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Proton-Transfer Reaction in Aqueous Propylamine Solution with Poly(vinyl alcohols) by Ultrasonic Absorption Method

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Ultrasonic absorption coefficients were measured in aqueous solutions of propylamine at 25 °C in both the absence and presence of 2.01 g dm^{-3} (poly(vinyl alcohols) (PVA's)) with the number average degree of polymerization of 500, 900, 1500, and 2000. No excess absorption was observed in solutions without propylamine. A single relaxational absorption was observed in the concentration range from 0.0241 to 0.201 mol dm^{-3} of propylamine in both the presence and absence of PVA's. The relaxational absorption was attributed to a perturbation of the equilibrium associated with a proton-transfer reaction from the concentration dependence of the relaxation frequency and the maximum absorption per wavelength. The rate and equilibrium constants and the standard volume change of the reaction were determined in individual solutions with PVA's. As a result, it was found that the diffusion-controlled reaction rate constant remains constant, or increases slightly, even though the solution viscosity increases. The effect of the polymers on the reaction was interpreted in terms of an interaction between the PVA's and the reaction intermediate and a solvent structural change.

Kinetic studies concerning a proton-transfer reaction in aqueous solutions of amino acids, amines and carboxylic acids were carried out using ultrasonic relaxation methods.[1–5] This type of information is particularly desirable for understanding more complex biological reactions and solute-solvent interactions. The additive effects of alcohols on the proton-transfer reaction have been examined in connection with water structural change.[6–8] A diffusion-controlled reaction is facilitated when the water structure is promoted, and is lowered if hydrogen-bond networks in the water structure are broken down. These results suggest dynamically that the proton-transfer reaction surely proceeds through the networks of the water hydrogen-bond. Previously, a poly(vinyl alcohol) effect on the proton-transfer reaction was examined by ultrasonic pulse method,[6] in which the frequency range was restricted to be above 15 MHz. The development of the apparatus by a resonance method provides a way to measure the ultrasonic absorption coefficients down to 0.8 MHz.[9] This situation has allowed us to obtain more accurate ultrasonic relaxation parameters associated with several reactions. Therefore, we have tried to precisely investigate in the present study how the proton-transfer reaction is affected when poly(vinyl alcohol)'s (PVA's) are added to the system with propylamine. By changing the degree of polymerization, it is hoped to receive how the dynamical interaction between the solute and solvent may be influenced because of a change in the water structure and the characteristics of the polymer.

Experimental

Chemicals: Propylamine and poly(vinyl alcohols) (PVA500, 1500, 2000) of reagent grade were purchased from Wako Pure Chemicals Co., Ltd. and were used without further purification. The saponification degree of PVA500, 1500, and 2000 was guaranteed to be 86–90 mol%, 86–90 mol% and more than 98.0 mol%, respectively. The saponification degree of PVA900 from Sigma Chemical Company was also guaranteed to be more than 99 mol%, and was used as received. {M_w = 22000 (abbreviation PVA500), M_w = 40000 (abbreviation PVA900), M_w = 66100 (abbreviation PVA1500), M_w = 88100 (abbreviation PVA2000)}. The sample solvent was distilled, deionized and filtered through a MilliQ SP-TOC filter System from Japan Millipore Ltd. The sample solutions were prepared from concentrated stock solutions (2.01 mol dm^{-3} of propylamine and 4.02 g dm^{-3} of PVA's), and were kept in a N_2 gas atmosphere.

Measurement: 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. A resonance method was used in the low frequency range from 0.8 to 7 MHz. The details of these apparatuses were described elsewhere.[9,10] The sound velocity was measured by a resonator at around 3 MHz. The density was obtained by a vibrating density meter (DMA 60/602, Anton Paar). The solution pH was measured by inserting a glass electrode into the test tube or into the ultrasonic absorption cell while the measurements were proceeding (HM-60S Toa Denpa). A water bath (EYELA UNI ACE BATH NCB-2200) controlled within ± 0.1 °C was used for the cells of the pulse method, and circulating water (LAUDA, RM20) was for the resonance cells which were controlled within ± 0.01 °C. The temperature was kept at 25 °C. An Ubbelohde-type viscometer was used to determine the viscosity coefficient in a water bath controlled within ± 0.01 °C. All of the measurements were always performed with a dry N_2 gas atmosphere in order to avoid, as much as possible, any contamination of carbon dioxide during the measurements.

