August, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 60, 2779—2783 (1987)* 2779

# Effects of Some Additives on Proton-Transfer Reaction Studied by Ultrasonic Methods

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(Received March 5, 1987)

Ultrasonic absorption and velocity were measured in aqueous solutions of propylamine at 25 °C both in the absence and in the presence of 2 g dm$^{-3}$ PVA(poly(vinyl alcohol)), 5 mol dm$^{-3}$ urea and 1 mol dm$^{-3}$ NaCl. No excess absorption was observed in these solutions without propylamine. A single relaxational absorption was observed in the concentration range from 0.0196 to 0.719 mol dm$^{-3}$ of propylamine both in the presence and absence of the additives. The ultrasonic parameters have been found to be quite dependent on the concentration of propylamine and also on the structure of additives. This relaxational absorption has been attributed to the perturbation of an equilibrium associated with a proton-transfer reaction. The rate constants and the standard volume change of the reaction have been determined from the concentration dependences of the relaxation frequency and the maximum excess absorption per wavelength. As a result, it was discovered that the forward rate in a solution with PVA increased and those with urea and NaCl, on the other hand, decreased; also, the standard volume change associated with the reaction increased in a series of the solutions with urea, no additive, NaCl, and PVA. The data have been interpreted by means of the structural changes of the solvent water.

Any mechanism by which protons get carried along particularly quickly has important implications for a large area of molecular biology. The proton-transfer reaction is directly followed by the ultrasonic absorption technique.[1] So far, investigations for the proton-transfer in aqueous solutions of various amines have been performed;[1,2] the present authors[3] have also reported some results of the rate constants with a revised analysis of the reaction mechanism. Recently, Yamashita et al.[4] have examined the effect of an additive on this reaction in the presence of the surfactant micelle; also, the decreasing effect on the proton-transfer rates has been reported. They have interpreted the effect as restricted reaction fields owing to the charged surface of the micelles. On the other hand, it is expected that the proton-transfer reaction in an aqueous solution of amine may be closely related to the water structure since the reaction is hydrolysis. From this view, the present study was undertaken in order to clarify this speculation by adding nonelectrolyte and electrolyte using ultrasonic methods. Propylamine was chosen as the solute since another type relaxation which is observed in the solutions of some amines with larger hydrophobic groups[5] was not expected to be observed. The phenomenon that the reaction rate is accelerated or decelerated by additives is also interesting from a pharmacological point of view.

## Experimental

All reagents, i.e. propylamine, urea, PVA(poly(vinyl alcohol)), and NaCl, were purchased from Wako Pure Chemical Industries Ltd. Propylamine was distilled once; however, the other reagents which were of the purest grade obtainable were used without further purification. Solutions were prepared by weight with doubly distilled water. The additive concentrations were fixed to be 2 g dm$^{-3}$, 1 mol dm$^{-3}$, and 5 mol dm$^{-3}$ for PVA (number-average molecular weight; 22000), NaCl and urea, respectively.

A semiautomatic pulse method was used for ultrasonic absorption measurements over a frequency range from 15 to 220 MHz. Two cells with fundamental crystals of 5 and 20 MHz were utilized at their odd harmonic frequencies. Details of the apparatus are described elsewhere.[6] The sound velocity was determined using an interferometer at 2.5 MHz. The ultrasonic cells were immersed in a water bath which was controlled within ±0.002 °C. The density of the solutions was measured by using a standard pycnometer, the volume of which was about 4 cm$^3$. The measurement of pH was performed using a HITACHI-HORIBA pH meter with a glass electrode. The standard buffer solutions at 9.18 and 11.88 were used as the standard references of the electrode. All pH and ultrasonic measurements were carried out under a dry nitrogen atmosphere because of the high basicity of the solution. They were all measured at 25 °C.

