

Effect of Poly(vinylpyrrolidone) on Proton-Transfer Reaction in Propylamine Aqueous Solution by Ultrasonic Relaxation Method

Sadakatsu Nishikawa* and Kazuhiko Ishikawa

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

Ultrasonic absorption coefficients in the frequency range from 0.8 to 220 MHz were measured in aqueous solution of propylamine in the presence of poly(vinylpyrrolidone) (PVP) with several polymerization degrees at 25 °C. In the solutions containing only the polymers, no relaxational absorption was found. However, a single Debye-type relaxational absorption was observed when propylamine coexists in solutions, and the cause of it was attributed to a perturbation of chemical equilibrium associated with a proton-transfer reaction. The protolysis and hydrolysis rate constants and the standard volume change of the reaction in the solutions with PVP were determined from the reactant concentration dependence of the relaxation frequency and the maximum absorption per wavelength. These results were compared with those in the solution with poly(vinyl alcohol) (PVA), and it was found that an interaction between propylamine and the polymer plays an important role in the proton-transfer reaction. The extent of the interaction between PVA and the reaction intermediate was proved to be smaller than that between PVP and the intermediate.

Introduction

Recognition of dynamic solute–solvent interactions is very important for the precise understanding of complex biological reactions. One of the popular solute–solvent interactions is hydrolysis or protolysis reaction in aqueous solutions. The protolysis for acids and bases in aqueous solutions is associated with a proton-transfer reaction that is occurring very rapidly. An ultrasonic relaxation method has been used to provide the direct information concerning the proton-transfer reaction in aqueous solutions of various amines and carboxylic acids.^{1–5} The reaction mechanism has been precisely clarified from the detail analysis of the ultrasonic relaxational absorption. Then, solution characteristics with various additives may be examined through the proton-transfer reaction. Actually, the present authors successfully applied the ultrasonic relaxation due to the proton-transfer reaction to elucidation of characteristics of alcohol/water mixed solvents.^{6–9} In addition, the effect of poly(vinyl alcohol) on the proton-transfer reaction was examined using the ultrasonic relaxation method.¹⁰ We desired to extend these studies to the effects of other polymers that are considered to affect the structure of the solvent water. For this purpose, poly(vinylpyrrolidone) with several polymerization degrees was chosen as additives, and the ultrasonic absorption measurements were carried out in propylamine aqueous solution with the polymers. The results are discussed in this study, comparing those in the system with poly(vinyl alcohols).

Experimental Section

Chemicals. Propylamine and poly(vinylpyrrolidone) (PVP3300) [M_w (molecular weight) $\sim 360\,000$ (K value,¹¹ 81.0–97.2)] of reagent grade were purchased from Wako Pure Chemicals Co., Ltd., and were used without further purification. PVP270 [$M_w \sim 29\,000$ (K value, 24.2)], PVP500 [$M_w \sim 55\,000$ (K value,

28.9)], PVP11900 [$M_w \sim 1\,300\,000$ (K value, 95.5)] of reagent grade were purchased from Aldrich Chemical Co. and were also used without further purification. The sample solvent was distilled, deionized, and filtered through a Milli-Q SP-TOC filter system from Japan Millipore Ltd. The sample solutions were prepared from the stock solutions (2.01 mol dm⁻³ of propylamine and 4.02 g dm⁻³ of PVP) and were kept in a N₂ gas atmosphere.

Apparatus. The ultrasonic absorption coefficients, α , were measured by pulse method using 5 and 20 MHz fundamental x-cut quartz crystals at their odd over-tones in the frequency range from 15 to 220 MHz. The sample solution under examination was maintained at constant temperature by using a thermostatic bath (Eyela Uni Ace Bath NCB-2200). In the resonance method, a cell with 3 MHz fundamental x-cut quartz plates (3-cm diameter) was applied to the measurement of the absorption coefficients in the range from 0.8 to 3 MHz. In the frequency range from 3 to 7 MHz, 5-MHz fundamental crystals (2-cm diameter) were used. The acoustic path length of these resonators is ~ 6 mm. The thermostated water was circulated around the resonator cavity in order to maintain the temperature of the sample solutions within ± 0.01 °C using LAUDA RM-20. The acoustic loss of the resonators was always checked using solvents before measuring the desired sample solutions. The details of the pulse and resonance apparatuses were described elsewhere.^{9,12}

Sound velocity was measured by the resonator at ~ 3 MHz. Density value was obtained by a vibrating density meter (DMA 60/602, Anton Paar). 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 Ubbelohde-type viscometer was used to determine the viscosity coefficient in a water bath controlled within ± 0.01 °C. All of the measurements were carried out, as much as possible, in a dry N₂ gas atmosphere, and measurement temperature was 25.0 °C.

