Isotope Effect in Proton-Transfer and Association–Dissociation Reactions for Butylamine by Ultrasonic Relaxation Methods

Hua Huang,[†,#] Sadakatsu Nishikawa,[*] and Shaojun Dong[†]

Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Saga 840-8502

†Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Jilin 130022, China

(Received February 10, 1999)

Ultrasonic absorption coefficients were measured for butylamine in heavy water (D_2O) in the frequency range from 0.8 to 220 MHz and at concentrations from 0.0278 to 2.5170 mol dm^{-3} at 25 °C; two kinds of relaxation processes were observed. One was found in relatively dilute solutions (up to 0.5 mol dm^{-3}), which was attributed to the hydrolysis of butylamine. In order to compare the results, absorption measurements were also carried out in light water (H_2O). The rate and thermodynamic parameters were determined from the concentration dependence of the relaxation frequency and the maximum absorption per wavelength. The isotope effects on the diffusion-controlled reaction were estimated and the stability of the intermediate of the hydrolysis was considered while comparing it with the results for propylamine in H_2O and D_2O. Another relaxation process was observed at concentrations greater than 1 mol dm^{-3} in D_2O. In order to examine the solution characteristics, proton NMR measurements for butylamine were also carried out in D_2O. The chemical shifts for the γ- and δ-proton in butylamine molecule indicate the existence of an aggregate. From profiles of the concentration dependence of the relaxation frequency and the maximum absorption per wavelength of sound absorption, the source of the relaxation was attributed to an association–dissociation reaction, perhaps, associated with a hydrophobic interaction. The aggregation number, the forward and reverse rate constants and the standard volume change of the reaction were determined. It was concluded from a comparison with the results in H_2O that the hydrophobic interaction of butylamine in D_2O is stronger than that in H_2O. Also, the isotope effect on this reaction was interpreted in terms of the solvent structure.

An ultrasonic absorption method has been widely utilized to investigate fast reaction kinetics.[1—3] Especially, a recent development of the apparatus over a wide frequency range (from 0.8 to 220 MHz in our case) is helping us to extend the observable time range and to examine various reactions. On the other hand, an isotope effect has been known to be very useful to elucidate the reaction mechanism, and has been used to study the static and slow dynamic behaviors in solutions. However, it has not so far been utilized for examinations in fast reaction kinetics in solutions.[4] Light water (H_2O) and heavy water (D_2O) are extremely closely matched in many properties, except for the most sensitive ones, i.e. the surface tension, the dielectric constant, etc.[5] In addition, the higher viscosity, higher heat capacity and higher temperature of the maximum density for D_2O reflect that D_2O is more structured than H_2O. However, it seems to be difficult to predict straightforwardly the change in the reaction rate when going from H_2O to D_2O, because a number of competitive processes involved proceed too quickly.

In recent years, the role of solvents in reaction kinetics has been paid much attention because the rates of various reactions are strongly dependent on the reactant environments. This is striking when the solvent molecules themselves participate in the reaction. One representative example is the hydrolysis of amines (diffusion-controlled reaction) in water, which has been directly observed by an ultrasonic relaxation method.[2,3,6—10] Also, aggregates are formed when the hydrophobicity of the molecule increases; the association–dissociation reaction is detected by the same method.[7—9] The proton-transfer and association–dissociation reactions for butylamine in H_2O were studied previously by the present authors.[8—10] A recent study[11] concerning the proton-transfer reaction of propylamine in D_2O has proved that a diffusion-controlled reaction rate is facilitated and the intermediate of the hydrolysis is stabilized when D_2O is used as a solvent. It is now necessary to clarify the isotope effect on the fast proton-transfer and aggregation reactions of other amines in order to see how much the isotope effect appears when the reactant molecular size is different. For this purpose, we have chosen butylamine as a solute, and ultrasonic studies have been carried out in detail. Also, a proton NMR method has been used to ascertain the existence of a butylamine aggregate. Understanding these kinds of reactions of amines is very helpful to reveal similar phenomena occurring in biological systems.

Experimental

Chemicals. Butylamine was the purest grade from Wako Pure Chemicals Co., Ltd. and was used without further purification.

H. H. was supported by AIEJ Short-term Student Exchange Promotion Program in 1998.

Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) and heavy water from the same Co., Ltd. were guaranteed to be more than 99 and 99.75%, respectively. Light water was distilled, deionized and filtered through a MilliQ SP-TOC filter System from Japan Millipore Ltd. The sample solutions were prepared one day before measurements, and were kept in a N_2 gas atmosphere. The desired concentrations of the samples were determined by weighing.

Measurements. Ultrasonic absorption coefficient measurements were performed by a pulse method over the frequency range from 15 to 220 MHz using 5 and 20 MHz fundamental X-cut quartz crystals to obtain the absolute values of the coefficient. A resonance method was used in the low frequency range from 0.8 to 7 MHz. The details concerning these apparatuses were previously described.[12,13] The sound velocity was measured by the resonator at around 3 MHz. Densities were achieved using a vibrating density meter (DMA 60/602, Anton Paar). The solution pH was measured by inserting a glass electrode (HM-60S Toa Denpa) into the ultrasonic absorption cell while the measurements were proceeding. A water bath (EYELA UNI ACE BATH NCB-2200) and circulating water (LAUDA, RM20) were utilized to keep the temperature at 25 °C.