## Results

No excess absorption was observed in any aqueous solutions of urea, PVA, or NaCl at the concentrations used in this work. However, the value of the absorption coefficient, $\alpha$, divided by the square of the frequency, $f$, has been found to be frequency dependent in all of aqueous solutions of propylamine both in the presence and in the absence of the additives. If an observed spectrum is due to a single relaxational process, it may be generally well expressed by[7]

$$\alpha/f^2 = A/(1+(f/f_r)^2)+B, \tag{1}$$

where $A$ is the excess absorption amplitude, $f_r$ the relaxation frequency and $B$ the back ground absorption. Figure 1 shows some representative absorption spectra in an aqueous solution of propylamine. The ultrasonic parameters have been determined in terms of a nonlinear least mean square method by microcomputer, and the solid curves in the figure represent the theoretical values. The fact that the agreements between experimental and theoretical values are excellent indicates that the relaxation phenomenon observed in the measured frequency range can be associated with a clear single relaxation process.

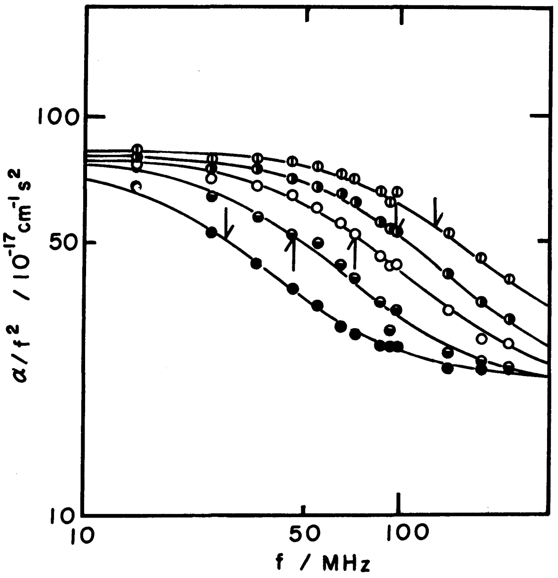

Fig. 1. The representative ultrasonic absorption spectra in aqueous solutions of propylamine at 25 °C. ●: 0.0196 mol dm$^{-3}$, ⊖: 0.0491 mol dm$^{-3}$, ○: 0.114 mol dm$^{-3}$, ◑: 0.236 mol dm$^{-3}$, ⦶: 0.631 mol dm$^{-3}$.

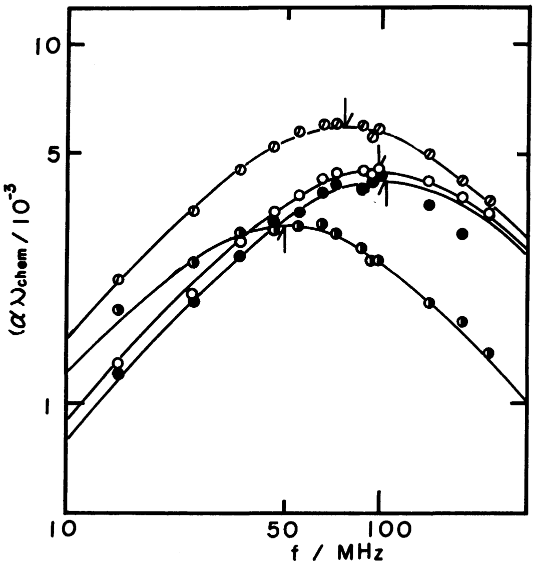

Fig. 2. The ultrasonic absorption spectra for aqueous solutions of propylamine at 0.236 mol dm$^{-3}$ in the absence and in the presence of additive. ○: No additive, ●: PVA, ⊘: NaCl, ◑: urea.

Table 1. Ultrasonic and Thermodynamic Parameters for Aqueous Solutions of Propylamine with Additives at 25 °C

