Solvent Effect on Proton Transfer Reaction Rate by Ultrasonic Absorption Method

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(Received January 5, 1994)

Some equipment for a resonance method was constructed in order to obtain ultrasonic absorption coefficients in a frequency range less than 10 MHz. Using this apparatus, the measurable frequency range was extended down to 2.5 MHz. No relaxational absorption was observed in an aqueous solution of 2-propanol at 2.70 mol dm^{-3} in the frequency range from 2.5 to 220 MHz. A relaxational absorption was observed in aqueous solutions of *n*-propylamine in the presence of 2.70 mol dm^{-3} 2-propanol. The frequency dependence of the absorption coefficient was analyzed by a usual Debye-type relaxational equation. Excellent agreement between calculated and experimental values was obtained in the frequency range measured. The relaxational absorption was attributed to the perturbation of equilibria associated with a proton transfer reaction:

$$\text{R-NH}_3{}^+ + \text{OH}^- \rightleftharpoons \text{R-NH}_3{}^+\cdots\text{OH}^- \rightleftharpoons \text{R-NH}_2 + \text{H}_2\text{O}.$$

The rate constants and the standard volume change for the first step of the reaction were determined from the concentration dependence of the relaxation frequency and the maximum absorption per wavelength. It was found that the forward rate constant decreased and the standard volume change increased when the values were compared with those in the absence of 2-propanol. The results were discussed in relation to water structure and hindrance for the proton transfer reaction by the additives.

Effects of additives on proton transfer reaction in aqueous solutions are of particular interest, because the reaction may be closely related to water structure and the additives may alter the solvent structure. There have been some reports which deal with how the proton transfer reaction is affected by additives. Harada et al.$^{1)}$ have examined the effect of surfactant micelles on the proton transfer reaction and have reported the decreasing effect on the forward rate constant in the following reaction: $\text{R-NH}_3^+ + \text{OH}^- \rightleftharpoons \text{R-NH}_2 + \text{H}_2\text{O}$. They have interpreted the effect as a restricted reaction field owing to the charged surface of the micelles. The reaction field may be also altered by the addition of nonelectrolytes which may cause some change in the solvent water structure. In our previous study,$^{2)}$ we have speculated that 2-propanol in aqueous solution promotes water structure considerably. In addition, we have been examining the proton transfer reaction in aqueous solution of amines with alkyl$^{3—8)}$ and alkene group.$^{9)}$ On the basis of our results so far, we desire to get an insight into the relation between the structural properties of the solution and the proton transfer reaction. Another purpose of the present investigation is to ascertain if other relaxation processes exist or not in the lower frequency range than that measured by a pulse ultrasonic absorption equipment. For this purpose, the absorption coefficient should be measured in the frequency range less than 10 MHz, because it is so hard to obtain the absorption coefficient by the pulse method when the absorption is comparable to or slightly larger than the solvent water. Therefore, we have tried to construct some resonance equipment.

Experimental

Apparatus: The resonance method which was originally developed by Eggers has been applied to some dynamical studies$^{10—12)}$ in liquids. The theoretical treatment for the resonance method has been shown elsewhere.$^{10,11,13)}$ Therefore, we only show briefly the technical procedures needed to handle the resonator. The equipment consists of a frequency synthesizer (PHILIPS model PM 5193), cylindrical resonator cells, a control computer (NEC PC-9801), an attenuator, an amplifier and voltmeter (KIKUSUI model 165A) which is improved to receive digital signals. The transducers used are 5 and 2 MHz X-cut crystals with diameter of 2 and 5 cm, respectively. The acoustical path length is about 6 mm. Signals from the resonator and the synthesizer are sent alternatively to the computer.

Since the output voltages are plotted as a function of frequency on a display, it is possible to see the resonance signals in real time. The half power bandwidth, Δf_n, was determined near the resonance frequency, f_n, by the next equation:

$$\Delta f_n = (f_n - f_{nl}) + (f_{nh} - f_n), \qquad (1)$$

where f_{nl} and f_{nh} are the lower and higher frequencies where the output voltage reaches $1/\sqrt{2}$ times of the peak voltage at f_n, respectively. When $(f_n - f_{nl})$ and $(f_{nh} - f_n)$ values were the same within the range of less than 10%, we admitted this Δf_n value as an available one. The measurement was repeated at least five times for every resonance curve. In the real measurements for solutions by the resonator, other peaks from the undesired modes are observed. The coupling of the principal peak with these peaks makes the absorption measurement meaningless. Therefore, the measurements were carried out in a frequency range where the principal peak is not affected by other peaks. The absorption coefficient, α, has been determined by the usual relation between the half power bandwidth and the absorption coefficient.$^{10—13)}$

In order to maintain the temperature of the sample solution, the thermostat water which was controlled within ±0.01°C was circulated around the resonator cavity. Furthermore, the resonator cell was placed in an air thermostat which was controlled within ±0.1°C.