Results

Figure 1 illustrates the frequency dependence of the ultrasonic absorption coefficients divided by the square of the frequency, α/f^2, for propylamine aqueous solutions. In our previ-

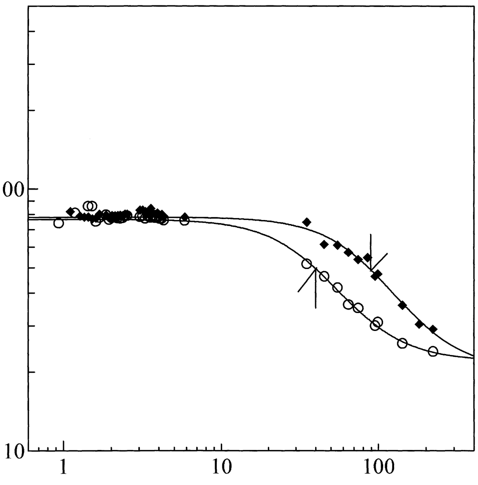

Fig. 1. The representative ultrasonic absorption spectra for aqueous solution of propylamine at 25 °C. ○: 0.0402 mol dm^{-3} ; ◆: 0.151 mol dm^{-3}. The arrow shows the location of the relaxation frequency.

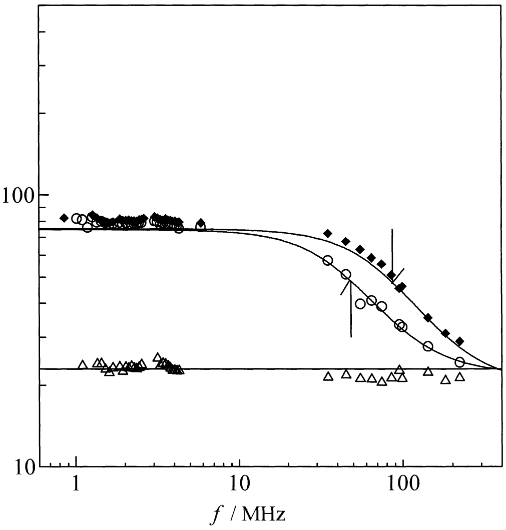

Fig. 2. The representative ultrasonic absorption spectra for aqueous solution of propylamine with 2.01 g dm^{-3} PVA-900 at 25 °C. △: 0 mol dm^{-3} ; ○: 0.0503 mol dm^{-3} ; ◆: 0.151 mol dm^{-3} propylamine.

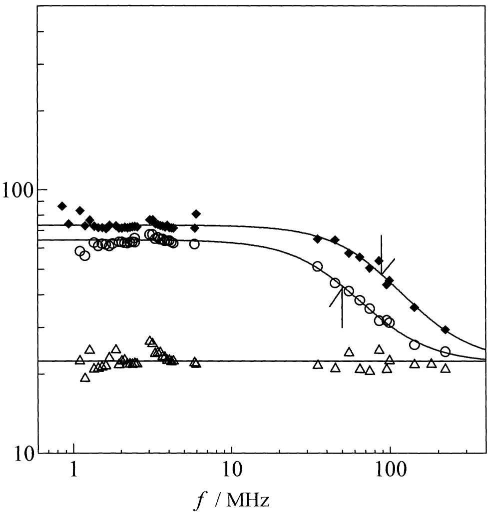

Fig. 3. The representative ultrasonic absorption spectra for aqueous solution of propylamine with 2.01 g dm^{-3} PVA-1500 at 25 °C. △: 0 mol dm^{-3} ; ○: 0.0503 mol dm^{-3} ; ◆: 0.151 mol dm^{-3} propylamine.

ous report,[6] the measurement frequency range was restricted to be above 15 MHz. The experimental results in the lower frequency range below 10 MHz provided constant values of $\alpha/f_0{}^2$ (equilibrium values). With an increase in the frequency, α/f^2 decreases. Absorption measurements were carried out in aqueous solutions of PVA's, the concentration of which was kept constant to be 2.01 g dm^{-3}. This corresponds to a constant molar fraction of monomer units (8.2×10^{-4}). No frequency dependence has been found in PVA solutions, as can be seen in Figs. 2 and 3. When propylamine and PVA's coexist in the solution, α/f^2 is also dependent on the frequency. The experimental absorption data have been analyzed by a Debye-type relaxational equation,[11]

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

where f_r and A are the relaxation frequency and the amplitude of the ultrasonic absorption, respectively, and B is the background absorption associated with the viscosity and thermal conductivity of the medium as well as that due to any processes with relaxation frequencies much higher than f_r for the process in question. All of the ultrasonic parameters (f_r, A, and B) listed in Table 1 have been determined by a nonlinear least-mean-squares method. The solid curves shown in Figs. 1, 2, and 3 are the calculated values using Eq. 1 with the help of such determined parameters. As can be seen, these observed absorption spectra are well fitted to the single relaxational equation. The obtained absorption amplitudes, A, are shown in Fig. 4 as a function of the propylamine concentration; they tends to reach plateaus with increasing the concentration, even if PVA's exist in the solutions. This trend is characteristic for relatively dilute aqueous solutions of amines.[6,8,9] Figure 5 shows the dependence of the relaxation frequency on the concentration of propylamine. From only this information it is hard to see the effect of PVA's on the solution characteristics. In a propylamine aqueous solution without additives, it has already been clarified that the ultrasonic relaxational absorption is associated with the proton-transfer reaction. The mechanism of the reaction was originally proposed by Eigen,[12] and it is expressed by

$$\mathrm{R{-}NH_3^+ + OH^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} R{-}NH_3^+\cdots OH^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} R{-}NH_2 + H_2O}, \qquad (2)$$

where k_{ij} is the rate constant at the individual steps. Following the conventional procedure of a relaxation analysis,[13] when the second step is faster than the first one ($k_{12}\gamma^2\{[\mathrm{R{-}NH_3}^+] + [\mathrm{OH}^-]\} + k_{21} \ll k_{23} + k_{32}$), the relationship between the relaxation time, τ, and the reactant concentrations is derived to yield Eq. 3, including the coupling effect of the perturbation of the two equilibria on the relaxation time,

