $\delta$-H (⊙) and the $\epsilon$-H (○) of 1-pentylamine.

$\delta$- and $\epsilon$-H's. If the critical micelle concentration exists in the solution, it may be between 0.40 and 0.45 mol dm$^{-3}$.

Therefore, the relaxation absorption observed is considered to be caused by an aggregation reaction of 1-pentylamine expressed by the following reaction mechanism

$$n\mathrm{A} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{A}_n \tag{7}$$

where A is 1-pentylamine monomer, $A_n$ is the aggregate, $n$ is the aggregation number, and $k_f$ and $k_r$ are the forward and reverse rate constants, respectively. According to eq 5, for this aggregation reaction, we have

$$\Gamma_2 = (1/RT)k_f(C_A)^n(2\pi f_{r2})^{-1} \tag{8}$$

where $C_A$ is the molar concentration of 1-pentylamine monomer. The relaxation process under consideration is not observed in 1-pentylamine hydrochloride aqueous solution. Therefore, the nonionized amine molecules are considered to participate in the aggregation reaction. When the dissociation constant, $K_b$, still holds in the concentrated solution of 1-pentylamine, the concentration of the 1-pentylamine monomer is obtainable through the relationship as $C_A = \gamma^2[OD^-]^2/K_b$. Then, the next equation is derived from eqs 3 and 8 as $\ln[A_2 f_{r2}^2/(\rho v)] = n \ln(\gamma^2[OD^-]^2) + \ln[(\Delta V_2)^2 k_f/(2RTK_b^n)]$. The plots of $\ln[Af_r^2/(\rho v)]$ vs $\ln(\gamma^2[OD^-]^2)$ shown in Figure 6 make it possible to evaluate the aggregation number $n$ to be 4.4. In this calculation, the original ultrasonic parameters in Table 1 have been used. When the ultrasonic parameters calculated from the subtracted values as $(\alpha/f^2)' = \alpha/f^2 - A_1/[1 + (f/f_{r1})^2]$ are used, $n = 3.3$ is obtained. In these determinations, the values at 2.5093 mol dm$^{-3}$ were not taken because the amplitude of the absorption in the two calculation procedures are considerably different from each other as seen in Table 1. We have adopted $n = 4$ as the average aggregation number (Table 4). Then, for the aggregation reaction in eq 7, the rate constants are derived from the dependence of the relaxation frequency on $[OD^-]$ as[4-6] $\tau_2^{-1} = 2\pi f_{r2} = n^2 k_f (\gamma^2[OD^-]^2/K_b)^{n-1} + k_r$. From the plots of $2\pi f_{r2}$ vs $(\gamma^2[OD^-]^2)^3$ for 1-pentylamine in $D_2O$ (Figure 7), the forward and reverse rate constants are obtained (Table 4). When the $f_{r2}$ values in parentheses in Table 1 are used, we obtain $k_f = 1.1 \times 10^7$ (mol dm$^{-3}$)$^{-3}$ s$^{-1}$ and $k_r = 3.7 \times 10^7$ s$^{-1}$. In Figure 7, these recalculated relaxation frequencies are also indicated.

Because $n$-molecular reaction is improbable, a stepwise reaction mechanism has been proposed for the aggregation reaction of surfactant by Kresheck et al.[22] The relation for the

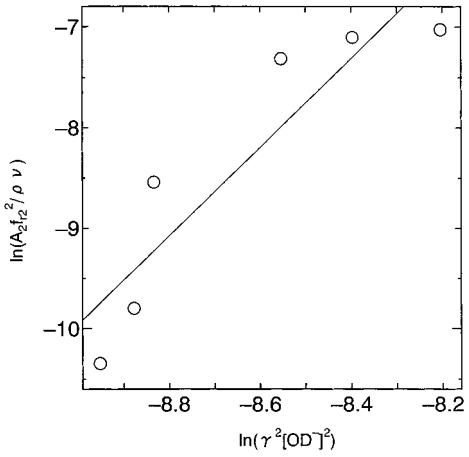


**Figure 6.** Aggregation number determination for the association−dissociation reaction in 1-pentylamine aqueous solution in $D_2O$. The slope of the fitted line is 4.4, and when the recalculated values in parentheses in Table 1 are used, the slope is 3.3. Thus the mean aggregation number is evaluated as 4.