Determinations of the NMR spectra were made with a JEOL JNM-GX-270 spectrometer, operating at 270 MHz using Fourier-transfer techniques. The chemical shifts were determined using DSS dissolved in D_2O as an internal standard.

Results and Discussion

The amino-hydrogen atoms of butylamine are exchanged with deuterium spontaneously when D_2O is used as a solvent.[14] The deuterated butylamine is represented as R-ND_2.

Figure 1 shows the frequency dependence of the ultrasonic absorption coefficients divided by the square of the frequency, α/f^2, for butylamine in D_2O. The experimental absorption data have been analyzed by the Debye-type relaxational equation,

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

where f_{ri} and A_i are the relaxation frequency and the amplitude of the ultrasonic absorption for the i-th process, respectively, and B is the background absorption. All of the ultrasonic parameters (f_{ri}, A_i, and B) which are listed in Table 1, have been determined by a nonlinear least-mean-squares method. The solid curves shown in Fig. 1 are the calculated values using Eq. 1 with the help of such determined parameters. It is clearly shown in this figure that the excess absorptions observed in relatively dilute solutions (below 1 mol dm^{-3}) are well characterized by a single relaxational equation, $i = 1$ in Eq. 1. Along with an increase in the concentration (from 1 to 1.3 mol dm^{-3}), the data do not obey the single relaxational equation, but they fit to relaxation curves with two relaxation frequencies, $i = 2$ in Eq. 1. Along with further increase in the concentration, it happens again that the data can be well described by the single relaxational equation. The details concerning the analytical and distinctive procedures for the single or double relaxational spectra have been described elsewhere.[12,15] These results mean that there exist at least two different relaxational processes in our

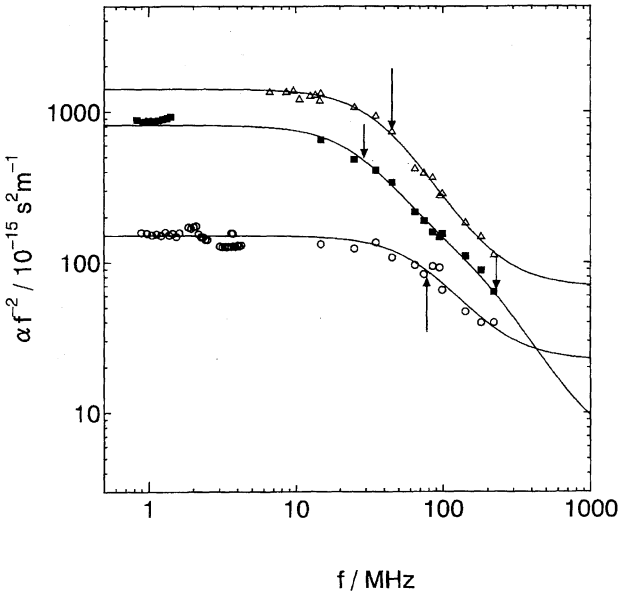

Fig. 1. The representative ultrasonic absorption spectra for butylamine in D_2O at 25 °C. ○: 0.5270 mol dm^{-3}; ■: 1.2028 mol dm^{-3}; △: 1.5209 mol dm^{-3}. The arrows indicate the relaxation frequencies.

frequency range. A similar phenomenon for butylamine and pentylamine has also been found in H_2O.[7,8,10]

First, let us consider the relaxation process which takes place in relatively dilute solutions in which the concentration of butylamine is less than 1 mol dm^{-3}. In order to compare the results with those in light water, absorption measurements for butylamine in H_2O were carried out under the same conditions. These ultrasonic parameters are indicated by f_{r1} and A_1 in Table 1. The profiles of the ultrasonic parameters are quite similar to each other in both solvents, D_2O and H_2O, as the results show in Table 1. That is, the relaxation frequency increases monotonically and the amplitude of the relaxation tends to reach a plateau with the concentration. Also, the absorption is very sensitively dependent on the solution pH. In such butylamine solutions, the absorption mechanism is considered to be related to a hydrolysis of amine proposed originally by Eigen,[16] expressed as

$$\text{R-NL}_3^+ + \text{OL}^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \text{R-NL}_3^+ \cdots \text{OL}^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \text{R-NL}_2 + \text{L}_2\text{O}, \quad (2)$$

where L represents H or D, and k_{ij} is the rate constant at individual steps. In this situation, the relationship between the relaxation frequency and the reactant concentration is given by[2,9]

$$\tau_1^{-1} = 2\pi f_{r1} = k_{12}\gamma^2([\text{R-NL}_3^+] + [\text{OL}^-]) + k_{21} = 2k_{12}\gamma^2[\text{OL}^-] + k_{21}, \quad (3)$$

where τ_1 is the relaxation time. Then, the rate constants, k_{12} and k_{21}, can be determined from the slope and the intercept of plots of $2\pi f_{r1}$ vs. $\gamma^2[\text{OL}^-]$ when the hydroxide or deuteroxide concentration is available. The coupling effect with other reactions is considered later, because this is usually taken into account in a treatment of the chemical relaxation