Figure 1 shows the experimental $\Delta f_n/f_n$ values for the 0.653 $\mathrm{mol\,dm^{-3}}$ NaCl aqueous solution which has the same acoustic impedance as that of 2.70 $\mathrm{mol\,dm^{-3}}$ 2-propanol aqueous solution as a function of the frequency. The solid line in this figure represents the calculated values using $\alpha/f^2=21.1\times10^{-15}\ \mathrm{s^2\,m^{-1}}$ and $c=1533\ \mathrm{m\,s^{-1}}$ which are for the above-mentioned NaCl aqueous solution. As may be seen in Fig. 1, it is possible to obtain the absolute values of the absorption coefficient in the frequency range from 6 to 7.5 MHz and from 2.5 to 3.3 MHz by 5 MHz crystal and 2 MHz one, respectively, because of no mechanical loss. However, the resonance peaks are not always symmetrical in real solutions depending on the magnitude of the ultrasonic absorption coefficient and the frequency. In other frequency ranges where the mechanical loss exists, we have subtracted it from the measured $\Delta f_n/f_n$ value for the determination of the absorption coefficient.

For the ultrasonic absorption coefficient measurement in the frequency range from 9.5 to 220 MHz, we used a pulse method, the details of which were described elsewhere.[14] The measurement of sound velocity was carried out using a sing-around meter at 1.92 MHz and the resonator. The measurements of pH and density were performed using a pH meter with a glass electrode (HM-60S Toa Denpa) and a vibrating density meter, respectively. All the measurements were carried out under a dry nitrogen atmosphere at 25.0 °C.

Chemical: The purest grade *n*-propylamine and 2-propanol were purchased from Wako Chemical Co., Ltd. 2-Propanol was further distilled once. *n*-Propylamine was used without further purification. Sample solutions were prepared with doubly distilled water through which N_2 gas was passed for about 15 min, and they were made from the stock solution. The concentration of 2-propanol was fixed to be 2.70 $\mathrm{mol\,dm^{-3}}$.

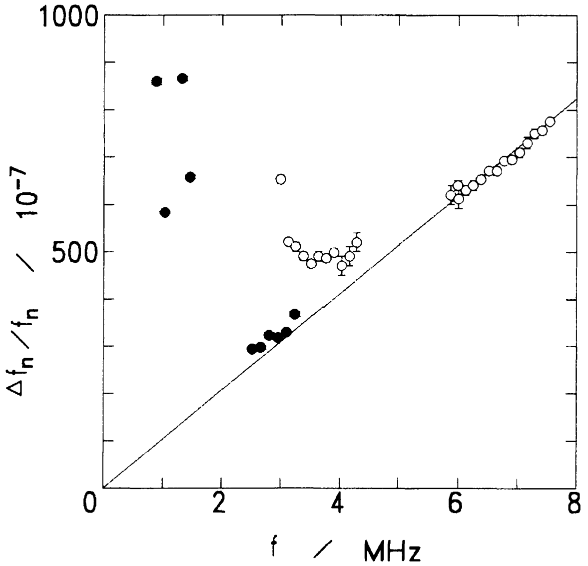

Fig. 1. The plots of $\Delta f_n/f_n$ vs. frequency for an aqueous solution of 0.653 $\mathrm{mol\,dm^{-3}}$ NaCl. The solid line represents the calculated values. ○: by 5 MHz crystal, ●: by 2 MHz crystal.

Results and Discussion

In the aqueous solution of 2-propanol with a concentration of more than 3.0 $\mathrm{mol\,dm^{-3}}$, the relaxational absorption is observed. The cause has been attributed to the perturbation of an equilibrium associated with the solute–solvent interaction.[2] In a slightly lower concentration than 3.0 $\mathrm{mol\,dm^{-3}}$, it is considered that the solvent water structure is also promoted by the addition of 2-propanol. Therefore, we have chosen the 2.70 $\mathrm{mol\,dm^{-3}}$ 2-propanol solution as the solvent for studying the proton transfer reaction of amine.

