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The Effect of Propyl Cellosolve on Water Structure Estimated from Ultrasonic Data

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Ultrasonic absorption and velocity have been measured in aqueous solution of Propyl Cellosolve (ethylene glycol monopropyl ether) in the frequency range of 7.5 to 220 MHz at 25 °C. A single relaxational process has been found and the mechanism has been attributed to the solute-solvent interaction, $AB \leftrightarrow A+B$. The rate constants obtained are $k_{12}=9.6\times10^{7}$ s^{-1} for the forward and $k_{21}=1.3\times10^{8}$ M^{-1} s^{-1} for the backward reaction. The effect of the solute on the water structure has been found to act slightly as the water structure promoter and the results have been discussed comparing with those of Butyl Cellosolve solution.

In the previous paper, we have been reporting ultrasonic properties of aqueous solutions of some alcohols.[1,2] The characteristic properties of the aqueous solutions are the observations of the Peak Sound Absorption and Peak Sound Velocity Concentrations. Depending upon the structure of the solute molecules, one or two relaxational absorptions have been found. One excess absorption which is due to the solute-solvent interaction is observed in most of the solutions of nonelectrolytes with a hydroxy group. The other excess absorption is only observed in the solutions in which the solute has a relatively large hydrophobic group, and the cause has been attributed to the perturbation of the equilibrium between the monomer and aggregate of the solute. In these respects, we have extended our dynamic studies of nonelectrolyte solutions by the ultrasonic method to ethers, one of which has been reported.[3] In this paper, we present the detail results of the ultrasonic properties in aqueous solution of Propyl Cellosolve. The result will be compared with that of Butyl Cellosolve solutions.

Experimental

Propyl Cellosolve (ethylene glycol monopropyl ether) was distilled once and the purity was more than 99.8%. Ultrasonic pulse method[4] was used to measure the absorption coefficient in the frequency range of 7.5 to 220 MHz. Sound velocity was measured at 2.5 MHz by a interferometer. A pycnometer of about 2.2 cm^3 was used to measure density of solutions. All the measurements were done at 25 °C.

Results and Discussion

The ultrasonic absorptions in aqueous solutions of Propyl Cellosolve are all characteristic of a single relaxation in the concentration range of 1.9 to 5.6 M in which the excess absorptions have been observed. The excess absorption, A, the background absorption, B, and the relaxation frequency, f_r, were determined so as to obtain the best fit of the experimental data to the single relaxational equation (Eq. 1), using a least mean square method by HITACHI Basic Master MB-6890 microcomputer.

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

where α is the absorption coefficient. Figure 1 shows the representative absorption spectra. In Table 1, these parameters are listed as a function of the concentration along with the values of the sound velocity and the density. The sound velocity goes through a maximum at the concentration of around 2.0 M, at which the excess absorption appears and increases up to 3.0 M. Subsequently, it decreases gradually.

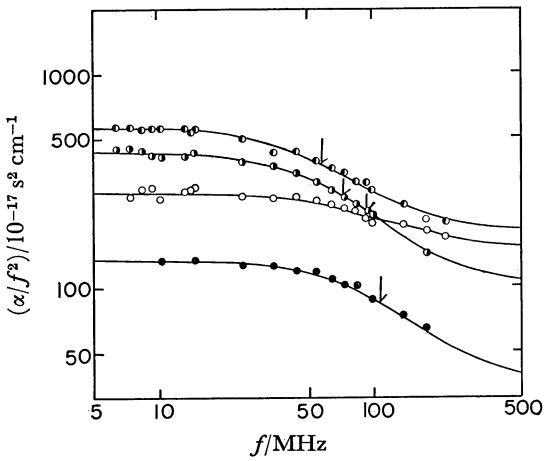

Fig. 1. Representative ultrasonic absorption spectra in aqueous solution of Propyl Cellosolve at 25 °C. The arrows show the positions of the relaxation frequencies. ●: 1.91 M, ◑: 2.69 M, ◐: 3.36 M, ○: 5.60 M.

