

Ultrasonic Absorption in Aqueous Solution of Propylamine in the Presence of Polymers

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Abstract

Ultrasonic absorption coefficients in the frequency range from 0.8 MHz to 220 MHz were measured in aqueous solutions of propylamine at 25°C in the presence of poly(ethylene glycol)(PEG) with different polymerization degrees and poly(propylene glycol)(PPG). The concentrations of the polymers were restricted to solutions in which no excess ultrasonic absorption was observed. In the above conditions, PEG and PPG concentrations were changed in order to see the effects of the polymers on acoustical characteristics. A single relaxational absorption was observed when propylamine was dissolved into the polymer solutions and the cause of the relaxation was attributed to a perturbation of chemical equilibrium as $\text{R-NH}_3^+ + \text{OH}^- \rightleftharpoons \text{R-NH}_3^+ \cdots \text{OH}^-$. The rate and equilibrium constants were determined from the dependence of the relaxation frequency on the reactant concentrations. The standard volume change for the reaction was also obtained from the dependence of a maximum absorption per wave-length. The viscosity coefficients were also measured in solutions in which propylamine and the polymers were coexisting. The effects of the polymers on the rate and thermodynamic constants were examined and it was found that the diffusion-controlled rate constant is independent of the existence of the polymers, while the reverse rate constant, i.e. the dissociation rate from the intermediate of the reaction increases with increasing the solution viscosity. All of the ultrasonic relaxation data obtained in this study have been compared with those in solutions with poly(vinyl alcohol)(PVA) and poly(vinylpyrrolidone)(PVP). As a result, it has been found acoustically that the polymers are classified into two groups depending on their hydrophilic groups.

Key word : Ultrasonic relaxation
Proton transfer reaction
Polymer effect:

1. Introduction

A large amount of acoustical data including ultrasonic absorption and velocity has been accumulated so far and these results are now exerted for the developments and utilizations of various sound tools in living and medical fields. The ultrasonic absorption and velocity are closely related to thermodynamic quantities, such as adiabatic compressibility and thermal expansibility, in liquids and solutions^{1,2}. Especially, relaxational phenomena obtained from measurements of frequency dependence of the ultrasonic absorption are, in many instances, due to perturbations of dynamic chemical equilibria in liquids. Although the ultrasonic relaxations have been conventionally analyzed in line with thermodynamics, computer simulation associated with quantum mechanics is now used to complement some results associated with energy changes obtained from the ultrasonic relaxations^{3,4}.

Hydrolysis or protolysis (proton transfer reaction) of amines in aqueous solution is one of the representative reactions observed directly by the ultrasonic absorption in the MHz frequency range. It has been clarified experimentally and theoretically that the rate for the ion recombination process is reasonable as a diffusion controlled reaction₁. By using such fast reaction as a probe, we have expected any possibilities to examine characteristics of more complicate solutions.

Interactions between amines and polymers are fundamentally conducive to actual causes of sound absorption in biological systems. We studied previously the ultrasonic relaxation in aqueous solution of propylamine in which poly(vinyl alcohol) (PVA)⁵ and poly(vinylpyrrolidone) (PVP) were coexisting⁶. Although the effect of the added polymers on the diffusion controlled reaction rate was not noticeable, the dissociation rate into the ions was found to be affected considerably when the polymers coexisted in solutions. In order to verify the effect of polymer on the reaction, we have desired that additional information concerning to the ultrasonic relaxation provides more precise and deep understanding for the interaction between amine and polymer. Poly(ethylene glycol) (PEG) and Poly(propylene glycol) (PPG) are popular water soluble polymers and PEG chemicals with different polymerization degrees are available. Then, they have been chosen as additives in aqueous solutions of propylamine in this study. The results obtained in this

study have been compared with those of the solutions with PVA and PVP.

2. Experimental

2-1. Apparatus and Measurements

Ultrasonic absorption coefficients were measured at odd harmonic frequencies of 5 MHz fundamental x-cut quartz crystals (from 15 MHz to 95 MHz) and 20MHz fundamental crystals (from 100 MHz to 220 MHz) by a pulse method. The distance between the sending crystal of sound and the receiving crystal was measured by a distal micrometer, and the sound propagating distance was sent to a microcomputer in which attenuation coefficients were calculated automatically⁷.