* To whom correspondence should be addressed. E-mail: nishikas@cc.saga-u.ac.jp.

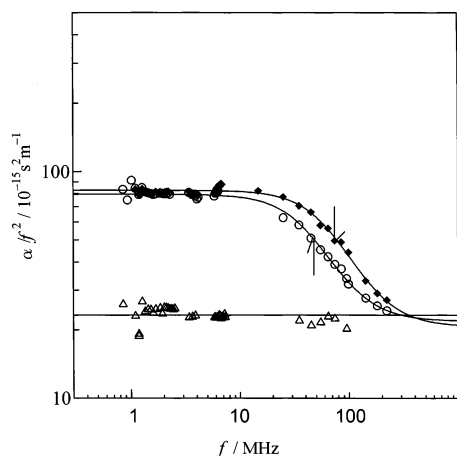


Figure 1. Representative ultrasonic absorption spectra for an aqueous solution of propylamine with 2.01 g dm⁻³ PVP3300 at 25 °C. Δ , no propylamine; \circ , 0.0503 mol dm⁻³ propylamine; \blacklozenge , 0.151 mol dm⁻³ propylamine. The arrows show the position of the relaxation frequency.

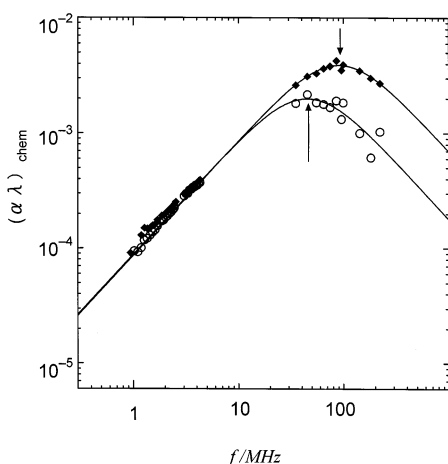


Figure 2. Representative ultrasonic absorption spectra for an aqueous solution of propylamine with 2.01 g dm⁻³ PVP270 at 25 °C. \circ , 0.0503 mol dm⁻³ propylamine; \blacklozenge , 0.150 mol dm⁻³ propylamine.

Results

Figures 1 and 2 illustrate the representative ultrasonic spectra for propylamine aqueous solutions in the presence of PVP3300 and PVP270. The concentration of the polymer was kept constant at 2.01 g dm⁻³. This corresponds to a constant molar fraction in monomer units (1.7×10^{-4}). No frequency dependence of the absorption coefficients divided by the square of the frequency, αf^2 , was found in aqueous solutions with only PVP, one of which is shown in Figure 1. Even when the solution pH of the PVAs was 10.3, excess absorption was not also observed. Similar absorption spectra were observed in the solutions with PVP500 and PVP11900.

The frequency dependence of the absorption on frequency was examined by a Debye-type relaxational equation as follows,¹²

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

or

$$(\alpha\lambda)_{\text{chem}} = (\alpha f^2 - B)f\nu = Af\nu/[1 + (f/f_r)^2] \quad (1')$$

where f_r , A , and B are the relaxation frequency, the amplitude of the relaxational absorption, and the background absorption, respectively and $(\alpha\lambda)_{\text{chem}}$ is the excess absorption per wavelength