Table 1. Ultrasonic Parameters for Butylamine in D_2O and in H_2O at 25 °C

C_0	pH	f_{r1}	f_{r2}	A_1	A_2	B	v	ρ
mol dm^{-3}		MHz			10^{-15} s^2 m^{-1}		m s^{-1}	kg dm^{-3}
			Butylamine	in	D_2O			
2.5170	12.98	—	105±9	—	705±25	32±18	1455	1.0405
2.0046	12.92	—	73±3	—	917±30	64±9	1461	1.0549
1.8009	12.87	—	52±3	—	1131±52	79±7	1465	1.0591
1.5209	12.83	—	43±1	—	1346±28	68±4	1470	1.0705
1.3488	12.82	127±29	29±2	224±40	1186±44	10±15	1475	1.0716
1.2028	12.80	202±134	31±8	99±31	713±44	5±40	1476	1.0777
1.0193	12.78	53±3	16±6	338±47	148±45	35±1	1470	1.0813
0.5270	12.50	80±6	—	128±6	—	22±2	1441	1.0920
0.3298	12.43	75±4	—	105±4	—	20±1	1427	1.0964
0.2530	12.32	62±2	—	85±2	—	24±1	1422	1.0985
0.1979	12.23	48±2	—	96±3	—	30.2±0.4	1419	1.0993
0.1064	12.17	34±1	—	113±3	—	28.7±0.3	1411	1.1011
0.0278	11.66	25±2	—	85±8	—	28.2±0.4	1399	1.1032
			Butylamine	in	H_2O			
0.5056	12.23	134±8		67±2		17±3	1529	0.9903
0.3860	12.14	107±5		73±1		16±1	1523	0.9925
0.1960	11.98	90±3		60±1		21.7±0.5	1512	0.9946
0.0820	11.76	58±2		61±2		21.1±0.4	1506	0.9961
0.0302	11.46	37±2		48±3		20.6±0.3	1503	0.9969

analysis.

The concentration of deuteroxide ions, $[OD^-]$, is calculated according to a pH meter reading using the following relation:[17—20]

$$pD_{\text{in } D_2O} = pH_{\text{meter reading in } D_2O} + 0.41. \quad (4)$$

The ionization constant, $pK_w = 14.955$ for D_2O at 25 °C, is also taken.[21] For butylamine in D_2O, the dissociation constant, K_b, is defined as

$$K_b = \gamma^2[OD^-]^2/([R\text{-}ND_3^+\cdots OD^-] + [R\text{-}ND_2]) = \gamma^2[OD^-]^2/(C_o - [OD^-]), \quad (5)$$

where γ is the activity coefficient calculated by Davis' equation.[22] A similar equation as Eq. 5 was applied to estimate the dissociation constant in H_2O. The obtained values are listed in Table 2, and the result in H_2O is very close to the literature value.[23] It is now possible, using a least-mean-squares method, to determine the rate constants from plots of $2\pi f_{r1}$ vs. $\gamma^2[OL^-]$, which are shown in Fig. 2; the results are tabulated in Table 2. The good linear relationships make us confirm that the cause of the relaxation is due to a perturbation of the first step in Eq. 2. Then, the isotope effects are obtained for the forward and backward rate constant (Table 2). The slightly greater forward rate constant for butylamine in D_2O is interpreted by a decrease in the activation energy at the transition state, i.e. by a decrease in the vibrational energy of the activated complex, because the rate constant is controlled by the activation free energy, following the Eyring rate theory. This may be caused by the greater reaction radius in D_2O than that in H_2O, which is estimated from the theoretical equation for the diffusion-controlled reaction proposed by Debye.[3,11,16] A similar isotope effect is also found in propylamine solutions.[11] Also, the isotope effect on the backward rate constant is explained by the more stable intermediate, as is done for propylamine solutions. That is, the intermediate, $R\text{-}ND_3^+\cdots OD^-$, which still includes several solvent molecules,[3] is stabilized due to deuterium additions, which cause a further decrease in the vibrational energy of the intermediate, even if the activated complex energy level is lowered. This situation is also seen in the equilibrium constant, K_{21}, defined as $K_{21} = k_{21}/k_{12}$. As can be seen in Table 2, the K_{21} values in D_2O are smaller than those in H_2O. Another equilibrium constant, K_{32}, in Table 2 is that for step II in Eq. 2. They were calculated from the relationship, $1/K_b = 1/K_{21} + 1/(K_{21}K_{32})$.[9,11]

For the deuteron- or proton-transfer reaction, the standard volume change, ΔV, is also related to the maximum absorption per wavelength, μ_{max1},

$$\mu_{max1} = 0.5A_1 f_{r1} c = \pi\rho c^2 \Gamma(\Delta V_1)^2/(2RT), \quad (6)$$

where $\Gamma = (1/[OL^-] + 1/[R\text{-}NL_3^+] + 1/[R\text{-}NL_3^+\cdots OL^-])^{-1}$, ρ is the solution density, c is the sound velocity, R is the gas constant, and T is the absolute temperature. Such determined mean values of ΔV_1 for a deuteron- or proton-transfer reaction are given in Table 2. The greater volume change for a deuteron-transfer reaction is considered to be caused by the stronger hydrogen-bond network in D_2O compared to that in H_2O because the hydrogen-bonded water molecules have a greater volume than the free ones. The trend of the isotope effects for butylamine is very close to those for propylamine, although the effect on the forward rate constant is not so notable.