Table 1. Ultrasonic and Thermodynamic Parameters for Aqueous Solutions of Propylamine with 2.01 g dm^{-3} PVA's at 25 °C

Propylamine	f_r	A	B	pH	v	$\rho^{a)}$
mol dm^{-3}	MHz	10^{-15} s^2 m^{-1}			m s^{-1}	kg dm^{-3}
no PVA						
0.603	130 ± 2	63.1 ± 0.4	21.7 ± 0.6	12.26	1532 ± 1	0.98929
0.302	120 ± 3	59.8 ± 0.5	20.2 ± 0.6	12.09	1515.3 ± 0.7	0.99323
0.201	90 ± 4	60 ± 2	20.7 ± 0.9	11.99	1510.4 ± 0.6	0.99456
0.151	82 ± 2	60.5 ± 0.8	20.1 ± 0.3	11.92	1507.5 ± 0.7	0.99520
0.101	67.0 ± 0.8	59.3 ± 0.5	20.8 ± 0.1	11.82	1504.8 ± 0.4	0.99602
0.0804	63 ± 1	58 ± 1	20.7 ± 0.2	11.77	1503.1 ± 0.8	0.99625
0.0503	49.8 ± 0.8	58.6 ± 0.9	20.5 ± 0.1	11.66	1501.4 ± 0.9	0.99653
0.0402	40.4 ± 0.7	54 ± 1	22.0 ± 0.1	11.60	1500.8 ± 0.6	0.99664
0.0302	36.8 ± 0.8	56 ± 1	21.4 ± 0.1	11.54	1500.8 ± 0.7	0.99689
0.0241	32 ± 1	52 ± 3	21.8 ± 0.2	11.49	1500.5 ± 0.9	0.99687
PVA500						
0.603	130 ± 4	58.8 ± 0.6	22.9 ± 0.8	12.21	1531.6 ± 0.7	0.99023
0.302	124 ± 2	59.7 ± 0.4	18.0 ± 0.5	12.03	1516.8 ± 0.7	0.99384
0.201	97 ± 2	56.6 ± 0.6	20.2 ± 0.4	11.91	1511.0 ± 0.9	0.99498
0.151	87 ± 3	55 ± 1	20.2 ± 0.5	11.82	1508.2 ± 0.8	0.99563
0.101	73 ± 2	48.3 ± 0.8	21.1 ± 0.2	11.68	1504.7 ± 0.7	0.99622
0.0503	63 ± 3	43 ± 1	19.4 ± 0.3	11.41	1501.7 ± 0.9	0.99718
0.0402	39 ± 2	40 ± 3	22.7 ± 0.3	11.30	1502.0 ± 0.8	0.99706
0.0302	39 ± 2	34 ± 2	21.8 ± 0.2	11.15	1501.8 ± 0.9	0.99731
0.0241	43 ± 3	22 ± 2	22.0 ± 0.2	11.02	1500.9 ± 0.8	0.99729
PVA900						
0.603	129 ± 2	62.2 ± 0.4	23.2 ± 0.5	12.30	1535.2 ± 0.6	0.99004
0.302	108 ± 2	62.9 ± 0.4	20.7 ± 0.4	12.10	1517.3 ± 0.5	0.99377
0.151	79 ± 1	61.8 ± 0.7	21.7 ± 0.2	11.84	1508.3 ± 0.8	0.99559
0.101	72 ± 1	57.0 ± 0.8	20.9 ± 0.2	11.71	1505.7 ± 0.4	0.99628
0.0503	48 ± 2	53 ± 2	22.1 ± 0.2	11.52	1502.5 ± 0.7	0.99693
0.0402	46 ± 1	55 ± 2	20.6 ± 0.2	11.47	1501.8 ± 0.8	0.99703
0.0302	42 ± 1	53 ± 1	20.7 ± 0.1	11.42	1500.8 ± 0.6	0.99716
0.0241	39 ± 1	51 ± 2	21.2 ± 0.2	11.38	1500.9 ± 0.6	0.99727
PVA1500						
0.603	127 ± 2	59.0 ± 0.4	25.2 ± 0.5	12.26	1531.6 ± 0.2	0.98981
0.302	104 ± 3	60.2 ± 0.7	21.4 ± 0.6	12.03	1514.7 ± 0.4	0.99369
0.151	88 ± 4	51 ± 1	22.3 ± 0.6	11.76	1508.3 ± 0.7	0.99557
0.101	69.2 ± 0.9	46.2 ± 0.5	23.2 ± 0.1	11.62	1506.1 ± 0.9	0.99622
0.0503	50 ± 1	43 ± 1	22.1 ± 0.1	11.37	1502.5 ± 0.7	0.99694
0.0402	41 ± 1	39 ± 1	21.9 ± 0.1	11.28	1504.3 ± 0.7	0.99701
0.0302	40.8 ± 0.9	36.8 ± 0.8	21.3 ± 0.1	11.17	1502.6 ± 0.8	0.99715
0.0241	37 ± 3	28 ± 3	21.3 ± 0.2	11.07	1501.1 ± 0.8	0.99721
PVA2000						
0.603	137 ± 4	61.5 ± 0.7	21.7 ± 0.9	12.20	1534.7 ± 0.7	0.99003
0.302	107 ± 3	61.5 ± 0.7	21.5 ± 0.6	12.02	1515.2 ± 0.7	0.99384
0.151	77 ± 3	57 ± 1	24.7 ± 0.4	11.82	1506 ± 1	0.99585
0.101	68.5 ± 0.7	61.9 ± 0.5	19.9 ± 0.1	11.70	1505.2 ± 0.5	0.99648
0.0503	56 ± 1	54 ± 1	18.6 ± 0.2	11.51	1502.4 ± 0.3	0.99717
0.0402	46 ± 2	49 ± 3	21.9 ± 0.3	11.46	1500.9 ± 0.7	0.99728
0.0302	39 ± 1	50 ± 2	22.1 ± 0.1	11.40	1501.2 ± 0.5	0.99740
0.0241	43 ± 1	46 ± 2	19.8 ± 0.2	11.36	1500.7 ± 0.4	0.99749

