Ultrasonic Absorption in Aqueous Solutions of Octylamine. Kinetic Investigation of Proton Transfer Reaction

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The ultrasonic absorption in the mesomorphic state of octylamine water system was characterized by double relaxations. One in the lower frequency range has been explained by the structural relaxation theory of the two state model. In order to clarify the mechanism of the relaxation in the higher frequency range, the ultrasonic absorption in a relatively dilute aqueous solution was measured. The mechanism of the absorption was attributed to hydrolysis from the concentration dependence of the relaxation time. The rate constant k_f for the proton transfer reaction, the equilibrium constant $K=k_b/k_f$, and the standard volume change ΔV resulting from the reaction were determined to be 1.0×10^{10} M^{-1} sec^{-1}, 7.6×10^{-3} M, and 32 cc mol^{-1} respectively.

A large amount of data has been accumulated on the equilibrium properties of aqueous solutions of amines. However, the knowledge of their dynamic properties in the solutions is limited. An ultrasonic absorption method has provided the very useful informations on dynamic properties in the liquid phase. In recent years, the ultrasonic absorptions in aqueous solutions of various amines have been measured and some mechanism associated with the excess absorptions have been proposed.[1-10]

The ultrasonic absorption in the mesomorphic state of octylamine water system is characterized by double relaxations. One in the lower frequency range was explained by the structural relaxation theory of the two state model. The explanation of the other in the higher frequency range remains unclarified.

The purpose of the present investigation is to report the results of the ultrasonic absorption measurement in the relatively dilute aqueous solutions of octylamine, to elucidate the mechanism and to clarify the relation between the excess absorption in the higher frequency range in the mesomorphic state and that in the relatively dilute solutions of octylamine.

In addition, an octylamine water system is one of lyotropic liquid crystals related very closely to biological systems.[11] Clarification of its dynamic properties, therefore, is of interest for understanding the biochemical reactions.

Experimental

The octylamine was of guaranteed grade and purified by distillation. The purity was verified to be higher than 99.9% by the gas chromatography. Deionized and distilled water was used as a solvent. Measurements of ultrasonic absorptions were carried out at odd harmonic frequencies of 0.5, 5, and 20 MHz X-cut quartz transducers by the pulse technique.[12] The frequency range was 2.5—220 MHz. The ultrasonic absorption measurement cell was air-tight and dry nitrogen gas was passed over the solution. The sing-around method was employed at 1.92 MHz to measure the sound velocity. Two kinds of picnometers were used for the measurement of density. The pH values of the solutions were measured by a Hitachi-Horiba Type F-5 pH meter. The temperature range of the ultrasonic absorption measurement was 12—36 °C and the concentration range 0.501—4.76 M.

Results

In general, the sound absorption caused by several relaxation processes is given by

$$\alpha/f^2 = \sum_j \frac{A_j}{1+(f/f_{rj})^2} + B \tag{1}$$

where f_{rj} is the relaxation frequency for the jth process and A_j and B are constants.

Representative ultrasonic absorption spectra at 3.79

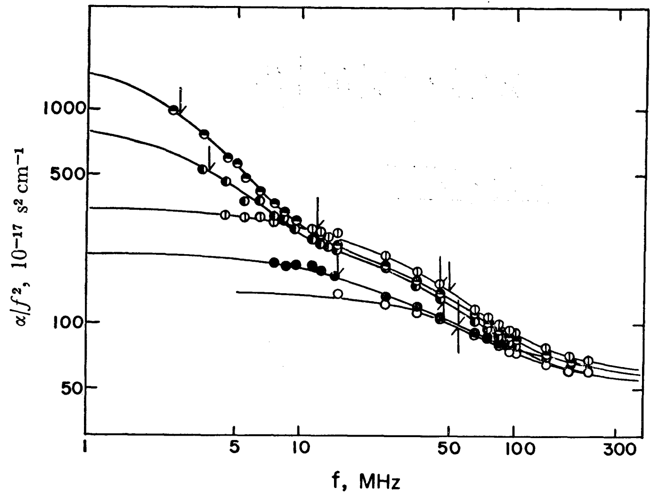

Fig. 1. Representative ultrasonic absorption spectra of the aqueous solution of octylamine at 3.79 M.
The arrows show the relaxation frequency:
⦶, 12 °C; ◐, 22 °C; ◓, 30 °C; ●, 35 °C; ○, 36 °C.