Next, we present the ultrasonic absorption results observed in concentrated solutions of butylamine in D_2O. In the con-

Table 2. Rate and Thermodynamic Constants of Deuteron or Proton Transfer Reaction for Propylamine and Butylamine in D_2O and in H_2O at 25°C

	k_{12}	k_{21}	k_{12}^H/k_{12}^D	k_{21}^H/k_{21}^D	K_{21}	K_{32}	K_b	ΔV_1
	10^{10} mol^{-1} dm^3 s^{-1}	10^7 s^{-1}			10^{-3} mol dm^{-3}		10^{-4} mol dm^{-3}	10^{-6} m^3 mol^{-1}
Propylamine[a] in D_2O	2.7±0.1	7.1±1.3	0.78	1.8	2.6	0.04	1.04±0.07	40±3
Butylamine in D_2O	3.1±0.3	5.4±2.8	0.90	1.7	1.8	0.07	1.17±0.23	34±1
Propylamine[a] in H_2O	2.1±0.2	13±4			6.2	0.10	5.6±1.5	33±8
Butylamine in H_2O	2.8±0.1	9.3±2.1			3.3	0.11	3.38±0.38	27±4

a) Quoted from Ref. 11.

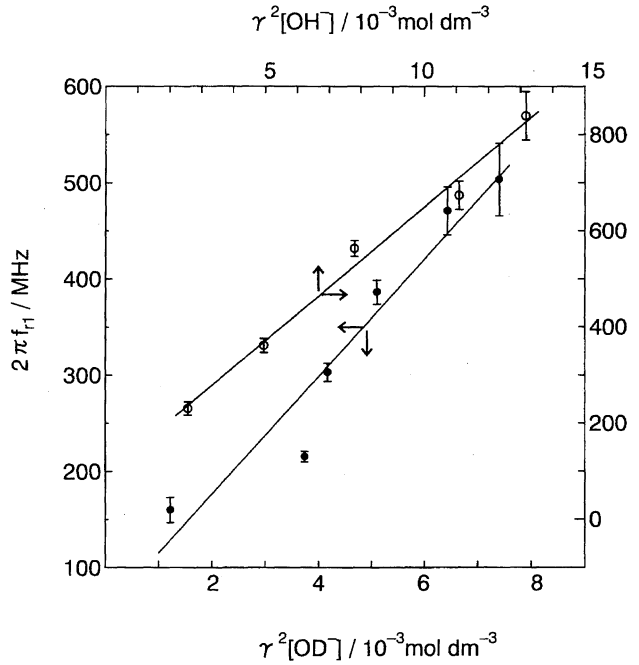

Fig. 2. Plots of $2\pi f_{r1}$ vs. $\gamma^2[OL^-]$ for butylamine in D_2O (●, corresponding to bottom and left axis.) and in H_2O (○, corresponding to top and right axis.).

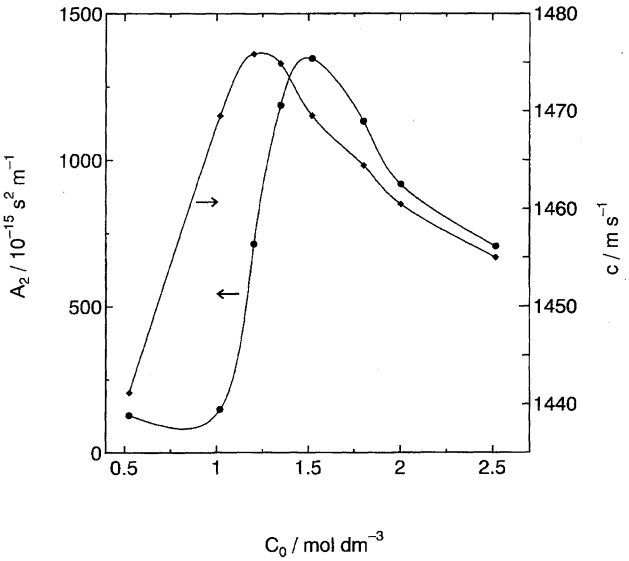

Fig. 3. The analytical concentration dependence of the excess absorption, A_2 (●) and the sound velocity, c (◆), for butylamine in D_2O.