A resonance method was applied to the absorption measurements in the frequency range from 0.8 to 7 MHz, by using 3 MHz, 5 MHz and 7 MHz fundamental x-cut quartz crystals. The measurement frequency was swept and the resonance signals were automatically analyzed to receive the absorption coefficients. The more details for these apparatus were described elsewhere^{8,9}. A water bath (Eyela Univ Ace NCB-2200) controlled within $\pm 0.1^\circ\text{C}$ was used for the cells of the pulse apparatus, and the temperature of solutions within the resonance cells was maintained at a constant better than $\pm 0.01^\circ\text{C}$ by circulating water (LAUDA, RM20). The temperature control for the resonance cells is especially important in order to maintain the resonance signals stable. The same water bath was used to keep the same temperature for the three resonance cells. All of the measurements of the absorption coefficients were always carried out in dry N₂ gas atmosphere in order to avoid any contamination, such as carbon dioxide, as much as possible. The sound velocity was measured by the resonator at around 3 MHz¹⁰. The density values were obtained by a vibrating density meter (DMA 60/602, Anton Paar). The solution *pH* was measured by a glass electrode (HM-60S Toa Denpa) just before the ultrasonic absorption measurements.

An Ubbelohde-type viscometer was used to determine the viscosity coefficient. The temperature for the measurements was kept at 25.0°C for which water bath was controlled within $\pm 0.01^\circ\text{C}$.

2.2. Chemicals

Propylamine was purchased from Wako Pure Chemical Co. Ltd. and poly(ethylene glycols) (PEG) with different polymerization degrees were obtained from Tokyo Kasei Co. Ltd. The average molecular weights of the chemicals are 300 (abbreviated as PEG7), 400 (abbreviated as PEG9), 3000 (abbreviated as PEG70), and 8500 (abbreviated as PEG190). Poly(propylene glycol) with 12 polymerization degree (abbreviated as PPG12) was also purchased from Wako Pure Chemical Co. Ltd.

Sample solutions with propylamine and the polymers were made from their concentrated stock solutions.

3. Results

The results of the ultrasonic absorptions in aqueous solutions of PEG with different polymerization degrees were previously reported and the absorption coefficients divided by the square of measurement frequency, a/f^2 , in concentrated solutions were dependent on the frequency in MHz range^{11,12}. This means that the ultrasonic relaxations exist in aqueous solutions of PEG in the same frequency range as that in the present study. Also, the relaxational absorption associated with a proton transfer reaction is surely

observed in propylamine aqueous solution in the similar frequency range^{5,6}. In order to simplify the system which is examined in our experimental study, the presence of the relaxations associated with only the polymers in aqueous solution is unfavorable because the plural relaxations cause the system complex. Therefore, the ultrasonic absorption properties in aqueous solutions of the polymers were examined firstly. Figure 1 shows the representative ultrasonic absorption spectra in aqueous solutions of PEG and PPG. When the concentration of PEG is below 20.0 g dm⁻³, the increase in a/f^2 is not observed. However, above that polymer concentration, the slight increase in a/f^2 is observed. In solutions of PPG, the trends are similar to those of PEG. Below 20.0 g dm⁻³, the values of a/f^2 are close to those of solvent water. The examination of the relaxation phenomena in polymer solutions is beyond the purpose of the present study. Therefore, the polymer concentrations have been restricted below the polymer concentrations of 20.0 g dm⁻³ in this study.

When propylamine is added in the polymer solutions, a clear frequency dependence of a/f^2 is found as can be seen in Fig. 2 in which the result of PEG7 solution of 2.00 g dm⁻³ without Propylamine is also indicated. The frequency dependences which were similar one