TABLE 1. ULTRASONIC PARAMETERS FOR AQUEOUS SOLUTION OF PROPYL CELLOSOLVE AT 25 °C

C_a	f_r	A	B	ρ	c
M[a]	MHz	10^{-17} s^2 cm^{-2}		g cm^{-3}	m s^{-1}
1.91	108	99.4	34.8	0.9929	1610
2.39	55.5	249	117	0.9920	1605
2.69	73.0	333	101	0.9908	1586
2.96	79.0	416	93.2	0.9891	1560
3.00	70.0	408	145	0.9886	1558
3.36	58.9	381	184	0.9858	1540
3.99	67.0	320	187	0.9803	1517
5.60	93.0	129	151	0.9627	1466

a) 1 M=1 mol dm^{-3}.

In order to interpret the excess absorption mechanism, we use the model which has been proposed for aqueous solutions of alcohols because the ultrasonic properties are very similar to those of alcohol solutions.[1,2] It is assumed that liquid water consists of two different states, that is, the hydrogen bonded and the nonhydrogen bonded water. Only the latter molecules may associate with the interaction with Propyl

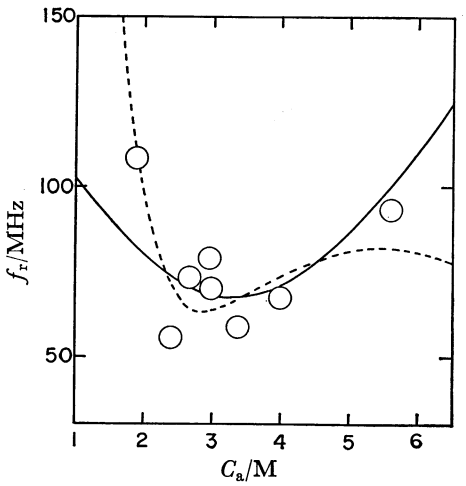

Fig. 2. Concentration dependence of the relaxation frequency for aqueous solution of Propyl Cellosolve. Solid line was calculated for the mechanism AB⟵⟶A+B, and dashed one was for AB_2⟵⟶A+2B mechanism.

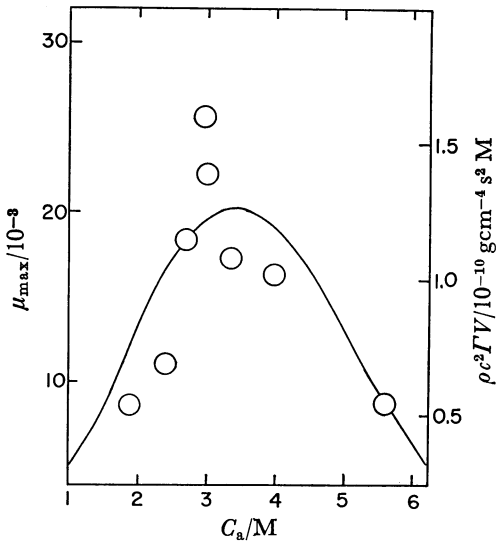

Fig. 3. The plots of μ_{max} and $\rho c^2\Gamma V$ as a function of Propyl Cellosolve concentration.

Cellosolve molecules.

$$\underset{C_1}{AB_m} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} \underset{C_2}{A} + \underset{C_3}{mB}, \qquad (2)$$

where A is the solute, B the monomer of liquid water, AB_m the complex and C_i the equilibrium concentration of each component. It has been shown in the previous studies[1-3] that the 1:1 complex is the most reliable. The relation between relaxation frequency and the concentration for the above reaction is given by the next equation.

$$2\pi f_r = k_{21}[(C_a-\beta C_w+K_{12})^2 + 4\beta C_w K_{12}]^{1/2}, \qquad (3)$$

where β is the mole fraction of the water monomer, C_a the analytical concentration of Propyl Cellosolve, C_w that of water and $K_{12}=k_{12}/k_{21}$. The rate constant, k_{21}, was determined so as to minimize the error defined by $r=0.675[\Sigma(p_i-\overline{k_{21}})^2/7]^{1/2}$ where $p_i=2\pi f_{ri}/[(C_{ai}-\beta C_{wi}+K_{12})^2+4\beta C_{wi}\overline{K_{12}}]^{1/2}$, and $\overline{k}_{21}$ is the most probable value of k_{21}, assuming the appropriate β value (the relation[1] between β and K_{12} is derived from the condition that the relaxation frequency goes through a minimum at 3.5 M). Figure 2 shows the plots of the experimental relaxation frequencies, f_r, and the calculated values (solid line). We have also tested the case of $m=2$, that is, the case in which two water molecules interact with a Propyl Cellosolve molecule. The relaxation frequency for this mechanism is expressed as