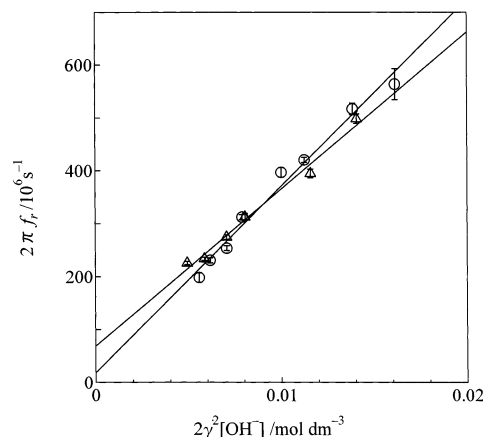
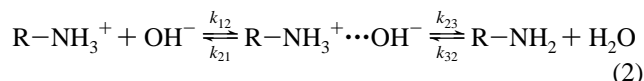


Figure 3. Representative plots of $2\pi f_r$ vs $2\gamma^2[\text{OH}^-]$ in the absence and in the presence of PVP. \circ , no additive; Δ , PVP500.

for the relaxation. The ultrasonic parameters (f_r , A , and B) in Table 1 were determined by a nonlinear least-mean-squares method using a slightly modified version of eq 1.¹⁴ The solid curves shown in Figures 1 and 2 are the calculated values represented by eqs 1 and 1'. The experimental results that the observed absorption coefficients are well fitted to eqs 1 or 1' indicate the existence of a single ultrasonic relaxation in the solutions. The relaxation frequency, f_r , increases with the propylamine concentration, while the amplitudes of the relaxational absorption, A , tend to reach plateaus with an increasing concentration, even if the additives (PVPs) are present in the solutions. These tendencies are characteristic of the relaxation due to a proton-transfer reaction in aqueous solutions of amines.⁶⁻⁹ The mechanism of the reaction was originally proposed by Eigen¹⁵ as



where k_{ij} is the rate constant at the individual steps. As was described in detail in the system with propylamine and poly(vinyl alcohol) (PVA),^{6,10} the cause of the relaxation is due to the perturbation of the first equilibrium in eq 2. Following the same analytical procedure, the relationship between the relaxation time, τ , or the relaxation frequency, f_r , and the reactant concentration is tested to apply

$$\tau^{-1} = 2\pi f_r = 2\gamma^2[\text{OH}^-]k_{12} + k_{21} \quad (3)$$

where γ is the activity coefficient calculated by Davies' equation. Figure 3 shows the representative plots of $2\pi f_r$ vs $2\gamma^2[\text{OH}^-]$, and they provide good linearity. From the slope and intercept, the forward and backward rate constants for the first step were determined using a linear least-mean-squares method, and they are listed in Table 2.

The equilibrium constants of the first and second steps, K_{21} and K_{32} , are defined as

$$K_{21} = k_{21}/k_{12} \quad \text{and} \quad K_{32} = k_{32}/k_{23} \quad (4)$$

These equilibrium constants can be combined with the dissociation constant, K_b , which is defined as

$$K_b = \gamma^2[\text{OH}^-]^2/([\text{R-NH}_3^+ \cdots \text{OH}^-] + [\text{R-NH}_2]) = K_{21}/(1 + K_{32}^{-1}) \quad (5)$$

TABLE 1: Ultrasonic and Thermodynamic Parameters for Aqueous Solutions of Propylamine with 2.01 g dm⁻³ PVP at 25 °C