a) The errors of the density values are within $\pm 1\times10^{-5}$ kg dm^{-3}.

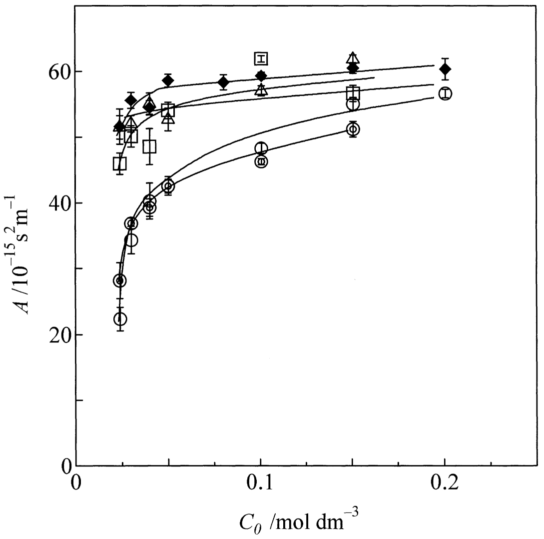

Fig. 4. Concentration dependence of the amplitude of the excess absorption, A, for aqueous solutions of propylamine in the absence and in the presence of PVA's. ◆: no PVA, ○: PVA500, △: PVA900, ◎: PVA1500, □: PVA2000.

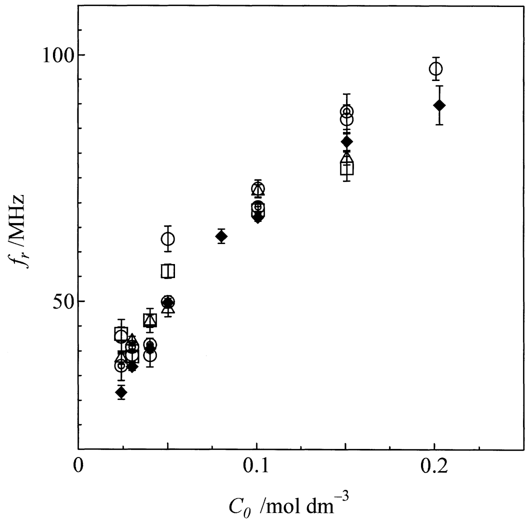

Fig. 5. Concentration dependence of the relaxation frequency, f_r, for aqueous solutions of propylamine in the absence and in the presence of PVA's. ◆: no PVA, ○: PVA500, △: PVA900, ◎: PVA1500, □: PVA2000.

$$\tau = 2\pi f_r = 2\gamma^2\,[\mathrm{OH}^-]k_{12} + k_{21}/(1 + k_{23}/k_{32}), \tag{3}$$

where γ is the activity coefficient calculated by Davies' equation, $\log \gamma = -0.5\{\sqrt{I}/(1+\sqrt{I}) - 0.3\times I\}$, where I is the ionic strength. The equilibrium constants of the first and second steps are defined as

$$K_{21} = k_{21}/k_{12} = \gamma^2[\mathrm{R{-}NH_3}^+][\mathrm{OH}^-]/[\mathrm{R{-}NH_3}^+\cdots\mathrm{OH}^-] \tag{4}$$

and

$$K_{32} = k_{32}/k_{23} = [\mathrm{R{-}NH_3}^+\cdots\mathrm{OH}^-]/[\mathrm{R{-}NH_2}], \tag{5}$$