| Concn | pH | $\rho$ | $c$ | $f_r$ | $A$ | $B$ |
|---|---|---|---|---|---|---|
| mol dm$^{-3}$ | | g cm$^{-3}$ | m s$^{-1}$ | MHz | $10^{-17}$ s$^2$ cm$^{-1}$ | |
| | | | (No additive) | | | |
| 0.0196 | 11.30 | 0.9970 | 1498 | 28 | 56 | 22 |
| 0.0491 | 11.90 | 0.9966 | 1500 | 46 | 60 | 21 |
| 0.114 | 11.83 | 0.9959 | 1503 | 72 | 60 | 21 |
| 0.236 | 12.05 | 0.9943 | 1513 | 97 | 61 | 21 |
| 0.476 | 12.26 | 0.9911 | 1526 | 120 | 62 | 23 |
| 0.631 | 12.38 | 0.9887 | 1536 | 130 | 60 | 24 |
| 0.719 | 12.41 | 0.9873 | 1539 | 134 | 58 | 26 |
| | | | (PVA) | | | |
| 0.0196 | 10.91 | 0.9970 | 1497 | 39 | 24 | 22 |
| 0.0491 | 11.34 | 0.9968 | 1499 | 58 | 38 | 22 |
| 0.114 | 11.47 | 0.9964 | 1504 | 76 | 52 | 21 |
| 0.236 | 11.65 | 0.9953 | 1510 | 103 | 54 | 21 |
| 0.476 | 11.87 | 0.9924 | 1525 | 132 | 57 | 22 |
| 0.631 | 11.95 | 0.9903 | 1533 | 143 | 59 | 22 |
| 0.719 | 11.98 | 0.9890 | 1541 | 146 | 56 | 24 |
| | | | (Urea) | | | |
| 0.0196 | 11.55 | 1.0740 | 1620 | 23 | 37 | 18 |
| 0.0491 | 11.90 | 1.0738 | 1620 | 27 | 66 | 18 |
| 0.114 | 12.20 | 1.0735 | 1621 | 38 | 68 | 17 |
| 0.236 | 12.38 | 1.7025 | 1626 | 49 | 79 | 18 |
| 0.479 | 12.59 | 1.0677 | 1637 | 61 | 82 | 19 |
| 0.631 | 12.72 | 1.0669 | 1643 | 65 | 80 | 20 |
| 0.719 | 12.86 | 1.0657 | 1645 | 68 | 80 | 20 |
| | | | (NaCl) | | | |
| 0.114 | 11.92 | 1.0366 | 1567 | 60 | 95 | 19 |
| 0.236 | 12.10 | 1.0357 | 1571 | 76 | 100 | 21 |
| 0.476 | 12.29 | 1.0318 | 1584 | 95 | 101 | 23 |
| 0.631 | 12.38 | 1.0306 | 1592 | 106 | 103 | 21 |
| 0.719 | 12.42 | 1.0301 | 1596 | 110 | 106 | 21 |

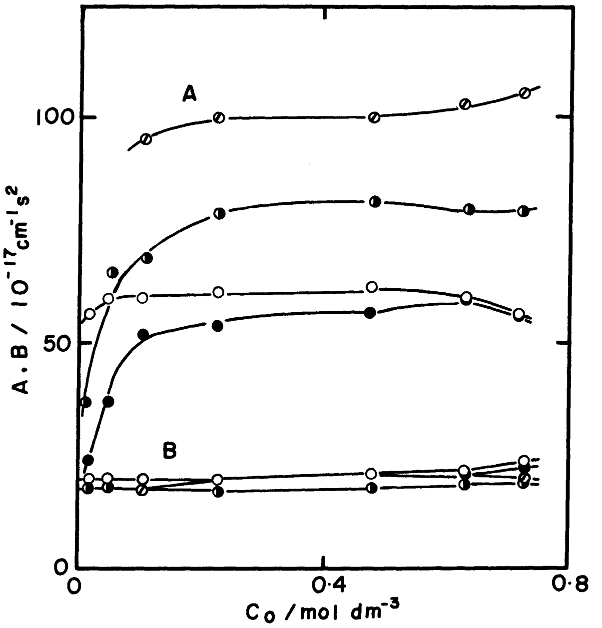

Fig. 3. Concentration dependence of the amplitude of the excess absorption, $A$, and the background absorption, $B$, for aqueous solutions of propylamine in the absence and in the presence of additives. ○: No additive, ●: PVA, ⊘: NaCl, ◑: urea.