propylamine mol dm ⁻³	f_r MHz	A 10 ⁻¹⁵ s ² m ⁻¹	B 10 ⁻¹⁵ s ² m ⁻¹	pH	ν m s ⁻¹	ρ^a kg dm ⁻³
PVP270 (M_w 29 000)						
0.151	90 ± 2	57.4 ± 0.9	19.9 ± 0.4	11.95	1507.1 ± 0.4	0.995 72
0.1206	71 ± 1	60.4 ± 0.7	21.4 ± 0.2	11.90	1506.7 ± 0.3	0.996 14
0.101	75 ± 1	55.1 ± 0.7	19.7 ± 0.2	11.85	1504.9 ± 0.9	0.996 41
0.0804	64 ± 2	52 ± 2	21.2 ± 0.3	11.79	1503.7 ± 0.2	0.996 63
0.0503	45 ± 2	59 ± 3	21.6 ± 0.3	11.66	1501.5 ± 0.4	0.997 01
0.0302	37 ± 1	57 ± 3	20.6 ± 0.2	11.48	1500.7 ± 0.5	0.997 27
0.0241	34 ± 1	55 ± 2	20.8 ± 0.2	11.37	1500.9 ± 0.4	0.997 31
PVP500 (M_w 55 000)						
0.151	79 ± 1	62.9 ± 0.7	20.6 ± 0.3	11.93	1507 ± 2	0.995 68
0.101	66 ± 1	61 ± 1	21.6 ± 0.2	11.83	1504.6 ± 0.2	0.996 29
0.0503	50 ± 1	55 ± 1	21.1 ± 0.1	11.66	1501 ± 1	0.997 01
0.0402	43.8 ± 0.7	53.7 ± 0.9	21.08 ± 0.08	11.60	1501.4 ± 0.1	0.997 12
0.0302	37.3 ± 0.5	56.4 ± 0.9	21.1 ± 0.06	11.52	150.8 ± 0.2	0.997 22
0.0241	36.0 ± 0.5	52.7 ± 0.8	20.63 ± 0.07	11.43	150.6 ± 0.2	0.997 28
PVP3300 (M_w 360 100)						
0.151	74 ± 1	62.1 ± 0.8	20.6 ± 0.3	11.87	1503.56 ± 0.02	0.995 92
0.101	66 ± 1	57.8 ± 0.8	21.8 ± 0.2	11.78	1501.76 ± 0.01	0.996 36
0.0503	47.6 ± 0.8	57.6 ± 0.9	21.8 ± 0.1	11.60	1499.36 ± 0.02	0.996 94
0.0402	41 ± 1	56 ± 2	21.8 ± 0.2	11.54	1499.17 ± 0.03	0.997 06
0.0302	40 ± 1	56 ± 2	21.1 ± 0.2	11.47	1498.75 ± 0.02	0.997 18
0.0241	38.1 ± 0.8	56 ± 1	20.1 ± 0.1	11.39	1498.47 ± 0.01	0.997 25
PVP11900 (M_w 1 300 000)						
0.151	80.1 ± 0.9	60.6 ± 0.4	21.4 ± 0.2	11.95	1507.4 ± 0.2	0.995 64
0.101	70.6 ± 0.9	59.8 ± 0.6	19.9 ± 0.2	11.85	1504.5 ± 0.4	0.996 30
0.0503	51.4 ± 0.7	54.5 ± 0.7	20.6 ± 0.1	11.66	1502.0 ± 0.3	0.996 98
0.0402	45.9 ± 0.8	53.1 ± 0.9	20.7 ± 0.1	11.59	1500.7 ± 0.3	0.997 08
0.0302	42 ± 1	55 ± 2	19.4 ± 0.1	11.48	1500.2 ± 0.3	0.997 23
0.0241	31.6 ± 0.7	53 ± 1	22 ± 1	11.37	1500.0 ± 0.4	0.997 30

^a The errors of the density values are within $\pm 1 \times 10^{-5}$ kg dm⁻³.

TABLE 2: Rate and Thermodynamic Parameters of Proton-Transfer Reaction of Propylamine in the Absence and Presence of the Additives at 25.0 °C

additive	k_{12} 10 ¹⁰ mol ⁻¹ dm ³ s ⁻¹	k_{21} 10 ⁸ s ⁻¹	K_{21} 10 ⁻³ mol dm ⁻³	K_{32} 10 ⁻²	ΔV 10 ⁻⁶ m ³ mol ⁻¹	K_b^a 10 ⁻⁴ mol dm ⁻³	K_{b1}^b 10 ⁻⁴ mol dm ⁻³	η 10 ⁻³ N s m ⁻²
none	3.51 ± 0.09	0.17 ± 0.09	0.49	481	25 ± 3	4.03 ± 0.08	3.7 ± 0.8	0.905
PVP270	3.4 ± 0.2	0.44 ± 0.16	1.3	44	25 ± 5	4.0 ± 0.7	3.4 ± 1.2	0.939
PVP504	3.0 ± 0.1	0.7 ± 0.1	2.3	21	27 ± 5	4.0 ± 0.1	3.8 ± 0.3	0.947
PVP3300	3.0 ± 0.1	0.94 ± 0.08	3.2	10.4	29 ± 7	2.95 ± 0.08	3.0 ± 0.3	1.22
PVP11900	2.5 ± 0.1	1.10 ± 0.09	4.4	10.6	28 ± 7	3.7 ± 0.8	3.8 ± 0.8	1.10

^a The calculated values from eq 6. ^b Those from eq 7.