No excess absorption was observed in aqueous solution of 2.70 $\mathrm{mol\,dm^{-3}}$ 2-propanol, as shown in Fig. 2. However, the value of α/f^2 was found to be frequency dependent when *n*-propylamine was added in the solution of 2.70 $\mathrm{mol\,dm^{-3}}$ 2-propanol. The frequency dependence of the absorption coefficient was analyzed by the Debye-type relaxational equation:

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

where f_r is the relaxation frequency, A the amplitude of the ultrasonic relaxation and B the background absorption. The ultrasonic parameters, A, B, and f_r, were determined by a nonlinear least-mean square method. The parameters obtained are listed in Table 1. Some representative ultrasonic absorption spectra are shown in Fig. 2 for aqueous solutions of *n*-propylamine in the presence of 2-propanol. The solid curves in the figure represent the values calculated using Eq. 2. The excellent agreement between calculated and experimental

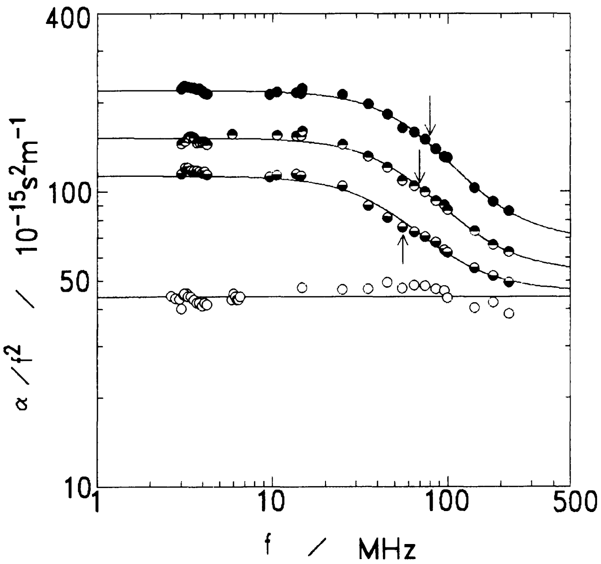

Fig. 2. The representative ultrasonic absorption spectra for aqueous solutions of *n*-propylamine in the presence of 2.70 $\mathrm{mol\,dm^{-3}}$ 2-propanol. ●: 0.469 $\mathrm{mol\,dm^{-3}}$, ◓: 0.261 $\mathrm{mol\,dm^{-3}}$, ◒: 0.101 $\mathrm{mol\,dm^{-3}}$, ○: without amine. The arrows show the position of the relaxation frequency.

Table 1. The Ultrasonic and Thermodynamic Parameters for Aqueous Solution of *n*-Propylamine in the Presence of 2-Propanol at 25.0 °C

Concn	pH	f_r	A	B
mol dm^{-3}		MHz	10^{-15} s^2 m^{-1}	
0.0507	11.779	44±2	56±2	44.8±0.3
0.0603	11.781	47±2	58±2	44.1±0.4
0.101	11.970	55±2	67±2	46.0±0.3
0.203	12.133	65±2	91±2	50.3±0.5
0.261	12.147	70±1	98±1	53.6±0.4
0.302	12.191	75±2	113±2	55.8±0.7
0.469	12.318	79±1	151±1	68.5±0.6
0.571	12.371	94±3	169±2	73 ±1

values shows that the Debye-type relaxational absorption is indeed observed in the solutions. Figure 3 represents the concentration dependence of the relaxation frequency, along with those reported previously in the solvent water and in that with urea.[3] The concentration dependence of the relaxation frequency is quite similar in these solutions, although the trends of the increments are different. The cause of the relaxation in water has been confirmed to be the proton transfer reaction. The mechanism of the reaction has been proposed originally by Eigen[15] and is given by next equation:

$$\begin{aligned} \mathrm{R\text{-}NH_3^+} + \mathrm{OH^-} &\underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{R\text{-}NH_3^+\cdots OH^-} (\text{or } \mathrm{R\text{-}NH_2\cdots H_2O}) \\ &\underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{R\text{-}NH_2} + \mathrm{H_2O}, \end{aligned} \tag{3}$$

where k_{ij} is the rate constant at each step. In general, a slower process is affected by a faster one when the two processes are not so apart. However, as has been described in previous paper,[4] the observed relaxation phenomena are well interpreted on the assumptions that the perturbation of the first equilibrium is the cause of the relaxational absorption and that the second step in Eq. 3 is too fast to affect the observed first process. Following this analytical procedure, we have estimated the rate constants from the dependence of hydroxide ion concentration by the following relation:

$$\tau^{-1} = 2\pi f_r = 2\gamma^2[\mathrm{OH^-}]k_{12} + k_{21}, \tag{4}$$

where τ is the relaxation time and γ the activity coefficient calculated by Davies' equation. Figure 4 shows the plots of f_r vs. $\gamma^2[\mathrm{OH^-}]$. From the slope and intercept of the plots, the rate constants, k_{12} and k_{21}, were determined. They are listed in Table 2 along with those previously reported in two solvents.[3] The forward rate constant, k_{12}, is reasonable for a diffusion-controlled reaction.