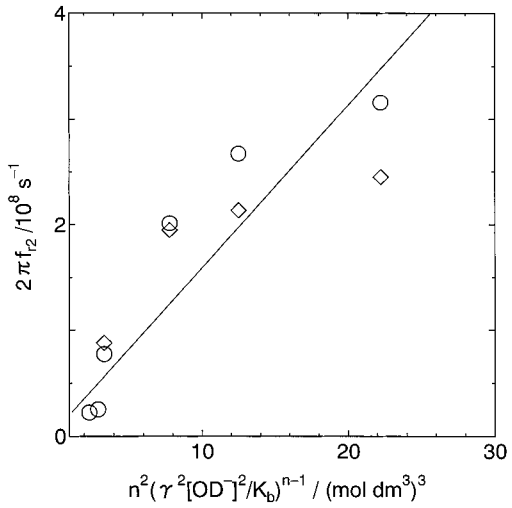


**Figure 7.** Rate constant determination of the association−dissociation reaction for 1-pentylamine in $D_2O$ by deuterioxide concentration dependence of the relaxation frequency, in which $n = 4$: ○, the results obtained from the original absorption data; ◇, those estimated after the subtraction of the absorption due to the deuteron transfer reaction.

**TABLE 4: Rate and Thermodynamic Constants of Aggregation Reaction for 1-Pentylamine in $H_2O$ and in $D_2O$ at 25 °C**

| reactants | $n$ | $k_f$ | $k_r$, $10^7\ s^{-1}$ | $\Delta V_2$, $10^{-6}\ m^3\ mol^{-1}$ |
|---|---|---|---|---|
| pentylamine in $H_2O$ | 5 | $1.2 \times 10^7\ (mol\ dm^{-3})^{-4}\ s^{-1}$ | 5.0 | 17 |
| pentylamine in $D_2O$ | 4 | $1.5 \times 10^7\ (mol\ dm^{-3})^{-3}\ s^{-1}$ | 2.2 | 15 |

relaxation time is given as $\tau_2^{-1} = k_r\{1 + n(C_0 - C_{cmc})/C_{cmc}\}$, where $C_0$ is the analytical concentration of solute. However, this expression is the same as that for eq 7 if the monomer concentration corresponds to the critical micelle concentration, $C_{cmc}$. Nakagawa[23] has proposed a new interpretation for the aggregation reaction for surfactant on the basis of the existence of polydispersed aggregates (micelles) and has given a preferable relation as $\tau_2^{-1} = k_r\{q + (C_0 - C_{cmc})/C_{cmc}\}$, where $q$ is constant. Assuming that $C_{cmc}$ for 1-pentylamine is 0.425 mol $dm^{-3}$, the plots of $\tau_2^{-1}$ vs $(C_0 - C_{cmc})/C_{cmc}$ are shown in Figure 8, which gives $\tau_2^{-1} = \{6.0 \times 10^7(C_0 - C_{cmc})/C_{cmc} + 1.8 \times 10^7\}\ s^{-1}$. When the recalculated values for the relaxation frequency are taken, we have $\tau_2^{-1} = \{5.3 \times 10^7\ (C_0 - C_{cmc})/C_{cmc} + 2.3 \times 10^7\}\ s^{-1}$. The slope value corresponds to $k_r$ according to Nakagawa's theory, and it is interesting to see that this value falls on the same straight line of the plots of $\log(k_r)$ vs $\log(C_{cmc})$ for various surfactants.[23] Also, it should be noticed that the intercept is close to the reverse rate constant, $k_r$, in Table 2. Aniansson and Wall,[24] Teubner,[25] and Kato et al.[26] have proposed a more realistic model to interpret the kinetics of micelles for surfactants assuming that the micelle distribution is Gaussian type. The relation for the relaxation time is given as $\tau_2^{-1} = k_r/\sigma^2 + (k_r/n)(C_0 - C_{cmc})/C_{cmc}$, where $\sigma$ is the variance of the size distribution function. Then, the above-mentioned numerical linear equation for $\tau_2^{-1}$ has a slightly different meaning. However, for 1-pentylamine, its hydrophobicity is not so much, compared with those of conventional surfactants. The aggregation number may be much smaller than those for surfactants. Therefore, it is not so certain that the aggregate distribution of 1-pentylamine is treated similarly (Gaussian).

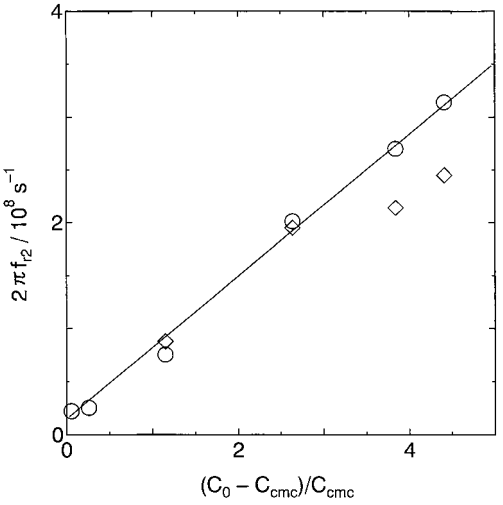


**Figure 8.** Plots of $2\pi f_{r2}$ vs $(C_0 - C_{cmc})/C_{cmc}$ following the analysis that is based on the distribution of the aggregate. ○ and ◇ have the same meaning as those in Figure 7.