centration range from 1 to 1.3 mol dm^{-3}, a double relaxation process is observed, and the absorption data above 1.3 mol dm^{-3} appear to be fitted to the single relaxational equation. This means that another relaxation process exists above 1 mol dm^{-3}, of which the parameters are given by f_{r2} and A_2 in Table 1. The slightly higher B values observed in the concentrated solutions (more than 1.3 mol dm^{-3}) indicate that the relaxational absorption due to the hydrolysis shifts to higher frequency range, that is, the higher B values are associated with a tail of the relaxation due to the hydrolysis of amines. Figure 3 shows the concentration dependence of the excess absorption, A_2. This phenomenon is called the peak sound absorption concentration (PSAC), and it is characteristic for aqueous solutions of nonelectrolytes. The concentration dependence of the sound velocity, c, which is also represented in Fig. 3, shows a similar trend, that is, the peak sound velocity concentration (PSVC), although the concentration of the maximum is lower than that for the maximum A_2. Similar phenomena were observed in solutions for butylamine in H_2O[8] and in binary mixtures,[24,25] and were interpreted by the molecular-aggregation reaction and the solute–solvent interaction. Butylamine molecules consist of hydrophilic and hydrophobic groups, which trend to associate in aqueous environment, as do those for surfactants.[26] The simplest association process may be expressed by the following reaction mechanism:

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

where B is the monomer, B_n is the aggregate, n is the aggregation number, and k_f and k_r are the forward and reverse rate constants, respectively. For solution in which aggregates form, the proton NMR signals can provide information about micelle formation. Haque[27] has reported that sodium propionate forms a small aggregate (micelle), of which the critical micelle concentration (cmc) is 1.33 mol dm^{-3}, using NMR. Muller and Birkhahn[28,29] have proposed a relation-

ship between the concentration and the chemical shift (δ) with the assumption that the reaction expressed by Eq. 7 occurs rapidly enough that the signals from the monomer and the micelle coalesce completely, when the over-all solute concentration, C_0, is greater than cmc:

$$\delta = \delta(B_n) + (\mathrm{cmc}/C_0)[\delta(B) - \delta(B_n)], \quad (8)$$

where $\delta(B)$ and $\delta(B_n)$ denote the chemical shift for the monomer and the aggregate, respectively. Below cmc, the chemical shifts are constant. Therefore, plots of δ vs. $1/C_0$ should consist of two straight lines, and the intersection of these two lines corresponds to cmc. These ideas have been applied to butylamine in D_2O, the plots of which are shown in Fig. 4. It is observed that the chemical shifts for γ- and δ-proton in butylamine fit to Eq. 8 well at greater than 1 mol dm^{-3}; also, the corresponding cmc has been estimated as ca. 1.0 mol dm^{-3}, which is close to the concentration where the ultrasonic relaxational absorption under consideration appears. However, the chemical shifts for the α- and β-proton in butylamine do not obey Eq. 8 very well. This is considered to be because the hydrophilic amine terminals are intact in D_2O molecules and, therefore, the α- and β-proton are still influenced by the solvent molecules. It has been well established that cmc for amphiphile in D_2O is lower than that in H_2O.[30—32] If the concentration where the ultrasonic relaxation appears corresponds to the cmc of butylamine, the present results are consistent, because the corresponding cmc in D_2O is 1 mol dm^{-3} or lower, and that in H_2O is 1.1 mol dm^{-3}. These concentrations are still lower than PSAC.

Since the existence of aggregates is speculated from a NMR measurement, it is natural that the cause of the observed relaxation may be associated with this aggregation process. Although the kinetics of the aggregation reaction of surfactants has been interpreted by the Aniansson–Wall

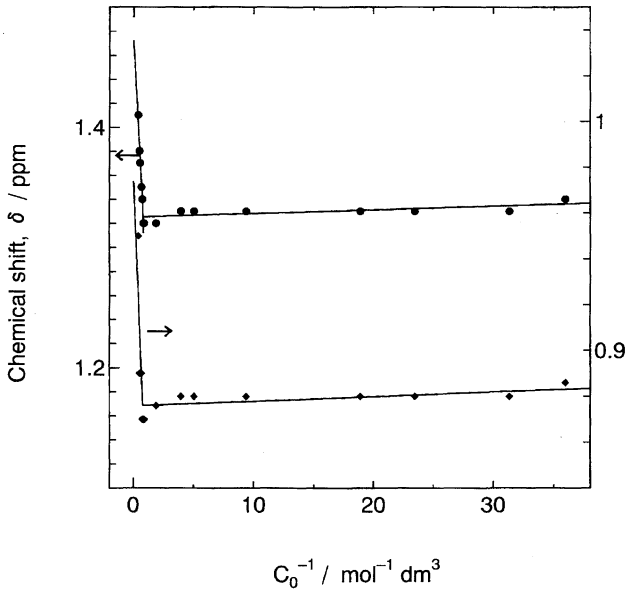

Fig. 4. Chemical shifts for butylamine in D_2O plotted against the reciprocal concentration. ●: γ-H, corresponding to left axis; ◆: δ-H, corresponding to right axis.