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Table 1. Relaxation parameters and density for aqueous solutions of octylamine at 20 °C

M	pH	ρ (g cm^{-3})	c (10^3 m sec^{-1})	f_r (MHz)		A (10^{-17} sec^2 cm^{-1})		B
			In the isotropic state					
0.501	11.47	0.9821	1.475	17.5		100		48.3
0.531	11.47	0.9818	1.474	18		121		46.1
0.782	11.53	0.9736	1.469	19		141		50.7
0.843	11.58	0.9715	1.470	20		130		55.3
0.978	11.74	0.9676	1.464	22		142		51.8
1.300	11.93	0.9597	1.456	27		146		56.5
			In the mesomorphic state					
				f_{r1}	f_{r2}	A_1	A_2	
3.10	—	0.9028	1.447	7	40	231	137	54.2
3.79	—	0.8782	1.456	6	50	346	138	57.6
4.76	—	0.9586	1.459	6	60	518	127	51.8

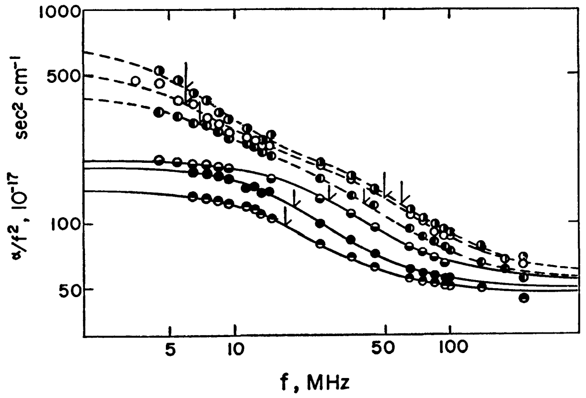

Fig. 2. Ultrasonic absorption in the aqueous solution of octylamine at various concentrations at 20 °C:
◑, 4.76 M; ○, 3.79 M; ◐, 3.10 M; ◒, 1.30 M;
●, 0.782 M; ◓, 0.501 M.

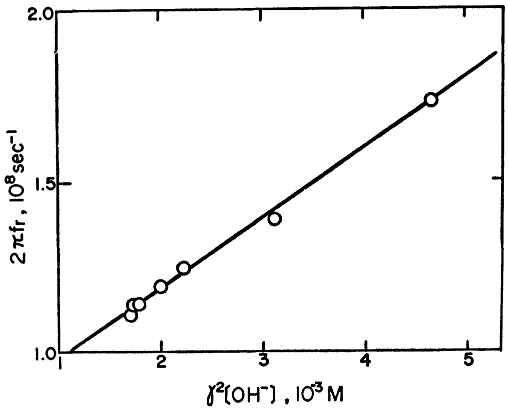

Fig. 3. The plots of $2\pi f_r$ *vs.* concentration at 20 °C. The straight line is a least-squares fit of the experimental points.

M (0.15 mol fraction of octylamine) at various temperatures are shown in Fig. 1. These spectra except one at 36 °C are characterized by double relaxations which correspond to the case of $j=1, 2$ in Eq. (1). The spectrum at 36 °C is described by the single relaxation equation which is the case $j=1$ in Eq. (1). The mesomorphic state of the octylamine water system is transformed to the isotropic one by heating. Since the transition temperature from mesomorphic to isotropic state is 35 °C at 3.79 M, the spectrum at 36 °C is that in the isotropic state. The excess absorption in the lower frequency range decreases abruptly as soon as the phase changes into the isotropic state, but that in the higher frequency range remains even in the isotropic state. The ultrasonic absorption spectra at various concentrations at 20 °C are shown in Fig. 2. The dashed lines are the spectra in the mesomorphic state, characterized by double relaxations. The solid lines are those for the relatively dilute solutions in the isotropic state, characterized by single relaxation. The values of relaxation frequency f_{rj} and constants A_j and B were determined so as to obtain the best fit of the data to Eq. (1). The values are listed in Table 1 together with the observed values of the sound velocity and density.