**TABLE 5: Isotope Effects on Aggregation Reaction for 1-Pentylamine and 1-Butylamine in $H_2O$ and in $D_2O$ at 25 °C**

| reactants | $k_r^H/k_r^D$ | $\Delta V_2^H/\Delta V_2^D$ |
|---|---|---|
| pentylamine | 2.3 | 1.1 |
| butylamine | 2.4 | 1.3 |

Once the forward rate constant is known, the standard volume change, $\Delta V_2$, is obtainable using the following equation derived from eqs 3 and 8 as $A_2 f_{r2}^2/\rho\nu = [(\Delta V_2)^2 k_f/(2RTK_b^n)](\gamma^2[OD^-]^2)^n$. For 1-pentylamine in $D_2O$, $\Delta V_2$ is estimated to be $15 \times 10^{-6}$ $m^3\ mol^{-1}$, and that in $H_2O$[1] is $17 \times 10^{-6}\ m^3\ mol^{-1}$ (Table 4). When the $A_2$ and $f_{r2}$ calculated from the subtracted absorption coefficients, $(\alpha/f^2)'$, are used, $\Delta V_2$ becomes $11 \times 10^{-6}\ m^3\ mol^{-1}$. The isotope effects for $k_r$ and $\Delta V_2$ are calculated for the above aggregation process (Table 5) using the original ultrasonic parameters in Table 1.

According to Teubner,[25] the maximum absorption per wavelength is given as

$$\mu_{max2} = 0.5A_2 f_{r2}\nu = [\pi\rho\nu^2(\Delta V_2)^2 C_{cmc}(\sigma^2/n)(C_0 - C_{cmc})/C_{cmc}]/[(2RT)\{1 + (\sigma^2/n)(C_0 - C_{cmc})/C_{cmc}\}] \quad (9)$$

Figure 9 shows the plots of $\mu_{max2}$ vs $(C_0 - C_{cmc})/C_{cmc}$, and they should have a simple increasing trend,[25,26] but the experimental result shows a maximum.

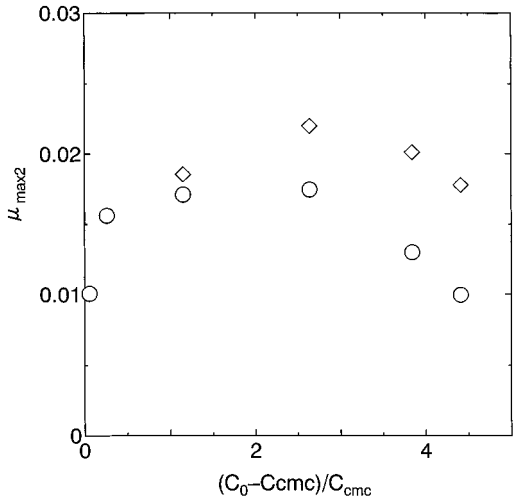


**Figure 9.** Maximum absorption per wavelength as a function of $(C_0 - C_{cmc})/C_{cmc}$. ○ and ◇ have the same meaning as those in Figure 7.

Following above interpretations, we have compared the kinetic results and have considered them on the basics of the analysis proposed by us, that is, by using the obtained rate and thermodynamic constants (Table 2). It should be noticed that the aggregation number for 1-pentylamine in $D_2O$ is smaller than that in $H_2O$, as observed in 1-butylamine solutions, which was interpreted by the relative hydrophobicity of the solute to the isotopic solvents.[3] The stronger hydrogen bond formed between hydrophilic amino groups and the solvent $D_2O$ makes the association trend decrease for 1-pentylamine, since it is considered that the amine molecules aggregate together by hydrophobic interaction. Concerning the difference in the rate constants, a different dimension for 1-pentylamine in $D_2O$ and that in $H_2O$ for the forward rate constants makes it inappropriate to compare them with each other. However, the isotope effect for the reverse rate constants, $k_r^H/k_r^D$, has been evaluated to be 2.3, which is almost the same value as that for 1-butylamine (Table 5). It indicates that the stability increases for the smaller aggregate in $D_2O$. Also smaller aggregate product causes smaller standard volume change for this reaction process.

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