Table 2. Parameters for pH Estimation in Aqueous Solution of 2.01 g dm^{-3} PVA's

Solution	The parameters for pH estimation		
	a mol^{-1} dm^3	b	c mol dm^{-3}
no PVA	1.50×10^2	7.17	−0.0131
PVA500aq	1.34×10^3	12.4	0.0097
PVA900aq	1.26×10^2	26.6	−0.0409
PVA1500aq	1.68×10^3	16.2	0.0027
PVA2000aq	4.49×10^2	24.8	−0.0362

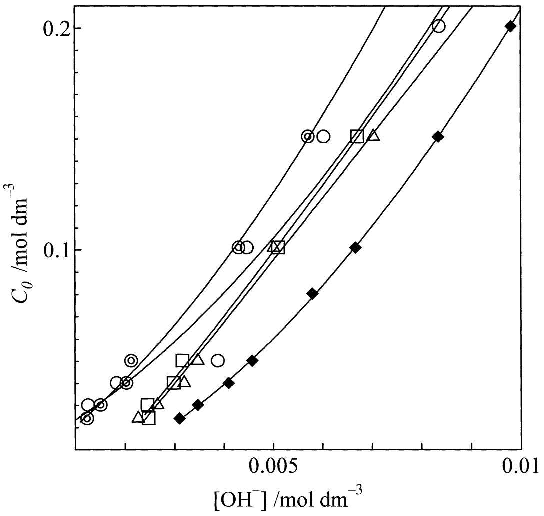

Fig. 6. Plots of propylamine concentration vs hydroxide ion concentration. ◆: no PVA, ○: PVA500, △: PVA900, ◎: PVA1500, □: PVA2000.

respectively. The dissociation constant or the equilibrium constant, K_b, can be expressed by the following equation when the intermediate is taken into account:

$$K_b = K_{21}/(1 + K_{32}^{-1}). \tag{6}$$

Although the concentration of [OH$^-$] is determined through a measurement by a pH meter, any slight error causes a large uncertainty in the determination of the rate constants. The dissociation constant, K_b, is simply expressed by the analytical concentration, C_0, for the over all reaction as

$$K_b = \gamma^2[\mathrm{OH}^-]^2/(C_0 - [\mathrm{OH}^-]). \tag{7}$$

Equation 7 shows that the analytical concentration may be expressed as a function of a polynomial of degree two of the hydroxide ion concentration. Then, as a first approximation, we employed the relation, $C_0 = a[\mathrm{OH}^-]^2 + b[\mathrm{OH}^-] + c$, where a, b, and c are constants. The a, b, and c values were determined (Table 2) and the results are shown in Fig. 6. It can be seen that the relation between the hydroxide ion and the analytical concentration is well expressed by a binomial. When a polymer exists in the solution, the reactant concentration, [OH$^-$], decreases, which is considered to be one of the polymer effects. In an analysis, the hydroxide ion concentrations were

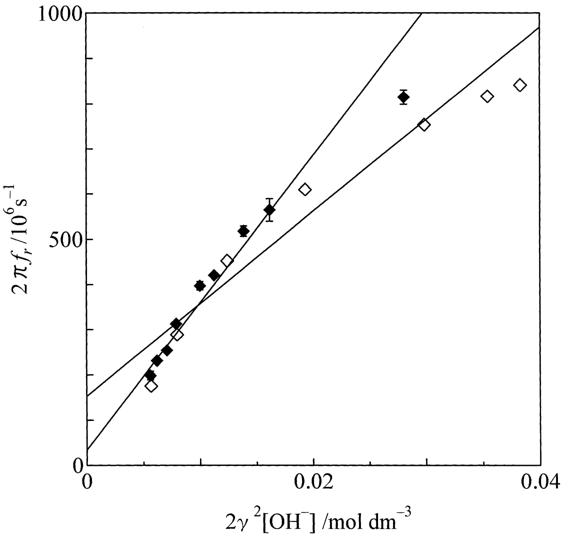

Fig. 7. Plots of $2\pi f_r$ vs $2\gamma^2[OH^-]$ for aqueous solutions of propylamine. ◆: this work, ◇: those in Ref. 6.