The rate constants obtained above enable us to determine the dissociation constant, K_b, on the assumption that the second step in Eq. 3 does not so affect the first step.[4] The relation between K_b and the analytical concentration, C_o, is derived as

$$\begin{aligned} K_b = &[(\tau^{-1})^2 + k_{21}{}^2 - 2\tau^{-1}k_{21}] \\ &/[k_{12}(4\gamma^2 C_o k_{12} + 2k_{21} - 2\tau^{-1})]. \end{aligned} \tag{5}$$

The calculated K_b value for the solution with 2-propanol is listed in Table 2 along with those in other two solvents. On the other hand, the dissociation constants for these solutions were also estimated from the results of pH measurements using the relation:

$$K_b = \gamma^2[\mathrm{OH^-}]^2/(C_o - [\mathrm{OH^-}]). \tag{6}$$

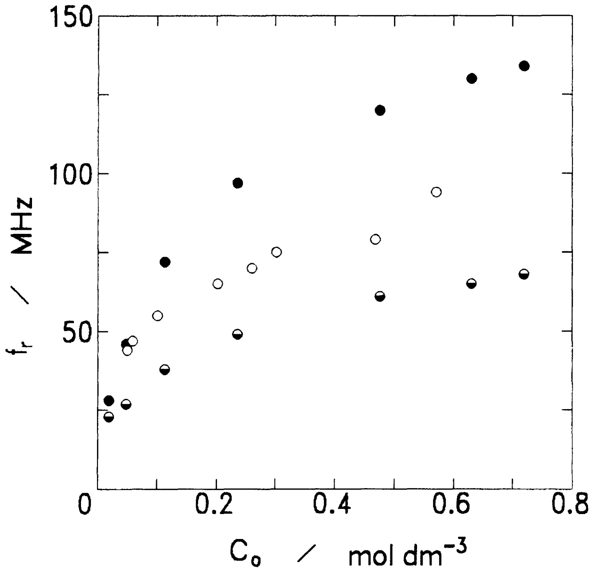

Fig. 3. The concentration dependence of the relaxation frequency, f_r, for aqueous solutions of *n*-propylamine in the absence and presence of additives. ●: no additive,[3] ⊖: urea,[3] ○: 2-propanol.

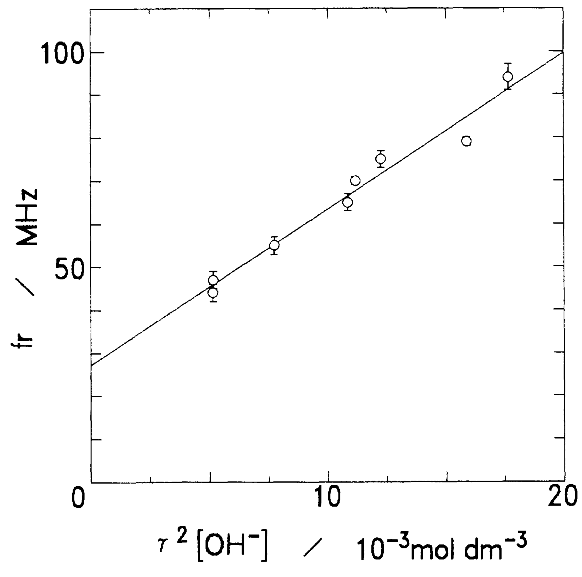

Fig. 4. The plots of f_r vs. $\tau^2[\mathrm{OH^-}]$ for aqueous solutions of *n*-propylamine in the presence of 2-propanol.

Table 2. The Rate and Thermodynamic Constants for the Proton Transfer Reaction in Aqueous Solution of *n*-Propylamine in the Absence and Presence of Additives at 25.0 °C

Additive		k_{12}	k_{21}	K_b[a)]	K_b[b)]
		$10^{10}\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	10^8s^{-1}	$10^{-4}\text{mol dm}^{-3}$	
No additive		1.9 ±0.2	1.5±0.4	5.7± 2.1	5.9± 1.7
Urea	(5.0 mol dm^{-3})	0.34±0.03	1.5±0.2	25 ±13	24 ±11
2-Propanol	(2.70 mol dm^{-3})	1.14±0.06	1.7±0.1	7.1± 0.7	7.1± 0.6

a) The calculated K_b values from Eq. 5. b) Those from Eq. 6.