model,[33—36] it seems not to be applicable when the aggregation number is small. Therefore, we simply assume that the aggregation process is expressed by Eq. 7. For this reaction, the aggregation number can be estimated from the relation between the maximum excess absorption per wavelength, μ_{max2}, and the monomer concentration, C_1, using the following equation;[7,8]

$$\mu_{max2} = 0.5A_2f_{r2}c = \pi\rho c^2(\Delta V_2)^2k_f(C_1)^n(2\pi f_{r2})^{-1}/(2RT), \quad (9)$$

where C_1 is the molar concentration of the butylamine monomer. It is assumed that the dissociation constant, K_b, still holds in a concentrated solution of butylamine; then, the concentration of the butylamine monomer is obtainable by the relation $C_1 = \gamma^2[OD^-]^2/K_b$ based on the assumption that the deionized amine molecules participate in the reaction because the relaxational absorption is not observed when the solution pH is lowered. Then, Eq. 9 can be rewritten as

$$\ln[A_2f_{r2}^2/(\rho c)] = n\ln(\gamma^2[OD^-]^2) + \ln[(\Delta V_2)^2k_f/(2RTK_b^n)]. \quad (10)$$

From the slope of the plots of $\ln[Af_r^2/(\rho c)]$ vs. $\ln(\gamma^2[OD^-]^2)$, the aggregation number, n, has been obtained (Table 3). Thus the obtained value of n is so considerably small that the aggregate of butylamine may not be estimated as a micelle. Therefore, it may not be appropriate to use the expression "cmc" for butylamine, and we thus use the corresponding cmc.

Also, for the aggregation reaction, the rate constants are derived from the dependence of the relaxation frequency on $[OD^-]$,[7,8]

$$\tau_2^{-1} = 2\pi f_{r2} = n^2k_f(\gamma^2[OD^-]^2/K_b)^{n-1} + k_r, \quad (11)$$

This is the same expression as that derived by Kresheck et al.[37] Figure 5 shows plots of $2\pi f_{r2}$ vs. $(\gamma^2[OD^-]^2)^2$ for butylamine in D_2O. From the slope and intercept of this line, the forward and reverse rate constants have been determined. The rate constants for butylamine in H_2O have been recalculated by the same procedure using previously reported absorption data.[8] The slightly different values for k_f, k_r, and ΔV_2 derived in this paper are from the data treatment. All of the results are listed in Table 3 for a comparison.

Once the forward rate constant is determined, the standard volume change is obtained using the following equation derived from Eq. 9:

$$A_2f_{r2}^2/\rho c = [(\Delta V_2)^2k_f/(2RTK_b^n)](\gamma^2[OD^-]^2)^n. \quad (12)$$

From the slope of the plots of $A_2f_{r2}{}^2/(\rho c)$ against $(\gamma^2[OD^-]^2)^3$, the standard volume change, ΔV_2, for the aggregation reaction of butylamine in D_2O is estimated to be 9×10^{-6} m^3 mol^{-1}, and that in H_2O is 12×10^{-6} m^3 mol^{-1}.

The adiabatic compressibility, β_s, is a powerful parameter to describe the structure of solutions. It is calculated from the solution density and the sound velocity by Laplace equation, as

$$\beta_s = -(1/V)(\partial V/\partial P)_s = 1/(\rho c^2). \quad (13)$$

Table 3. Rate and Thermodynamic Constants of Aggregation Reaction for Butylamine in D_2O and in H_2O at 25°C

	n	k_f	k_r	ΔV_2
			10^{-7} s^{-1}	10^{-6} m^3 mol^{-1}
Butylamine in D_2O	3	3.4×10^6 (mol dm^{-3})$^{-2}$ s^{-1}	3.8	9
Butylamine in H_2O[a)]	4	1.1×10^6 (mol dm^{-3})$^{-3}$ s^{-1}	9.2	12

a) Recalculated results from the data of Ref. 8.

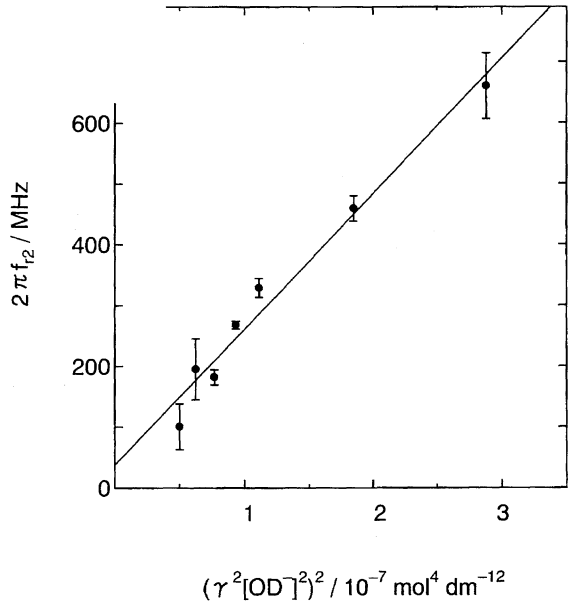

Fig. 5. Plots of $2\pi f_{r2}$ vs. $(\gamma^2[OD^-]^2)^2$ for butylamine in D_2O.