If the mechanism of the excess absorption in the relatively dilute solutions is attributed to the perturbation of the equilibrium[1-6)]

$$\text{R-NH}_3^+ + \text{OH}^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{R-NH}_2 + \text{H}_2\text{O} \qquad (2)$$

where k_f and k_b are forward and backward rate constants respectively, the relation between the relaxation frequency and the rate constants is given by

$$1/\tau = 2\pi f_r = k_f([\text{R-NH}_3^+]+[\text{OH}^-])\Pi\gamma_i + k_b \qquad (3)$$

where τ is relaxation time and γ_i an activity coefficient of species i. If the activity coefficient and concentration of R–NH$_3^+$ ion are equal to those of OH$^-$ ion respectively at each concentration, Eq. (3) can be written as

$$1/\tau = 2\pi f_r = 2k_f\gamma^2[\text{OH}^-] + k_b \qquad (4)$$

where γ is the mean activity coefficient. The activity coefficients were calculated by the Davies equation[13)]

$$-\log\gamma = 0.5\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right] \qquad (5)$$

where I is the ionic strength. Figure 3 shows the plots of $2\pi f_r$ *vs.* γ^2[OH$^-$]. The forward and backward rate constants were determined from the slope and inter-

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[13)] C. W. Davies, "Ion Association," Butter Worths, London (1962).

TABLE 2. RATE AND EQUILIBRIUM CONSTANTS AND STANDARD VOLUME CHANGE AT 20°C

System	k_f (M^{-1} sec^{-1})	k_b (sec^{-1})	K (M)	ΔV (cc mol^{-1})	Reference
$NH_4^+ + OH^- \rightleftarrows NH_3 + H_2O$	3.6×10^{10}	6.0×10^5	1.7×10^{-5}	26.8	(2) (3)
$CH_3NH_3^+ + OH^- \rightleftarrows CH_3NH_2 + H_2O$	3.7×10^{10}	1.6×10^7	4.2×10^{-4}	26.1	(2) (3)
$(C_2H_5)NH_3^+ + OH^- \rightleftarrows (C_2H_5)NH_2 + H_2O$	3.2×10^{10}	1.4×10^7	4.7×10^{-4}	24.3	(2) (3)
$(C_3H_7)NH_3^+ + OH^- \rightleftarrows (C_3H_7)NH_2 + H_2O$	3.0×10^{10}	1.2×10^7	4.0×10^{-4}	24.0	(2)
$(C_4H_9)NH_3^+ + OH^- \rightleftarrows (C_4H_9)NH_2 + H_2O$	4.1×10^{10}	1.1×10^8	2.5×10^{-3}	32	(6)
$(C_8H_{17})NH_3^+ + OH^- \rightleftarrows (C_8H_{17})NH_2 + H_2O$	1.0×10^{10}	7.6×10^7	7.6×10^{-3}	32	this work

cept, respectively, by the least-mean-squares method. The standard volume change ΔV resulting from the reaction could be determined as follows. The excess absorption per wavelength shows a maximum at a frequency $f=f_r$ and is given by

$$(\alpha\lambda)_{\max} = \frac{1}{2}Af_r c \tag{6}$$

where $(\alpha\lambda)_{\max}$ is the maximum excess absorption per wavelength and c the velocity of sound. For a chemical process of the type represented by Eq. (2), the maximum excess absorption per wavelength is given by

$$(\alpha\lambda)_{\max} = \frac{1}{2}\pi\rho c^2V^2RT\Gamma_c\left\{\left(\frac{\beta\Delta H}{C_pRT}\right)-\left(\frac{\Delta V}{VRT}\right)\right\}^2 \tag{7}$$

$$\Gamma_c = \left(\frac{1}{[OH^-]}+\frac{1}{[R\text{-}NH_3^+]}+\frac{1}{[R\text{-}NH_2]}\right)^{-1} \tag{8}$$

where ρ is density, V the molar volume, R the gas constant, β the thermal expansion coefficient, C_p the specific heat at constant pressure, and T the absolute temperature. In the case of a relatively dilute solution of amine, the first term in the bracket of Eq. (7) is negligibly small compared with the second term. The standard volume change resulting from the hydrolysis of octylamine was calculated by means of Eqs. (6) and (7). The values of rate constants, equilibrium constant, and standard volume change are listed in Table 2 together with those for other monoamines.

Since the aqueous solution of octylamine is separated into two phases below 0.5 M at 20 °C, measurements were impossible below 0.5 M.