estimated from the quadratic function curves, and used to determine the rate and thermodynamic parameters. Plots of $2\pi f_r$ vs. $2\gamma^2[OH^-]$ in the absence of PVA are shown in Fig. 7 along with previously reported data.[6] When all of the results were used, the slope and the intercept gave the same values as those in a reference.[6] However, we noticed that the plots tend to curve at a high concentration range. This kind of trend was also observed by Dickson et al.[14] When results in s range less than 0.201 mol dm^{-3} of propylamine were used, the linearity proved to give the straight line. When PVA's were added, very good linear relations were found in the same concentration range as shown in Fig. 8. The observed ultrasonic absorption has been declared to be clearly expressed by a single relaxational equation; also, the maximum absorption per wavelength can be interpreted by the single equilibrium perturbation (described soon). Therefore, we focused our attentions on the results in a concentration range less than 0.201 mol dm^{-3} of propylamine in this study. According to Eq. 3, the ratio $\{k_{21}/(1 + k_{23}/k_{32})/k_{12}\}$, which was calculated from the values of the slope and the intercept, should have been close to the dissociation constant, K_b, which is defined as $K_b = \gamma^2[OH^-]^2/([R\text{–}NH_3^+\cdots OH^-] + [R\text{–}NH_2])$ or Eqs. 6 and 7; the result in solution without PVA's differs from that described in the literature.[15] Because the dissociation constant, K_b, of samples containing PVA's have not been reported, we tried to determine the K_b values in solutions with PVA's. These were obtainable from the pH dependence in aqueous solutions using Eq. 7; they are listed in Table 3. The K_b values from pH measurements are, again, different from those obtained from the ratio of the intercept and the slope by Eq. 3. Even if the condition $k_{23}/k_{32} \gg 1$ is satisfied, the ratio $(k_{21}/k_{12})/(k_{23}/k_{32})$ must be close to the dissociation constant, K_b. Therefore, we have simply considered that the perturbation of the first step in Eq. 2 is the cause of the observed relaxation. Thus, the slope and intercept of plots of $2\pi f_r$ vs $2\gamma^2[OH^-]$ may provide the rate constants, k_{12} and k_{21}, respectively, because $2\pi f_r = 2\gamma^2[OH^-]k_{12} + k_{21}$. These rate constants are listed in Table 3. The equilibrium constant, K_{32}, was calculated by Eq. 6, and is also given in Table 3. The forward rate constants are reasonable for a diffusion-controlled reaction, and are almost the same, or slightly increase, with the degree of polymerization. The relationship between the relaxation time, τ, and the analytical concentration, C_0, was derived to yield the following equation under the same assumption:

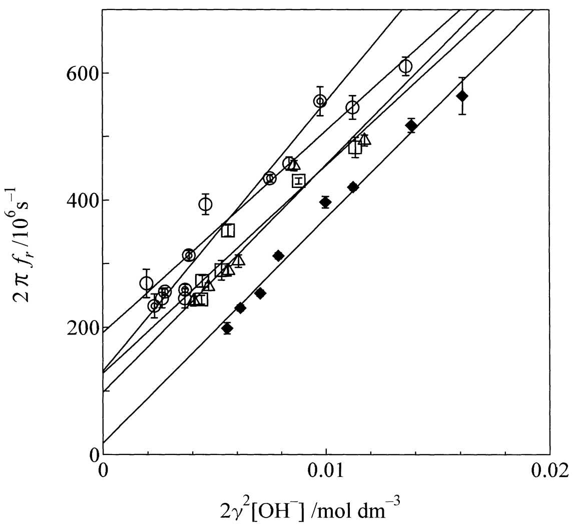

Fig. 8. Plots of $2\pi f_r$ vs $2\gamma^2[OH^-]$ in the absence and in the presence of PVA's. ◆: no PVA, ○: PVA500, △: PVA900, ◎: PVA1500, □: PVA2000.

$$\tau^{-1} = 2\pi f_r = k_{12}\{-K_b + (K_b{}^2 + 4\gamma^2 C_0 K_b)^{1/2}\} + k_{21}. \quad (8)$$

Consequently, by solving for K_b, we obtain

$$K_b = [(\tau^{-1})^2 + k_{21}{}^2 - 2\tau^{-1} k_{21}]/ [k_{12}(4\gamma^2 C_0 k_{12} + 2k_{21} - 2\tau^{-1})]. \quad (9)$$

Using the experimental relaxation time, the analytical concentration and the rate constants, the K_b values were calculated,

Table 3. Rate and Thermodynamic Parameters of Proton Transfer-Reaction of Propylamine in the Absence and Presence of the Additives at 25.0 °C

	k_{12}	k_{21}	K_{21}	K_{32}	ΔV	K_b[a)]	K_b[b)]
Additive	10^{10} mol^{-1} dm^3 s^{-1}	10^8 s^{-1}	10^{-3} mol dm^{-3}	10^{-2}	10^{-6} m^3 mol^{-1}	10^{-4} mol dm^{-3}	10^{-4} mol dm^{-3}
no PVA	3.51 ± 0.09	0.17 ± 0.09	0.49	481	25 ± 3	4.03 ± 0.08	3.7 ± 0.8
PVA500	3.2 ± 0.2	1.9 ± 0.2	5.8	2.7	33 ± 9	1.6 ± 0.7	1.6 ± 0.7
PVA900	3.6 ± 0.3	1.0 ± 0.2	2.8	9.3	32 ± 7	2.3 ± 0.2	2.3 ± 0.3
PVA1500	4.2 ± 0.1	1.3 ± 0.1	3.1	3.8	34 ± 9	1.1 ± 0.1	1.1 ± 0.3
PVA2000	3.3 ± 0.3	1.3 ± 0.2	3.9	6.1	33 ± 9	2.25 ± 0.09	2.3 ± 0.4

a) The calculated values from Eq. 7. b) Those from Eq. 9.