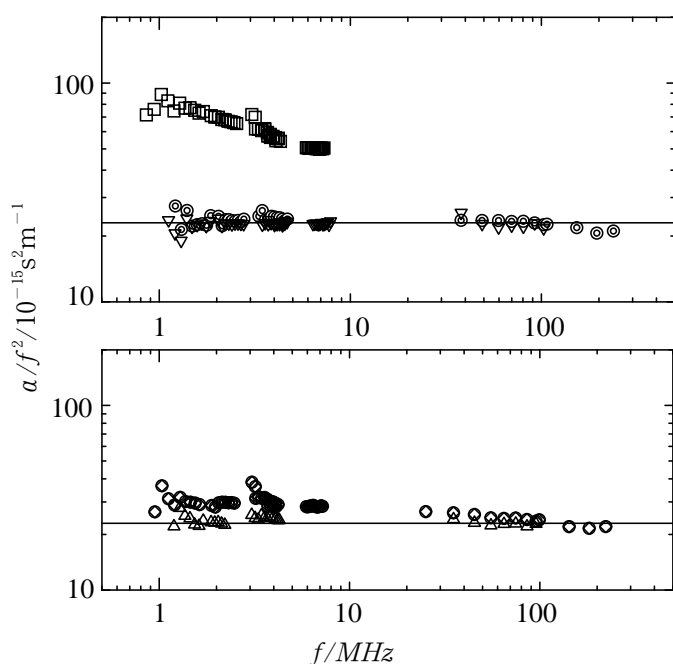


Fig. 1. Ultrasonic absorption spectra in aqueous solutions of several polymers.

△ : 20.0 g dm⁻³ of PEG70, ◇ : 40.0 g dm⁻³ of PEG70,
○ : 60.0 g dm⁻³ PEG70, ◎ : 20.0 g dm⁻³ of PPG12,
▽ : 2.00 g dm⁻³ of F127, □ : 20.0 g dm⁻³ of F127.

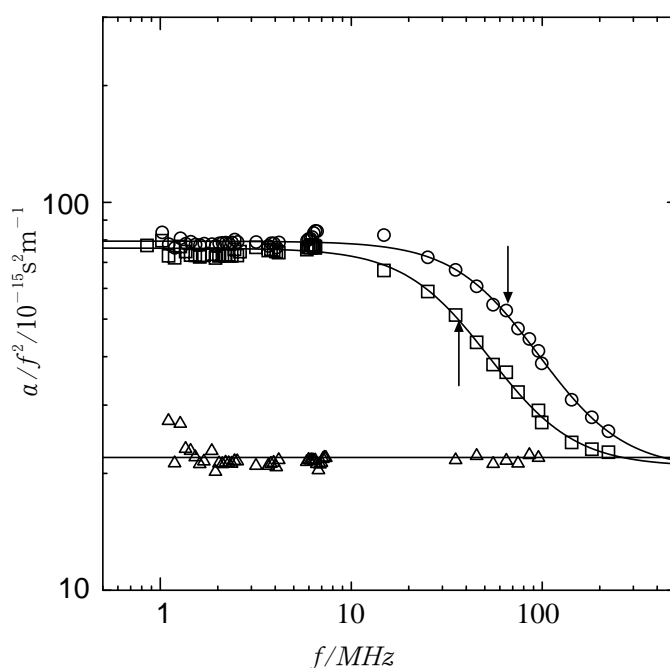
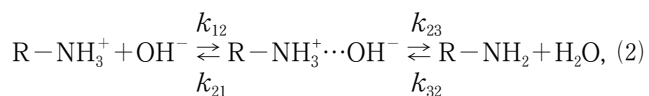


Fig. 2. Representative ultrasonic absorption spectra in aqueous solutions of propylamine (○ : 0.100 mol dm⁻³ and ◇ : 0.030 mol dm⁻³) with 2.00 g dm⁻³ of PEG7 and spectrum in 2.00 g dm⁻³ of PEG7 only (△).

another were observed in other propylamine solutions with the polymers. The dependence has been tested by using a Debye-type single relaxational equation as^{1,2},

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

where f_r is the relaxation frequency, A is the amplitude of the excess absorption and B is the background absorption. These ultrasonic parameters, f_r , A and B , have been determined by a nonlinear least-mean squares method. The solid curves in Fig. 2 indicate the calculated values by using the determined parameters. All of the spectra in the present study have been well fitted to the single relaxational equation. The characteristic acoustical aspects are 1) that the relaxation frequency increases with propylamine concentration and 2) that the amplitudes of the excess absorptions tend to reach constant values. These dependences are characteristics of the relaxation associated with proton transfer reaction of amines^{5,6}. The mechanism of the reaction was originally proposed by Eigen as follows^{1,2},



where k_{ij} is the rate constant at the individual steps. The cause of the relaxation is due to the perturbation of the equilibrium of the first step in Eq. (2) although the coupled reaction mechanism may be taken into account². The reasons why we consider the first step is associated with the observed relaxation are described in detail elsewhere¹³.