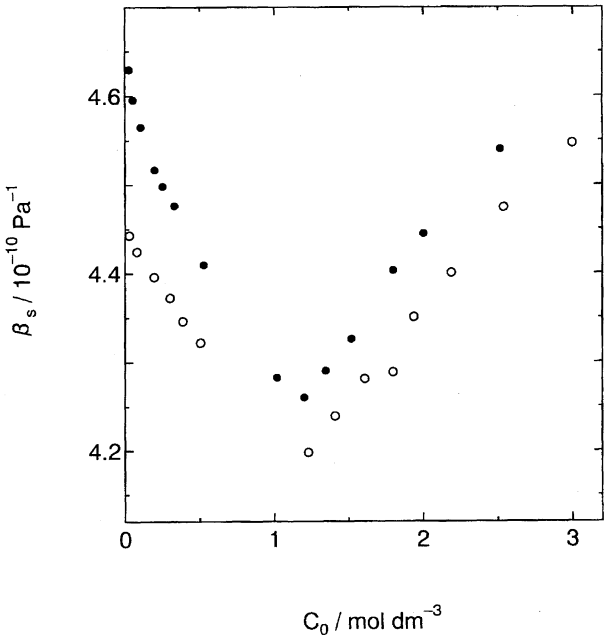

Fig. 6. The concentration dependence of the adiabatic compressibility, β_s, for butylamine in D_2O (●) and in H_2O (○).

Figure 6 shows the concentration dependence of β_s for butylamine in D_2O and that in H_2O. It is clearly shown that the adiabatic compressibility values in D_2O are greater than those in H_2O. It is considered that a solution with D_2O is bulkier than that with H_2O because of the further reorganized hydrogen-bond network in the D_2O solution. Such a network may cause hydrophobic interactions (or bond) that are stronger in D_2O than in H_2O. Also, a stronger hydrophobic interaction makes the concentration where the aggregate starts to be formed (the corresponding cmc) to decrease. This trend has been focused on in some surfactant solutions.[32]

It should be noticed that the observed aggregation number for butylamine in D_2O is smaller than that in H_2O. This may be because of the stronger hydrophobic interaction in D_2O. That is, it is considered that the aggregation number should be related to the relative hydrophobicity of the solute to solvent, and that the aggregate may be formed by a hydrophobic interaction. The end tails of the hydrocarbons in butylamine molecules are expected to be twining together. Such a small aggregate has also been found in an aqueous solution of perfluoro propionate, the aggregation number of which is three.[27] Concerning the difference in the rate constants, the forward rate constants have a different dimension for butylamine in D_2O and that in H_2O and, therefore, it is impossible to compare them with each other. However, the reverse rate constants are comparable. The isotope effect for the dissociation of the butylamine aggregate in H_2O and in D_2O, k_r^H/k_r^D, has been obtained to be 2.4. The decrease in the reverse rate constant for butylamine in D_2O indicates that even a smaller aggregate is more stable in D_2O. This may be because D_2O molecules are substantially structured. Such an isotope effect has also been observed in surfactant solutions,[4] although the isotope effects on fast reactions were seldom performed previously. In addition, the difference in the standard volume change for the aggregation reaction has also been attributed to the different aggregation number. That is, a reaction with a smaller aggregate product may cause a smaller volume change.

Though the proton- or deuteron-transfer reaction and the aggregation reaction have been interpreted independently in this paper, the general procedure of the chemical relaxation method needs the coupling effect for their reactions. Because the nonionized amine molecules participate in the aggregation reaction, all of the reactions under consideration are elucidated as

$$\begin{array}{l} \text{R-NL}_3^+ + \text{OL}^- \overset{\text{StepI}}{\rightleftharpoons} \text{R-NL}_3^+ \cdots \text{OL}^- \overset{\text{StepII}}{\rightleftharpoons} \text{R-NL}_2 + \text{L}_2\text{O} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow\uparrow \text{StepIII} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (1/n)(\text{R-NL}_2)_n. \end{array} \quad (14)$$

The observed relaxation for concentrations lower than 1 mol dm^{-3} has been attributed to a perturbation of Step I. When the coupling effect between Step I and Step II is taken into account, a reasonable dissociation constant, K_b, is not obtained, the details of which have been described previously.[2,9] Step II is considered to almost be an intramolecular reaction, and is too fast to affect Step I. With increasing the concentration, the relaxation frequency associated with Step I shifts to a higher frequency. Further increasing the concentration, the Step III process is observed in the MHz frequency range. Therefore, the relaxation frequency for Step III is much lower than that for Step I. If step II does not influence Step I, it is considered that Step II does not affect Step III. A more precise interpretation of the coupling effect has been shown in the ultrasonic results of butylamine and pentylamine in H_2O.[8]

In conclusion, from the results in the deuteron- or proton-transfer reaction for butylamine, we can see that the more structured hydrogen-bond networks in D_2O facilitate the deuteron-transfer reaction, and the intermediate is more stable when it is deuterated. It is noticed that the deuteron- or proton-transfer reaction proceeds slightly faster for butylamine than that for propylamine (Table 2). This may be explained by an enhancement of the hydrogen-bond structure of water by the hydrophobic alkyl group. A similar effect has been investigated in aqueous solutions of ethylenediamine, diethylenediamine and triethylenediamine by Dickson et al.[38] In addition, for the association–dissociation reaction for butylamine, it has been found that the aggregation number is smaller; also a slower reverse rate constant and a smaller standard volume change are obtained in D_2O compared to those in H_2O. These results are related to the structure of the solvent and the interaction between the solute and the solvent.