Therefore, the equilibrium constant in the second step is available from the ultrasonic data if the dissociation constant is determined in the solutions with the polymers. The dissociation constant, K_b , is simply expressed by the analytical concentration, C_0 , as

$$K_b = \gamma^2 [\text{OH}^-]^2 / (C_0 - [\text{OH}^-]) \quad (6)$$

The obtained value for K_b without PVP is very close to the literature value.¹⁶ We determined K_b values, therefore, in the solutions with PVP from the pH measurements, and they are also listed in Table 2.

The dissociation constant, K_b , is also expressed by the relaxation time, the rate constants, and the analytical concentration as follows:⁶

$$K_b = [(\tau^{-1})^2 + k_{21}^2 - 2\tau^{-1}k_{21}] / [k_{12}(4\gamma^2 C_0 k_{12} + 2k_{21} - 2\tau^{-1})] \quad (7)$$

Using the experimental results for rate constants and the relaxation time, the K_b values were also calculated, and they are listed in Table 2.

The amplitude of the relaxational absorption, A , also gives useful information about the reaction. In the ultrasonic relaxation study, the maximum absorption per wavelength, μ_{\max} , is widely used, and it is given by the next equation,¹³

$$\mu_{\max} = A f_r \nu / 2 = \pi \rho \nu^2 \Gamma \Delta V^2 / 2RT \quad (8)$$

where ν is the sound velocity, ρ is the density, R is the gas constant, T is the absolute temperature, ΔV is the standard volume changes of the reaction, and Γ is the concentration term as $\Gamma = (1/[\text{OH}^-] + 1/[\text{R}-\text{NH}_3^+] + 1/[\text{R}-\text{NH}_3^+ \cdots \text{OH}^-])^{-1}$. The ΔV values were determined from the plots of $\mu_{\max} 2RT / (\pi \rho \nu^2)$ vs Γ , some of which are shown in Figure 4. The obtained values are listed in Table 2. As can be seen, the standard volume changes of the reaction tend to increase slightly when the polymers coexist in the solution.

To examine the effect of solution viscosity on the reaction rate, viscosity coefficients, η , were measured in solutions of propylamine with PVP. Although η also increases very slightly with increasing propylamine concentration, the mean values in the solutions with PVP are listed in Table 2.

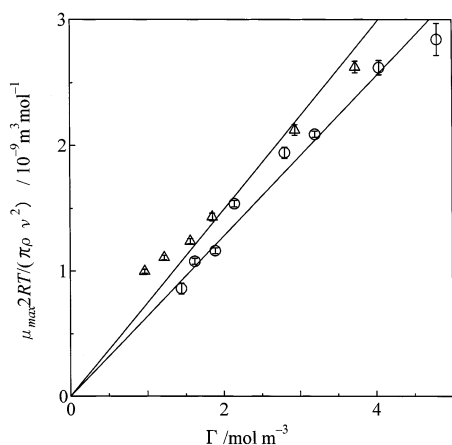


Figure 4. Representative plots of $\mu_{\max} 2RT/(\pi\rho v^2)$ vs Γ term in the absence and in the presence of PVP. O, no additive; Δ , PVP500.

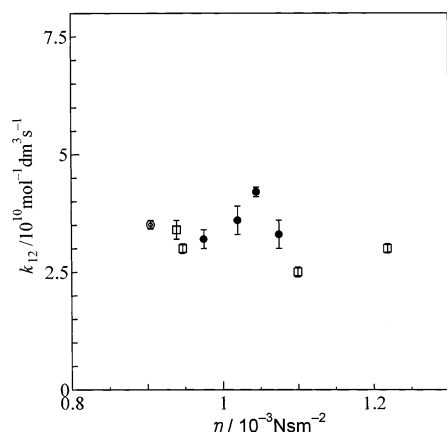


Figure 5. Viscosity dependence of the forward rate constant, k_{12} , for an aqueous solution of propylamine in the absence (\odot) and in the presence of PVA (\bullet) and PVP (\square).