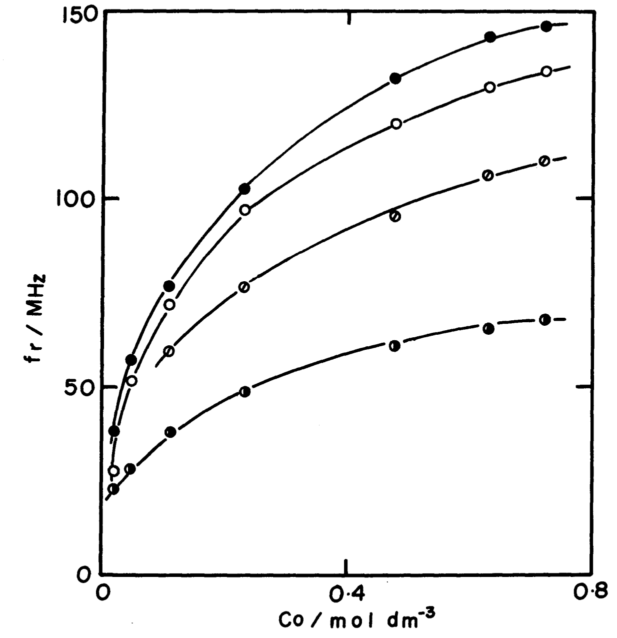

Fig. 4. Concentration dependence of the relaxation frequency for aqueous solutions of propylamine at 25 °C. ○: Without additive, ●: with PVA, ⊘: with NaCl, ◑: with urea.

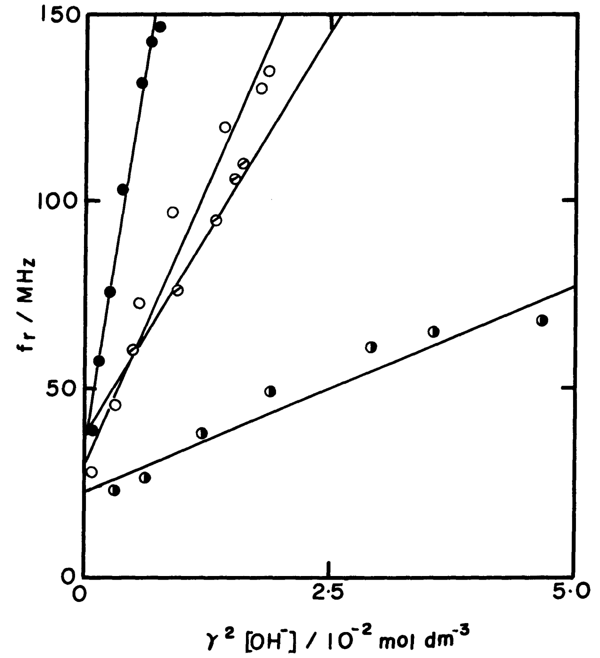

Fig. 5. The plots of $f_r$ vs. $\gamma^2[OH^-]$ for aqueous solutions of propylamine at 25 °C. ○: No additive, ●: PVA, ⊘: NaCl, ◑: urea.

Another relation, which is a modification of Eq. 1, is the plot of the chemical absorption per wavelength, $(\alpha\lambda)_{chem}$ against the frequency:

$$(\alpha\lambda)_{chem}=Afc/(1+(f/f_r)^2). \qquad (2)$$

Here, $(\alpha\lambda)_{chem}$ is calculated from the relation $(\alpha\lambda)_{chem}=(\alpha/f^2-B)fc$, where $c$ is the sound velocity. Figure 2 shows the spectra observed in the aqueous solutions in the absence and in the presence of additives at 0.236 mol dm$^{-3}$ of propylamine. The spectra can also be well expressed by a single relaxational equation. It can clearly be seen that the absorption amplitude and the relaxation frequency strongly depend on the additives. The obtained excess absorption amplitude, $A$, and the background absorption, $B$, are shown in Fig. 3 as a function of propylamine concentration. In Table 1, they are also tabulated along with other values obtained in this study. The background absorptions are close to those of solvent water, though they decrease slightly when NaCl and urea are added. On the other hand, the excess absorption amplitudes differ from each other, depending upon the additives. They increase at a low-concentration range and tend to show a plateau. These concentration dependences are very similar to the result for the ultrasonic absorption due to proton-transfer reaction reported previously.[3,5] Figure 4 shows the analytical concentration dependence of the relaxation frequency, $f_r$ for the solutions in the absence and the in presence of additives. Obviously, $f_r$ shifts to higher or lower values, and its degree depends upon the additives. These results imply that the additives affect the dynamic properties of the aqueous solutions. However, these similar concentration dependences of the ultrasonic parameters, that is, the plateau of the excess absorption amplitude and the monotonical increase of the relaxation frequency, have let us to predict that the cause of the relaxation in all of the solutions is the same and that it may be associated with the hydrolysis of amine. A detailed reaction mechanism has been proposed origi-