Following the similar determining procedure as that in our previous report¹³, the rate constants have been determined by using the next relation.

$$2\pi f_r = \gamma^2 \{ [\text{OH}^-] + [\text{R-NH}_3^+] \} k_{12} + k_{21} \\ = 2\gamma^2 [\text{OH}^-] k_{12} + k_{21}, \quad (3)$$

where γ is the activity coefficient calculated by Davies' equation¹⁴ and the concentration of hydroxide ion is determined from solution pH . Figure 3 shows the representative plots of $2\pi f_r$ as a function of $2\gamma^2[\text{OH}^-]$. All of the plots for solutions studied in our experiment have given good linear relationships like those in this figure. From the slope and intercept, the forward

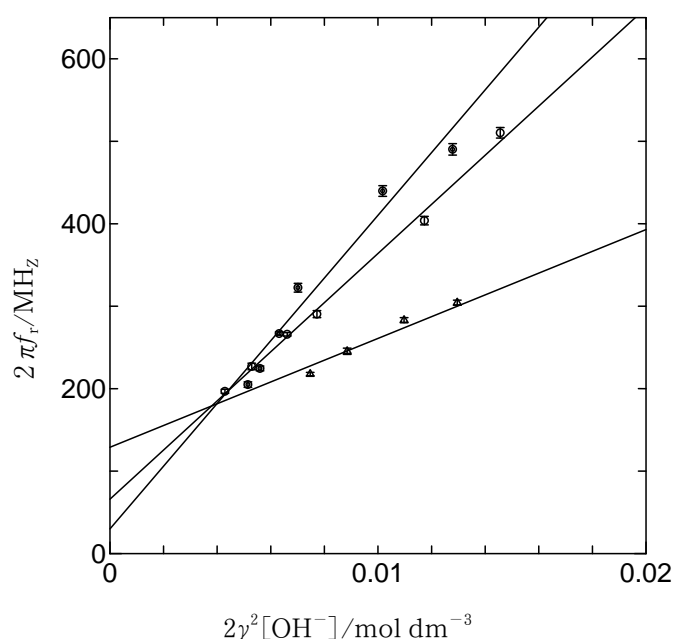


Fig. 3. The plots of $2\pi f_r$ vs $2\gamma^2[\text{OH}^-]$ for aqueous solutions of propylamine with PEG9 (\circ : 2.00 g dm^{-3}), PPG12 (\triangle : 20.0 g dm^{-3}) and F127 (\odot : 2.00 g dm^{-3}).

Table 1. Rate and Thermodynamic Parameters for Protolysis and Hydrolysis of Propylamine in the Presence of the Polymers at 25°C. The concentrations of the polymers are 2.00 g dm^{-3} except the concentrations with 20gPEG70 and 20gPPG12 (20.0 g dm^{-3} polymers coexist).

Polymer	$\frac{k_{12}}{10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}}$	$\frac{k_{21}}{10^8 \text{ s}^{-1}}$	$\frac{K_b}{10^{-4} \text{ mol dm}^{-3}}$	$\frac{K_{21}}{10^{-2}}$	$\frac{K_{32}}{10^{-2}}$	$\frac{\Delta V}{10^{-6} \text{ m}^3 \text{ mol}^{-1}}$	$\frac{\eta}{10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}}$
None	3.51 ± 0.09	0.17 ± 0.09	4.03 ± 0.08	4.9	481	25 ± 3	0.95
PEG7	3.1 ± 0.2	0.7 ± 0.2	3.3 ± 0.3	24	16	28 ± 6	0.915
PEG9	2.98 ± 0.07	0.66 ± 0.06	3.5 ± 0.6	22	19	27 ± 6	0.914
PEG70	3.5 ± 0.1	0.6 ± 0.1	3.3 ± 0.3	18	22	28 ± 4	0.924
PEG190	2.8 ± 0.1	0.7 ± 0.1	4.5 ± 0.1	25	22	25 ± 5	0.941
20gPEG70	2.5 ± 0.2	1.7 ± 0.1	2.4 ± 0.8	70	4	31 ± 9	1.12
PPG12	2.77 ± 0.08	0.60 ± 0.08	5.6 ± 0.5	22	35	25 ± 4	0.913
20gPPG12	1.32 ± 0.03	1.29 ± 0.04	11 ± 2	98	14	22 ± 6	0.999

and backward rate constants, k_{12} and k_{21} , have been determined using a linear least-mean squares method. The obtained values are listed in Table I .