Discussion

In our previous report,¹⁰ it was found that one of the effects of PVA on solution characteristics is a decrease in the dissociation constant of propylamine, K_b . This effect was interpreted by the interaction between the polymer and the intermediate of the reaction shown in eq 2. However, such a dominant effect is not found in the solution with PVP, as is seen in Table 2. This means that the extent of the interaction between PVP and the intermediate is different from that between PVA and the intermediate.

Concerning the results for the forward rate constant, k_{12} , the obtained values on the order of $10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ are reasonable, because the process is diffusion-controlled, even if the PVP coexists in the solution. Figure 5 shows the viscosity dependence of the diffusion-controlled reaction rates in the presence of PVP along with those with PVA. It is seen that the rate constants are not very affected by the existence of the polymers, although the solution viscosity increases with an increase in the degree of polymerization. The diffusion-controlled rate constant for ions in solutions is, in general, inversely proportional to the solution viscosity. The observed viscosity-independent phenomenon for the rate constant, k_{12} , may be interpreted by the compensation of two opposing effects. That is, the existence of the polymers causes an increase in viscosity and a decrease in the rate constant. On the other hand, water structures around the polymer molecules are created to form the hydrogen bond network further, and the mobility of the hydroxide ion may be facilitated (Grotthuss mechanism). It

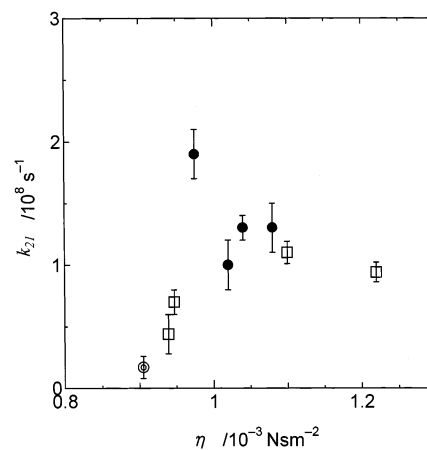


Figure 6. Viscosity dependence of the backward rate constant, k_{21} , for an aqueous solution of propylamine in the absence (\odot) and in the presence of PVA (\bullet) and PVP (\square).

is considered that these opposing effects make the rate constant seem independent of the solution viscosity.

The effect of the polymers on the proton-transfer reaction is reflected in the results for the backward rate constant, k_{21} , as seen in Table 2. The obtained rate constants are relatively greater than that in the solution without the polymers. To compare the results with those in PVA solutions, the results with the system with PVP are shown in Figure 6 as a function of the solution viscosity. The increase in the k_{21} value for the solution with PVA looks greater than that for the solution with PVP. This may indicate that the solution characteristics with PVA are different from those in the solutions containing PVP. Sinyashiki et al.^{16,17} examined dynamics of water in which several polymers (PVP, poly(ethylene glycol) (PEG), PVA, poly(acrylic acid) (PAA), poly(ethyleneimine) (PEI), and poly(allylamine) (PAIA)) coexist in water. They classified the polymer solutions into two groups depending on the solution characteristics from detailed microwave dielectric measurements. It is said that the interaction between the hydrophilic groups of PVA and water is stronger than that between the hydrophilic groups of PVP and water. It was predicted previously¹⁰ that the interaction between the intermediate in the protolysis reaction (eq 2) and the polymer plays an important role in the backward rate constant. The stronger the interaction with water is, the greater the backward rate dissociating into the ions is observed. This means that the extent of the interaction between the PVA and the reaction intermediate is lower than that between the PVP and the intermediate because of the stronger interaction between the PVA and the water molecule. This speculation is also confirmed in the variation of the equilibrium constant, $K_{32} = [\text{R-NH}_3^+ \cdots \text{OH}^-]/[\text{R-NH}_2]$, which is greater in the solution with PVP. However, K_{32} values in the solutions with PVP are still smaller than that in the solution without additive, as is seen in Table 2. This means that the PVP and intermediate interaction is yet affecting the proton-transfer reaction mechanism of propylamine.

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