$$2\pi f_r = k_{21}(4C_2C_3+C_3^2) + k_{12}. \qquad (4)$$

Assuming appropriate values of β and K_{12} because no simple relation between β and K_{12} is held, contrary to that for 1:1 complex formation, each equilibrium concentration was calculated with the relations of $C_a=C_1+C_2$, $\beta C_w=2C_1+C_3$, and $K_{12}=C_2C_3^2/C_1$ and the ratio, k_{12}/k_{21} was determined from the slope and intercept of the plots of $2\pi f_r$ *vs.* $(4C_2C_3+C_3^2)$ so as to get the same value as that of assumed K_{12} and so as that the excess absorption went through a maximum. In the range of $\beta=0.13$ to 0.17, it may be possible to obtain the parameters of β and K_{12} which seem to satisfy the above conditions. One of the results is shown in Fig. 2 by a dashed line which has been determined when $\beta=0.150$ and $K=0.715$. However, the errors of the rate constants are too large ($k_{12}=(5.7\pm1.3)\times10^7$ s^{-1} and $k_{21}=(4.2\pm10.2)\times10^7$ M^{-2} s^{-1}), and the concentration dependence of the calculated relaxation frequency exhibits a minimum and a maximum as is seen in Fig. 2. The mechanism due to the interaction between plural water molecules and one solute may not be considered as the cause of the observed excess absoprtion from the following reasons. First, even if the calculated curve for the case of $m=2$ in Fig. 2 seems to fit to the experimental relaxation frequency, reasonable rate constants were not obtained. Propyl Cellosolve may not be special or exceptional in the ultrasonic properties compared with various alcohols and ethers reported so far because the relaxation frequencies in other solute solutions only go through a minimum.[1,2,3,5] Second is the fact that the observed absorption data is fairly well expressed by a single relaxational equation, and it seems to be unplausible that many water molecules bind the solute at a fixed characteristic time.

Another parameter determined from the ultrasonic absorption measurement is the maximum excess absorption per wave length, μ_{max} which is related to the volume and enthalpy change of the reaction. It is a good approximation that μ_{max} is proportional to $\rho c^2\Gamma V$, where ρ is the density, c the sound velocity and $\Gamma=(1/C_1+1/C_2+1/C_3-1/C_T)^{-1}(1/V)$.[3] The comparison between the μ_{max} and $\rho c^2\Gamma V$ may be used to make sure if the cause of the absorption is due to the perturbation of the equilibrium expressed by Eq. 2. The solid curve in Fig. 3 represents the calculated $\rho c^2\Gamma V$ and the circles are the experimental values of the μ_{max}. These plots confirms that the excess absorption mechanism is associated with the solute-solvent interaction. In Table 2, the rate and thermodynamic constants obtained in this study are given

Table 2. Rate and thermodynamic constants determined from ultrasonic data

	k_{12} / 10^7 M^{-1} s^{-1}	k_{21} / 10^8 s^{-1}	β	Reference
Pure water			0.26	6
Propyl Cellosolve	9.6±1.3	1.3±0.2	0.10	This work
Butyl Cellosolve	4.2±0.7	1.7±0.3	0.029	3

along with those of Butyl Cellosolve[3] and pure water.[6]

The mole fraction of water monomer in the aqueous solution of Propyl Cellosolve is smaller than that in pure water, but is larger than that in Butyl Cellosolve solution. This means that Propyl Cellosolve acts as the structure promoter for liquid water. However, the effect is not so large, comparing with that of Butyl Cellosolve. This may be because of the smaller hydrophobic group of Propyl Cellosolve than that of Butyl Cellosolve. Though the excess absorption due to the aggregation reaction is observed in the Butyl Cellosolve solution, it is not found in the Propyl Cellosolve solution. Propyl Cellosolve molecule may not have enough hydrophobicity to form the aggregate in aqueous media. Aggregation by hydrogen bonding may be possible, but the rate for this process seems to be beyond our time scale.[7]

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