The equilibrium constants, K_{21} and K_{32} , for the first and second steps in Eq. (2) are reasonably defined as $K_{21}=k_{21}/k_{12}$, and $K_{32}=k_{32}/k_{23}$. These equilibrium constants are related to base dissociation constant as $K_b = \gamma^2 [\text{OH}^-]^2 / ([\text{R-NH}_3^+ \cdots \text{OH}^-] + [\text{R-NH}_2]) = \gamma^2 [\text{OH}^-]^2 / (C_0 - [\text{OH}^-]) = K_{21}(1 + K_{32}^{-1})^{-1}$ where C_0 is the analytical concentration of propylamine. The value of K_{21} has been calculated from the ratio of the rate constants for the first step. The base dissociation constant, K_b , has been determined from the concentration dependences of solution pH and the analytical concentration. They are also listed in Table I. The evaluated value is very close to the literature value in solution without additive¹⁵, and therefore the K_b values in solutions with the polymers are considered to be reasonable. Then, the equilibrium constants for the second step, K_{32} , has been determined and they are listed in Table I.

The standard volume change of reaction, ΔV , was obtained from a maximum absorption per wave-length, μ_{max} , which is given by the next equation¹².

$$\mu_{\text{max}} = A f_r v / 2 = \pi \rho v^2 \Gamma (\Delta V)^2 / 2RT, \quad (4)$$

where R is the gas constant, T is the absolute temperature and Γ is the concentration term given by

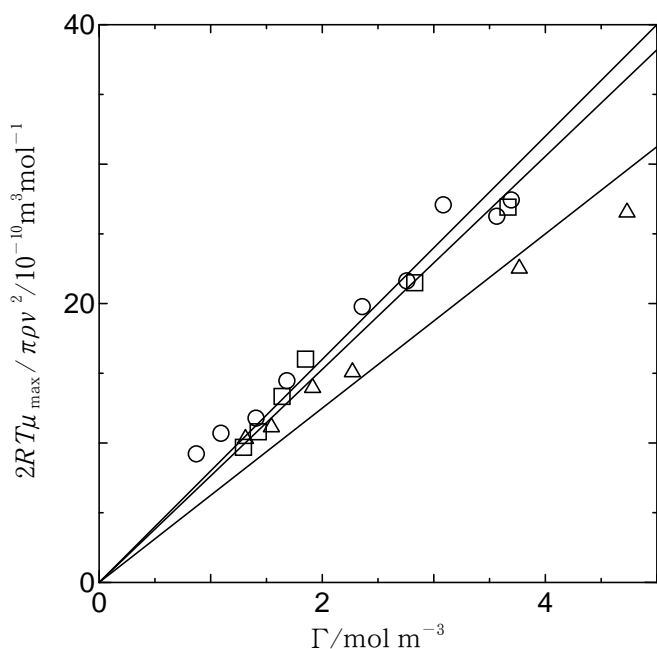


Fig. 4. For the determination of the standard volume change of reaction, the plots of $2RT\mu_{\text{max}} / \pi\rho v^2$ vs Γ for the solutions with PEG70 (\circ : 2.00 g dm⁻³), F127 (\square : 2.00 g dm⁻³) and PPG12(\triangle :2.00 g dm⁻³).

$\Gamma = (1/[\text{OH}^-] + 1/[\text{R-NH}_3^+] + 1/[\text{R-NH}_3^+ \cdots \text{OH}^-])^{-1}$ for the reaction under consideration. The values of ΔV have been determined from the slope of the plots of $2RT\mu_{\text{max}} / \pi\rho v^2$ as a function of Γ and some of the examples are shown in Fig. 4. The obtained values are also tabulated in Table I.

The viscosity coefficients, η , have been measured in all solutions of propylamine with the polymers. The dependence of η on propylamine concentration is not notable though it has been significant in the solution of the polymers. The mean values are also shown in Table I.