Such calculated values are also shown in Table 2. The K_b value for the solution without additive is very similar to that in the literature.[16)] The equality of the K_b values determined by Eqs. 5 and 6 proves that the observed relaxation is only due to the first process in Eq. 3.

Another important parameter obtained from the absorption measurement is the maximum absorption per wavelength, $\mu_{\max}$, which is related to the standard volume change of the reaction, ΔV, as follows:

$$\mu_{\max} = Af_rc/2 = \pi\rho c^2\Gamma(\Delta V)^2/2RT. \tag{7}$$

where ρ is the solution density, R the gas constant, T the absolute temperature and Γ the concentration term given by the next equation,

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

Figure 5 shows the dependence of the standard volume change on the analytical concentration along with those previously reported.[3)] In this calculation, the values of the sound velocity and the density were approximately equal to those for individual solvents. In the case of aqueous solutions with 2-propanol, it has been confirmed that the sound velocity is almost independent of the concentration of *n*-propylamine.

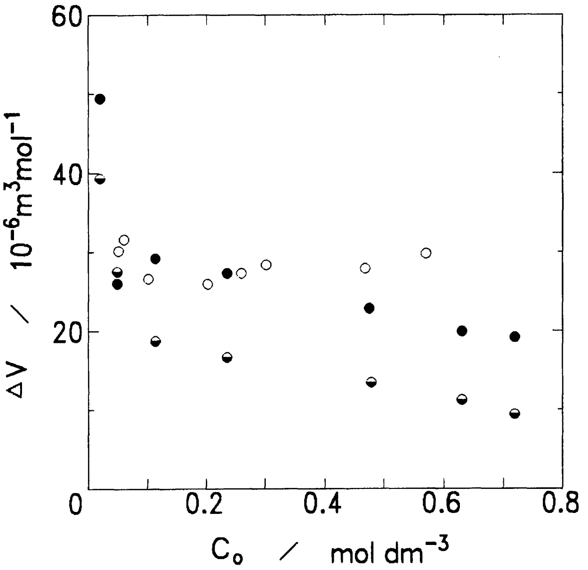

Fig. 5. The concentration dependence of the standard volume change of the reaction, ΔV, for aqueous solutions of *n*-propylamine in the absence and presence of additives. ●: no additive,[3)] ◒: urea,[3)] ○: 2-propanol.

It is interesting to compare the kinetic and thermodynamic parameters for the proton transfer reaction obtained in this study with those in the solution with urea and in the solution without additive. It is said that the urea in aqueous solution acts as the water structure breaker; the dense water increases when urea is added.[17)] On the other hand, the bulky water may be further created when 2-propanol coexists.[2)] It is considered that the diffusion of one of the reactants may be facilitated by the network of water hydrogen bonds. The forward rate constant, k_{12} which is the diffusion-controlled one, is considerably influenced by the additives. Actually, the diffusion of the reactants may be blocked by the additives. However, the urea effect on the rate constant seems to be more remarkable than that of 2-propanol. On the other hand, the backward rate constants, which are for the dissociative process of the intermediate in Eq. 3, are almost the same even if the additives coexist. These results may imply an opposing effect of the two additives on water structure. The notable decrease of the forward rate constant for the solution with urea may be because of the blocking of the diffusing reactants and the increase of the dense water. The slight decrease of the forward rate constant in the solution of 2-propanol may be due to compensation between the blocking and the increase of bulky water.

It is seen in Fig. 5 that the standard volume change of the reaction in the aqueous solution with 2-propanol tends to be larger than that just in the aqueous solution and also that the standard volume change in the urea solution is the smallest in the three solutions. These changes for the proton transfer reaction may also imply the structural change of the solvent. If more bulky water molecules participate in the proton transfer reaction, a larger volume change of the reaction is expected, because the bulky water or hydrogen-bonded water will occupy a larger volume.

In conclusion, it has been proved in this study that only one ultrasonic relaxation process is observed in the aqueous solution of *n*-propylamine with 2.70 mol dm^{-3} 2-propanol in the frequency range from 2.5 to 220 MHz. It has been attributed to the perturbation of equilibrium associated with the proton transfer reaction. The rate and thermodynamic parameters are found to be affected by the addition of 2-propanol, when they are compared with other data reported previously.

Further experimental studies concerning how the additives affect the proton transfer reaction are now in progress. The results will be reported in due course.

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