Discussion

The excess absorption mechanism in the mesomorphic state in the higher frequency range can not be interpreted quantitatively since the ionic concentration in that state is not determined accurately. However, excess absorption is observed even in the isotropic state as is seen in Fig. 1 and the relaxation frequencies seem to increase continuously with concentration as is seen in Fig. 2. The mechanism of the excess absorption in the mesomorphic state is therefore regarded to be identical with that in the relatively dilute solution. The linearity of the plots of $2\pi f_r$ *vs.* $\gamma^2[OH^-]$ in Fig. 3 indicates that the cause of the excess absorption is attributed to the perturbation of the equilibrium given by Eq. (2). The value of the rate constant k_f obtained is pertinent to the proton transfer reaction, since it is, in general, of the order 10^{10}—10^{11} M^{-1} s^{-1}. However, the equilibrium constant determined by the relation $K=k_b/k_f$ does not agree with the value reported 4.5×10^{-4} M at 25 °C[14] which was obtained in various dilutions of alcohol such as to permit satisfactory extrapolation to pure water in a concentration less than 0.016 M because of the limited solubility of octylamine in water. Since our investigation was carried out in concentrations higher than 0.5 M, a comparison of the results may not be suitable.

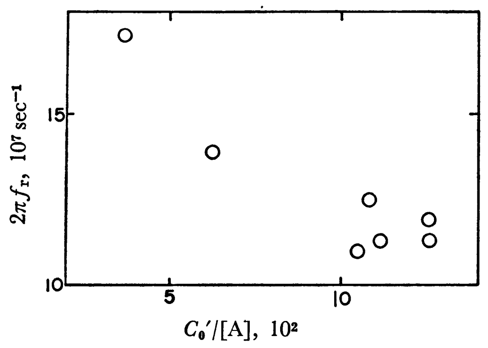

Fig. 4. The plots of $2\pi f_r$ *vs.* $C_0'/[A]$ at 20 °C.

The process of hydrolysis of amine[3] is not so simple as that expressed by Eq. (2). It proceeds through a complex formation by hydrogen bonding as follows

$$R\text{-}NH_3^+ + OH^- \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} R\text{-}NH_3^+\cdots OH^- \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} R\text{-}NH_2 + H_2O \tag{9}$$

Under the conditions[3] of $k_{23}\gg k_{21}$, the rate constants in Eq. (2) are expressed as follows

$$k_f = k_{12},\quad k_b = k_{21}\frac{k_{32}}{k_{23}} \tag{10}$$

Consequently, the collision frequency of reaction partners, $R\text{-}NH_3^+$ and OH^- ions, might affect the magnitude of the rate constant k_f. The octylamine molecule consists of a long hydrophobic chain and a small hydrophilic group, *viz.*, the reaction site might be so small compared with the size of the molecule. Therefore, the effective collision frequency for the reaction might decrease. As is seen in Table 2, the rate constant k_f for octylamine is small compared with those for other monoamines.[2,3]

The excess absorption mechanism attributed to the perturbation of the equilibrium expressed as $nA\underset{k_2}{\overset{k_1}{\rightleftarrows}}A_n$

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[14] C. W. Hoerr, M. R. McCorkle, and A. W. Rals, *J. Amer. Chem. Soc.*, **65**, 328 (1943).

by McKellar and Andreae[7] should be reconsidered. The relation between relaxation time and concentration for this mechanism is derived as follows.

$$1/\tau = 2\pi f_r = -k_2(n-1) + nk_2C_0'/[\mathrm{A}] \qquad (11)$$

where n is the aggregation number, [A] the concentration of monomer, k_2 the rate constant and $C_0' = [\mathrm{A}] + n[\mathrm{A}_n]$. If the cause of the excess absorption were attributed to the association-dissociation reaction, the plots of $2\pi f_r$ *vs.* $C_0'/[\mathrm{A}]$ should be a straight line with a positive slope and a negative intercept according to Eq. (11). However, the results do not obey Eq. (11), *viz.*, the plots of $2\pi f_r$ *vs.* $C_0'/[\mathrm{A}]$ seems to have a negative slope and positive intercept as is shown in Fig. 4. The mechanism due to the aggregation reaction might, therefore, be ruled out as that of the excess absorption.