Table 2. The Rate and Thermodynamic Constants for the Hydrolysis of Propylamine in the Absence and in the Presence of Additives at 25 °C

| Additive | $k_{12}$ | $k_{21}$ | $K_b^1$ | $K_b^2$ | $\Delta V$ |
|---|---|---|---|---|---|
| | $10^{10}$ mol$^{-1}$ dm$^3$ s$^{-1}$ | $10^8$ s$^{-1}$ | $10^{-4}$ mol dm$^{-3}$ | | cm$^3$ mol$^{-3}$ |
| a) | 1.8±0.1 | 1.9±0.3 | 5.1±2.0 | 4.8±1.3 | 33±8 |
| PVA | 4.8±0.2 | 2.1±0.2 | 0.78±0.24 | 0.84±0.18 | 45±8 |
| Urea | 0.34±0.03 | 1.5±0.2 | 25±12 | 25±10 | 21±7 |
| NaCl | 1.4±0.1 | 2.5±0.1 | 4.0±0.7 | 5.3±0.6 | 27±3 |

$K_b^1$: The calculated values from Eq. 5. $K_b^2$: Those from the pH measurements. a) The obtained rate constants without additives are slightly different from those reported previously.[5] This is because the present study was undertaken in the wider concentration range of propylamine than the previous one.

nally by Eigen,[1] and is expressed by

$$\mathrm{R\text{-}NH_3^+ + OH^-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{R\text{-}NH_3^+ \cdots OH^-} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{R\text{-}NH_2 + H_2O}, \qquad (3)$$

where $k_{ij}$ is the rate constant at each step. Usually, the relation between the relaxation frequency and the reactant concentrations is derived on the bases of the coupled reactions;[8] that is, the faster process influences the slower one. However, as has been reported in a previous paper,[3] the analysis based on the assumption that the only first step is associated with the observed relaxation process gives us a reasonable result. This means that the second step in Eq. 3 may not so affects on the observed process even if the relaxation associated with the second step may exist in other time region. Then, the relation between the relaxation frequency and the reactant concentrations is simply represented by

$$\tau^{-1} = 2\pi f_r = \gamma^2 k_{12}([\mathrm{R\text{-}NH_3^+}] + [\mathrm{OH^-}]) + k_{21}, \qquad (4)$$

where $\tau$ is the relaxation time and $\gamma$ a mean activity coefficient which is calculated using Davies equation.[9] Figure 5 shows plots of $f_r$ vs. $\gamma^2[\mathrm{OH^-}]$. The linearity of these plots confirms that the cause of the relaxational sound absorption is due to the hydrolysis of propylamine. The rate constants, $k_{12}$ and $k_{21}$, were determined from the slope and intercept of the straight lines, respectively. The obtained results are listed in Table 2. These results enable us to determine the dissociation constant, $K_b$.[3] The relation between $K_b$ and the analytical concentration, $C_o$, is derived as

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

The calculated $K_b$ values for each solution are listed in Table 2.

The dissociation constants for these solutions have been estimated from the results of pH measurements using the relation $K_b = \gamma^2[\mathrm{OH^-}]/(C_o - \gamma[\mathrm{OH^-}])$, which are also listed in Table 2. The value for a solution without any additives is very close to that in the literature.[10] The smaller $K_b$ value in the solution with PVA indicates the smaller concentrations of the ionic species in Eq. 4. The larger value in the solution with urea, on the other hand, shows the opposite condition. It should be noticed that the relaxation frequency in the PVA solution is higher than that in the urea solution.