Table 4. Viscosity for Aqueous Solution of Propylamine with 2.01 g dm^{-3} PVA's

Propylamine	no PVA	PVA500	PVA900	PVA1500	PVA2000
Mol dm^{-3}			η/m Pa•s		
0	0.890	0.960	1.01	1.03	1.06
0.024	0.895	0.963	1.01	1.03	1.06
0.101	0.911	0.982	1.02	1.05	1.09
0.151	0.922	0.996	1.04	1.06	1.10

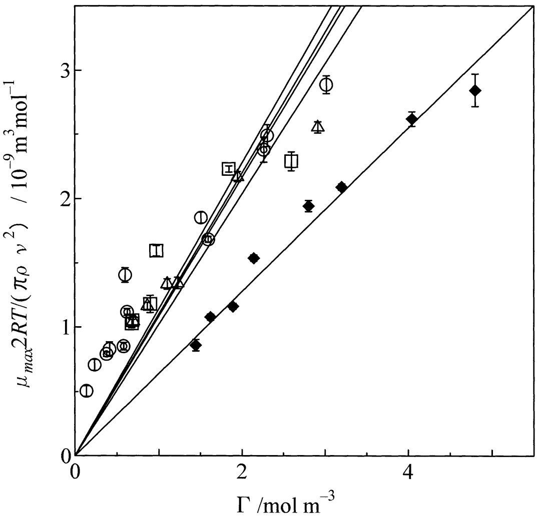

Fig. 9. Plots of $\mu_{max}2RT/(\pi\rho v^2)$ vs Γ in the absence and in the presence of PVA's. ◆: no PVA, ○: PVA500, △: PVA900, ◎: PVA1500, □: PVA2000.

and are also listed in Table 3. Reasonable dissociation constants have been obtained because they are close to those calculated by Eq. 7.

Another important parameter obtained from ultrasonic absorption and velocity measurements is the maximum absorption per wavelength, μ_{max},[11]

$$\mu_{max} = Af_r v/2 = \pi\rho v^2 \Gamma [\Delta V - \alpha_p \,\Delta H/(\rho C_p)]^2/2RT, \qquad (10)$$

where v is the sound velocity, ρ the density, R the gas constant, T the absolute temperature, ΔV the standard volume changes of the reaction, α_p the thermal expansion coefficient, C_p the specific heat at a constant pressure, ΔH the standard enthalpy change of the reaction, and Γ the concentration term, given by

$$\Gamma = (1/[OH^-] + 1/[R\text{–}NH_3^+] + 1/[R\text{–}NH_3^+\cdots OH^-])^{-1}. \qquad (11)$$

The contribution of the activity coefficient on the Γ term is negligibly small and the enthalpy term in Eq. 10 is also negligible because of the aqueous solutions. The coupling effect of the second step on the first step in Eq. 2 is ignored for the same reason for interpreting the relaxation time. As a result, the concentration dependence of μ_{max} provides a value of the standard volume change of the reaction because the intermediate concentration is calculated from the K_b and K_{21} values. In these calculations, the values of the sound velocity and the density were approximated to be equal to those for individual solvents with PVA's, because the changes in the sound velocity and density do not affect the magnitude of μ_{max}. The ΔV values have been determined from plots of $\mu_{max}2RT/$ $(\pi\rho v^2)$ vs Γ, which are shown in Fig. 9; the results are listed in Table 3.

The viscosity coefficient, η, of the solutions of PVA's was measured in order to see the effect of the solvent viscosity on a diffusion-controlled reaction. They are listed in Table 4. As can be seen, the viscosity coefficient increases in the solution with PVA's.

Discussion

One of the effects of PVA's on the solution characteristics under study is a decrease in the dissociation constant, K_b (Table 3). This decreasing effect was not observed in mixed solvents with several alcohols.[8] The effect by PVA's is very remarkable because the concentration of PVA's in the monomer unit is 0.044 mol dm^{-3} while the concentrations of the alcohols are more than 1 mol dm^{-3}. Therefore, the decreasing effect by PVA's may arise from localized hydroxyl groups in the polymers. This effect is considered to be due to an interaction between the hydroxyl groups in PVA's and the reactants in Eq. 2. The ionic species of the reactants are considerably hydrated, and may prefer to exist in the bulk phase. Thus, the most plausible intermolecular interaction between them is among the intermediate, $R\text{–}NH_3^+\cdots OH^-$, and OH groups in PVA's. It is possible that two adjacent hydroxyl groups in PVA's interact specifically with the one intermediate because the intermediate may include water molecules.[16]

Once such an attractive interaction is effective, the stability of the reaction intermediate decreases, which causes an increase in the backward rate constant, k_{21}, as can be seen Table 3. Also, the concentration of the intermediate decreases because of this interaction. This is reflected in the smaller values of K_{32} when they are compared with that without the polymer. The extent of the decrease in the intermediate is more than those of the reactant concentrations, $[R\text{–}NH_3^+]$ or $[OH^-]$. This causes an increase in the equilibrium constant, K_{21}. Thus, the dissociation constant, K_b, decreases when PVA's exist in the solution from Eq. 6. Theses can be seen in an actual calculation of the individual species in Eq. 2 at the same analytical concentration.