The determined ultrasonic parameters at various concentrations of propylamine is available on request from one of authors, S. N. along with solution pH , sound velocity, v , density, ρ , and viscosity coefficient, η .

4. Discussion

The forward rate constants, k_{12} , in Eq. (2) are on the order of $10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ in all solutions with the polymers and they are reasonable as the diffusion controlled reaction. The rate constant can be calculated independently by the theoretical equation derived by Debye¹, and the agreements between the experimental and theoretical values are coincide. The detail calculation procedure has been shown elsewhere⁵. The diffusion controlled reaction associated with proton or hydroxide ion (Grotthuss mechanisms) is considered to be influenced by the presence of the polymers because water molecule participates in the reaction and water structure may be changed by the presence of the polymers. Theoretically, the diffusion controlled rate decreases with increase in solution viscosity because diffusion coefficients of reactants decrease with solution viscosity. In our previous paper, however, we reported that the rate constants were not so dependent on the viscosity of propylamine aqueous solutions in which PVA and PVP coexisted. The results were interpreted by the compensation of two opposing effects⁵. One is that the existence of the polymers causes an increase in solution viscosity and it brings about the decrease in the rate constant. The other is that water structures around the polymer molecules are developed to form hydrogen bond network and the network causes the increase in the reactant movements. Figure 5 shows the dependence of the diffusion controlled reaction rate constant, k_{12} , on solution viscosity. The results

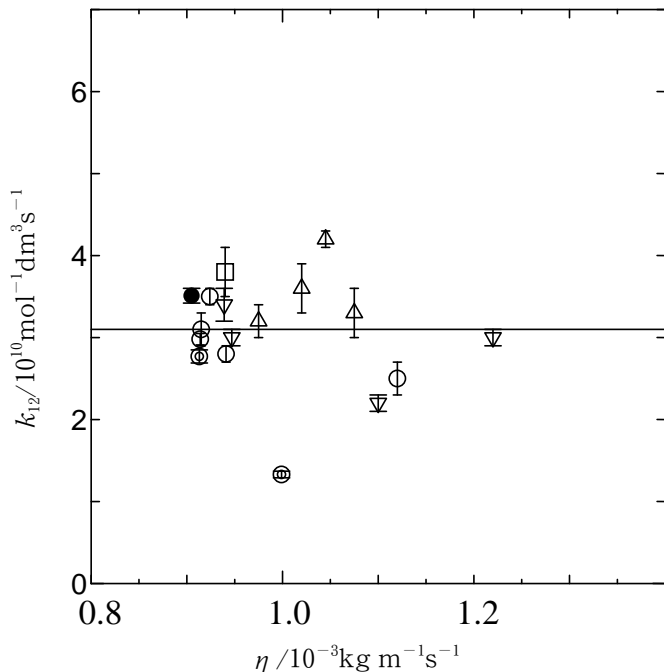


Fig. 5. Viscosity dependence of the forward rate constant, k_{12} , for aqueous solutions of propylamine in the absence (●) and in the presence of polymers (○ : PEG, ⊙ : PPG, △:PVA and PVP:▽).

for solutions with PVA and PVP are also shown for comparison. Clear dependence on the solution viscosity has not been seen. Then, we have concluded that the above interpretation is again confirmed by the results of the present experiments in aqueous solutions with PEG and PPG. However, it is probable that solution viscosity affects the proton transfer reaction in more concentrated polymer solution.

The effect of the polymers on the reverse rate constant, k_{21} , is now considered. As can be seen in Fig. 6, the additions of PEG and PPG cause an increase in the rate constants even if solution viscosity increases. The results in solutions with PVA and PVP are also shown in Fig. 6 for comparison. The results indicate that the reaction is not diffusion controlled as the rate constants are not on the order. It is noteworthy that the rate constants are almost same even if the degree of polymerization is different for solutions of PEG. The result in solution with PPG is also close to that in solutions with PEG. This means that the effect of hydrophobicity in the polymers on the reaction is not so notable. However, the results in solutions with PVP in which oxygen atom is linked with double bond have indicated that the rate constant increases with solution viscosity.⁶ The concentration of PEG in the monomer unit is $0.045 \text{ mol dm}^{-3}$ at 2.00 g dm^{-3} and the concentrations of PPG and PVP in the monomer unit are less than that for PEG. Therefore,