Another parameter obtained from ultrasonic absorption measurement along with the sound velocity is the maximum excess absorption per wavelength, $\mu_{max}$. It is related to the thermodynamic parameters as

$$\mu_{max} = A f_r c/2 = \pi \rho c^2 \Gamma \Delta V^2 / 2RT. \qquad (6)$$

where $\rho$ is the density, $\Delta V$ the standard volume change of the reaction, and $\Gamma$ the concentration term which is expressed for the reaction under consideration as

$$\Gamma = (1/[\mathrm{R\text{-}NH_3^+}] + 1/[\mathrm{OH^-}] + 1/[\mathrm{R\text{-}NH_3^+ \cdots OH^-}])^{-1} \qquad (7)$$

With the help of Eqs. 6 and 7, standard volume changes could be calculated at each concentration (listed in Table 2).

## Discussion

As has been described previously, it is certain that the cause of the relaxation process observed by the ultrasonic absorption measurement in the aqueous solutions of propylamine with some additives is due to the hydrolysis of the amine. The additives have been found to considerably affect the rate processes. The micellar effect on the hydrolysis seems to be associated with the restricted reaction field by micelles.[4] However, the present additive effects are not associated with such a microscopic heterogenious reaction field. They seem to be associated with structural changes of the solvent water.

First, the effect of PVA on the hydrolysis is considered. When PVA is added, the relaxation frequency shifts to a higher frequency range and the reactant concentration, i.e. $[\mathrm{OH^-}]$ decreases, even if the analytical concentration of propylamine is identical (Table 1). Therefore, as a result, the forward rate constant, $k_{12}$ has been found to increase considerably when PVA is added. This may be considered as follows. Adding a small amount of the polymer with the hydroxyl groups to the solution, the water structure may be changed by an extension of the hydrogen-bond network. Consequently, it can be expected that hydrogen or hydroxide ion mobility increases. It is said that the proton-transfer rate in a more hydrogen-bonded network is faster than that in less hydrogen-bonded types.[11] The above experimental evidence is consistent with the proton-transfer proposed reaction mechanism so far. The obtained standard volume change for the reaction also reflects the solvent structural change by an addition of PVA. That is, it is larger than that in only water (Table 2). The considerably large volume change may be caused by a breaking of the constructed water hydrogen-bonds by PVA.

Second, the additive effect of urea on the hydrolysis is now considered. Urea is a so-called water structure-breaker.[12] When it is added to water, it breaks the water hydrogen bonds; then, the sound velocity increases, the absorption decreases and the solution density increases. These trends are also observed in aqueous solutions of propylamine (Table 1). This means that the solvent water may be in a less structured state. Then, the diffusion-controlled reaction rate may decrease. This expectation has been supported by the concentration dependence of the relaxation frequency. That is, the relaxation frequency shifts to a lower range when it is compared wiht that in the absence of additive. The smaller volume change for the reaction has also reflected this situation. The reaction may proceed through breaking hydrogen bonds just around the reaction site.

Third, in a solution with NaCl, it has been observed that the relaxation frequency is lower than that without additives (Fig. 4). The recent investigation[13] for the proton-transfer reaction by a fluorimetry has shown that the effect of NaCl on the decreasing rate is due to the structure breaking for solvent water. This seems to be sonsistent with the result obtained in our study. However, it is not so reasonable to compare the rate constants with those obtained in the solutions with urea and PVA because they are at quite different ionic strengths each other. In order to obtain more information concerning the effect of electrolytes on the proton-transfer reaction, it should be necessary to clarify the concentration dependence of the salts on the rate.

In conclusion, the additive effects on the proton-transfer reaction have been well interpreted on the bases of the structural changes of solvent water. This is, when the water structure is promoted by the addition of PVA, the rate for the proton transfer is accelerated. On the other hand, when water hydrogen-bonds are partly broken by the addition of urea, the proton-transfer rate is diminished. It may be expected that the fast proton-transfer reactions are now utilized in order to investigate the structural properties of liquids and solutions. The concentration dependences of the additives on the hydrolysis of various amines are now under investigation and the results will be reported in due course.

This work was partly supported by The Naito Foundation.

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