Another effect of PVA's on the solution characteristics is found in the diffusion-controlled reaction rate constant, k_{12}. Even though the reactant concentration, $[OH^-]$, decreases, the experimental relaxation frequencies still exist in a similar frequency range. This situation means that the rate constant, k_{12}, remains constant, or increases slightly when PVA's are added to the solutions. The obtained values are reasonable as a diffusion-controlled reaction. According to Debye, the diffusion controlled rate constant is calculated by,[17]

$$\begin{aligned} k_{12} = {} & \sigma (D_{\mathrm{R\text{–}NH_3^+}} + D_{\mathrm{OH^-}}) (Z_{\mathrm{R\text{–}NH_3^+}} Z_{\mathrm{OH^-}} N_{\mathrm{A}}\, e^2) \\ & /\varepsilon_r \varepsilon_0 k_B T \,[\, \exp \{\, (Z_{\mathrm{R\text{–}NH_3^+}} Z_{\mathrm{OH^-}} e^2) \\ & /\, (4\pi\varepsilon_r\, \varepsilon_0\, k_B\, T\, r^*)\} - 1\,], \end{aligned} \tag{12}$$

where σ is the steric factor, N_{A} Avogadro constant, Z_I the algebraic charge of ions, e the electronic charge, D_I the diffusion coefficient of the reacting ions, ε_0 the dielectric constant in a vacuum, ε_r the relative dielectric constant of the solvent, k_B the Boltzmann constant, and r^* the effective radius for the reaction. Equation 12 is appropriately used to compare the theoretical proton-transfer reaction rate with the results obtained experimentally.[4,17] When the steric factor, 1, is taken for propylamine solution, good agreements between the calculated and experimental rate constants are obtained in solution without PVA to yield the reaction radius, $r^* = 4.2\times10^{-10}$ m.

In order to see the applicability of Eq. 12 to a system with PVA's, the effects of the solvent dielectric constant, ε_r, the diffusion coefficient of the reactants, D_I, and the reaction radius, r^*, on the reaction must be taken into account. Akerlof[18] reported on the dielectric constants in mixtures of various alcohols and water. At concentrations less than 30 wt% of alcohols, the dielectric constants decrease linearly with the alcohol concentration. The decreasing effect is slightly greater with an increase in the hydrophobicity of the alcohols. The concentration of PVA's in this study was kept constant at 0.20 wt%. If the effect of a decrease in the dielectric constant on a PVA solution is close to those of ethanol and propanol, its decrease is estimated to be only 0.13 unit in ε_r. This change in the dielectric constant causes a negligibly small change in the rate constant in Eq. 12 (0.03×10^{10} mol^{-1} dm^3 s^{-1}). This means that the effect of the dielectric constant on the rate constant may not be predominant under this experimental condition. The reaction radius is also sensitive in a calculation of the rate constant by Eq. 12.[4,19] However, because one of the reactants is supplied by water molecules, it is approximated that the reaction radius is still the same, even if PVA's are added to the solutions. The only factor that is left is the diffusion coefficient of the reactant, $D_{\mathrm{OH^-}}$, which should be reciprocally proportional to the solution viscosity. As shown in Table 4, the viscosity coefficients increase when PVA molecules exist in the solution, while the experimental diffusion-controlled rate constants, k_{12}, are almost the same, or slightly increase, along with the degree of the polymerization of PVA's. This means that the diffusion coefficient is not lowered. Even if the frequency of collisions between the reactants decreases with the solution viscosity, the rate constants are still similar. The migration of protons or hydroxide ions in water is well interpreted by the Grotthuss mechanism.[20,21] It has been reported that the addition of PVA's creates the hydrogen-bonds around the hydrophobic regions, although the bond defects are also found.[22] If the hydrogen-bond network is promoted as a whole in the solution used in this study, their movements are facilitated. We have considered that when PVA's are added to aqueous solutions of propylamine, water structure may be developed owing to hydrophobic hydration near the PVA's, and thus the k_{12} values still remain at similar values, or are slightly greater. A similar viscosity dependence on the diffusion-controlled rate constant is observed in a mixed solvent with 2-propanol where the alcohol acts as water structure promoter.[23] However, a clear dependence of the degree of polymerization for PVA's on the forward and backward rate constants and the standard volume change for the proton-transfer reaction was not found under our experimental conditions.

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