The authors acknowledge Professor Osada for the treatment of the NMR apparatus. Partial financial support of a Grant-in-Aid for Science Research No. 09440202 from The Ministry of Education, Science, Sports and Culture is gratefully appreciated.

References

1 S. Nishikawa, N. Yokoo, and N. Kuramoto, *J. Phys. Chem. B*, **102**, 4830 (1998).

2 S. Nishikawa and M. Satoh, *J. Acoust. Soc. Am.*, **102**, 3779 (1997).

3 N. Kuramoto and S. Nishikawa, *J. Acoust. Soc. Am.*, **104**, 2490 (1998).

4 J. Gettins, P. L. Jobling, M. F. Walsh, and E. Wyn-Jones, *J. Chem. Soc., Faraday Trans. 2*, **76**, 794 (1980).

5 G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, **41**, 680 (1964).

6 N. Kuramoto and S. Nishikawa, *J. Phys. Chem.*, **100**, 10629 (1996).

7 S. Nishikawa, T. Yasunaga, and K. Takahashi, *Bull. Chem. Soc. Jpn.*, **46**, 2992 (1973).

8 S. Nishikawa and T. Yasunaga, *Bull. Chem. Soc. Jpn.*, **46**, 1098 (1973).

9 Y. Yoshida and S. Nishikawa, *Bull. Chem. Soc. Jpn.*, **59**, 1941 (1986).

10 S. Nishikawa, T. Nakamoto, and T. Yasunaga, *Bull. Chem. Soc. Jpn.*, **46**, 324 (1973).

11 H. Huang, S. Nishikawa, and S. Dong, *J. Phys. Chem. A*, **103**, 3804 (1999).

12 S. Nishikawa and K. Kotegawa, *J. Phys. Chem.*, **89**, 2896 (1985).

13 N. Kuramoto, M. Ueda, and S. Nishikawa, *Bull. Chem. Soc. Jpn.*, **67**, 1560 (1994).

14 D. L. Pavia, G. M. Lampman, and G. S. Kriz, "Introduction to Spectroscopy," Harcourt Brace College Publishers, 1996, p. 209.

15 S. Nishikawa and F. Matsuo, *J. Phys. Chem.*, **95**, 437 (1991).

16 M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry," ed by A. Weissberger, Jr., Wiley, New York (1961), Vol. VIII, Part 2.

17 A. G. Marshall, "Biophysical Chemistry. Principles, Techniques, and Applications," John Wiley & Sons, New York (1978), p. 456.

18 P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **44**, 188 (1960).

19 H. H. Hyman, A. Kaganove, and J. J. Katz, *J. Phys. Chem.*, **64**, 1653 (1960).

20 F. G. K. Baucke, *J. Phys. Chem. B*, **102**, 4835 (1998).

21 "Handbook of Chemistry and Physics," 54th ed, CRC Press, Boca Raton (1973—1974), D-131.

22 R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London (1959), p. 232.

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

24 J. Andreue, P. D. Edmonds, and J. F. McKeller, *Acustica*, **15**, 74 (1965).

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

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

27 R. Haque, *J. Phys. Chem.*, **72**, 3056 (1968).

28 N. Muller and R. H. Birkhahn, *J. Phys. Chem.*, **71**, 957 (1967).

29 N. Muller and R. H. Birkhahn, *J. Phys. Chem.*, **72**, 583 (1968).

30 P. Mukerjee, P. Kapauan, and H. G. Meyer, *J. Phys. Chem.*, **70**, 783 (1966).

31 Y. F. Maa and S. H. Chen, *J. Colloid Interface Sci.*, **115**, 437 (1987).

32 G. C. Kresheck, *J. Phys. Chem. B*, **102**, 6596 (1998).

33 E. A. G. Aniansson and S. N. Wall, *J. Phys. Chem.*, **78**, 1024 (1974).

34 M. Teubner, *J. Phys. Chem.*, **83**, 2917 (1979).

35 S. Kato, S. Harada, and H. Sahara, *J. Phys. Chem.*, **99**, 12570 (1995).

36 T. Telgmann and U. Kaatze, *J. Phys. Chem. B*, **101**, 7766 (1997).

37 G. C. Kresheck, E. Hamorz, G. Dauenport, and H. A. Scheraga, *J. Am. Chem. Soc.*, **88**, 246 (1966).

38 L. Dickson, W. H. Nomura, R. E. Verrall, T. Suzuki, and S. Kato, *J. Phys. Chem.*, **85**, 2273 (1981).