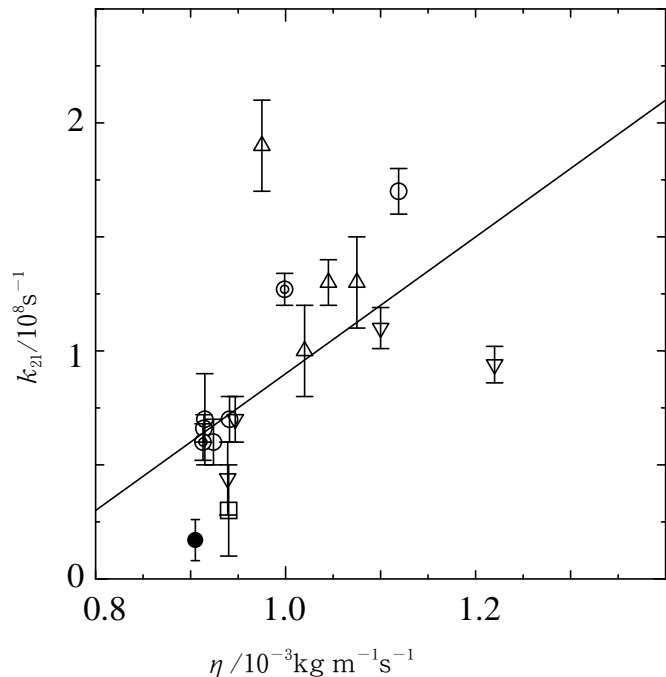


Fig. 6. Viscosity dependence of the backward rate constant, k_{21} , for aqueous solutions of propylamine in the absence (●) and in the presence of polymers (○ : PEG, ⊙ : PPG, △ : PVA, and PVP : ▽).

an interaction between the polymer themselves may be scarce in our experimental conditions. From these experimental results, we have proposed that the increasing tendency of the k_{21} values, when the polymers coexist, may be explained by the weak interactions between the reaction intermediate, $\text{R-NH}_3^+ \cdots \text{OH}^-$, and the hydrophilic moiety of the polymers. When the intermediates bind to the hydrophilic sites of the polymers, the bond between the ammonium and hydroxide groups is weakened. As the result, the rate of the departure from the intermediate to the individual ions increases. It is possible to interpret the polymer concentration dependence on the k_{21} as follows. With increase in the amount of the polymers (20 g PPG in Table I), the reaction rate surely increases because the concentration of the intermediates increases. From the profile of the viscosity dependence of the reverse rate constant as can be shown in Fig. 6, it may possible to divide the polymers into two groups if one result for solution with PVA is ignored. One is the group 1 to which PVA, PEG and PPG belong and the other is the group 2 with PVP. This clarification is due to the hydrophilic group in the polymers and it is accordance with the results reported previously by microwave experiment¹⁶.

The dependence of the standard volume change of the first step on the polymers is not so notable as can be seen in Table I. This indicates that the cause of the

observed relaxation is due to the first step in Eq. (2).

5. Conclusion

The ultrasonic relaxation due to proton transfer reaction has been examined when water soluble polymers, PEG and PPG, coexist in solution. The results have been compared with those reported previously, for PVA and PVP. The diffusion controlled rate is not so influenced by the presence of the polymers, while the dissociation process into ions depends on solution viscosity. From the profile, it is found acoustically that the polymers are classified into two groups depending on their hydrophilic groups.

和文概要

ポリエチレングリコール、ポリプロピレングリコールが共存するプロピルアミン水溶液の超音波吸収測定を0.8～220MHzの領域で行った。アミンが存在する場合にのみ超音波の単一緩和現象が観測された。超音波の緩和周波数および一波長あたりの最大吸収量のアミン濃度依存性を調べ、その緩和の原因がアミンの加水分解反応によるものであることを解明した。それらの結果を用いて反応の速度定数、平衡定数および反応の体積変化を決定した。以上の結果は高分子が共存すると拡散律速反応速度よりもその逆反応に影響することが分かった。また、溶液の粘度依存性についても考察した。今回得られたこれらの速度論的結果をポリビニルアルコール、ポリビニルピロリドンが共存する場合の結果と比較検討をおこなった。

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