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The Temperature Dependence of the Ultrasonic Relaxation Process Due to Interaction between Water and Allyl Cellosolve

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Ultrasonic absorption and velocity measurements have been performed in aqueous solutions of Allyl Cellosolve (ethylene glycol monoallyl ether) as functions of the concentration and the temperature. Only a single relaxational absorption has been observed in the frequency range from 15 to 220 MHz and, it has been attributed to the perturbation of the equilibrium expressed as $AB \rightleftarrows A+B$, where A and B are the solute and the solvent molecule respectively. The rate constants at various temperatures have been determined from the concentration dependence of the relaxation frequency, and the thermodynamic parameters associated with the reaction have been calculated. The enthalpy change has also been estimated from the concentration dependence of the maximum excess absorption per wavelength. From these results, it has been concluded that Allyl Cellosolve molecules act as water structure promoters and that the interaction between the solute and the solvent is due to hydrogen bonding. Furthermore, the rate and the thermodynamic properties obtained are compared with those for aqueous solutions of other ethers.

It has been recognized that the interaction between water and biological compounds play important roles in living systems. However, the dynamical properties of the interactions have not been well interpreted because the rates are too fast and the complex reactions proceed at the same time. The ultrasonic absorption method has been used to investigate the dynamical properties in solutions. The present authors have also reported some ultrasonic results for aqueous solutions of alcohols and ethers.[1-5] In these solutions, we have found that the excess absorption associated with the interaction between the solute and the solvent is observed in the MHz frequency range, and have predicted from the concentration dependence of the absorption that the interaction may be due to hydrogen bonding. In order to confirm the origin of the interaction, an investigation of the temperature dependence of the absorption is required; it may provide useful information about the rate and the thermodynamic properties. For this purpose, Allyl Cellosolve (ethylene glycol monoallyl ether) has been chosen as a solute; in this report the results are compared with those of other ethers.

This kind of fundamental informations seems to be very important for the understanding of more complex interactions.

Experimental

The Allyl Cellosolve was purchased from the Tokyo Kasei Co., Ltd. and was distilled once under reduced pressure. The purity was confirmed to be more than 99.8% by means of the gas-chromatographic method. The sample solutions were prepared using doubly distilled water by weighing.

The ultrasonic absorption coefficients, α, were measured by a pulse method. The 5 MHz x-cut crystal was used in the frequency range from 15 to 95 MHz and the 20 MHz crystal, in the range from 60 to 220 MHz. An ultrasonic interferometer was used to measure the sound velocity, c, at 2.5 MHz. All the measurement cells were immersed in a water bath which was maintained within ±0.005 °C. The measurements were carried out at 20, 25, and 30 °C.

Results and Discussion

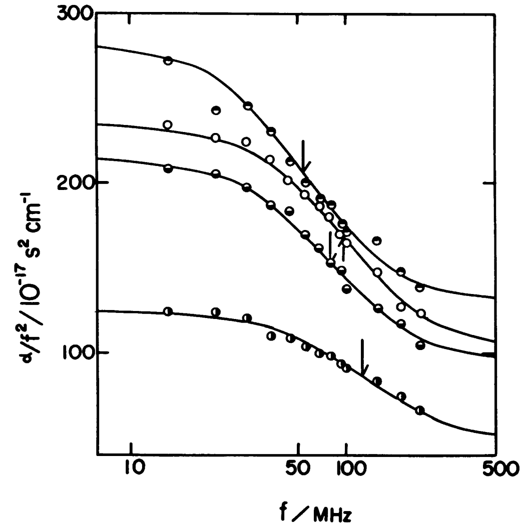

Fig. 1. Ultrasonic absorption spectra in aqueous solution of Allyl Cellosolve at 25 °C. Arrows show the positions of the relaxation frequency. ◑; 3.01 M, ◒; 3.50 M, ◓; 4.00 M, and ○; 4.50 M.

Figure 1 shows an illustrative example of the ultrasonic absorption spectra for aqueous solutions of Allyl Cellosolve at 25 °C. They are all characteristic of a single relaxation process and are well described by the following equation.

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

where f is the frequency; f_r the relaxation frequency, and A and B, constants. These ultrasonic parameters, f_r, A, and B, were determined so as to obtain the best fit of the experimental data to Eq. 1, using a nonlinear least-meansquare method.[3] They are listed in Table 1 as a function of the analytical concentration of Allyl Cellosolve, C_e. The sound velocity shows a maximum at 2.5 M, $1\ M = 1\ mol\ dm^{-3}$, above which the excess absorption appears. The value of A which is the relaxation amplitude also shows a maximum at around 4.0 M though it is dependent on the temperature. These concentration dependences of ultrasonic properties are characteristic of aqueous solutions of nonelectrolytes, and we predict that the same mechanism as that proposed previously[1-5] is associated with the excess absorption in the aqueous solution of Allyl Cellosolve.

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

C_e / M[a]	f_r / MHz	A	B	$r.m.s.$[b]	c / m s^{-1}	ρ / g cm^{-3}
		10^{-17} s^2 cm^{-1}				
3.01	118	75.3	49.3	2.75	1606	1.000
3.10	118	76.5	60.6	4.85	1603	1.000
3.27	89.8	120	95.9	4.41	1594	0.9999
3.50	84.6	119	94.7	3.19	1593	0.9987
3.75	65.0	140	116	4.51	1584	0.9979
4.00	63.5	150	131	4.60	1576	0.9960
4.23	88.9	140	116	3.55	1566	0.9950
4.51	96.7	130	103	2.78	1564	0.9942
4.77	102	115	105	3.25	1557	0.9937

a) 1 M=1 mol dm^{-3}. b) *r.m.s.* is defined as $\sum[[(\alpha/f^2)_{\mathrm{calcd}\,i}-(\alpha/f^2)_{\mathrm{exptl}\,i}]^2/N]^{1/2}$; the details of the procedure of the analysis are described in Ref. 3.

The model is as follosw:

$$\underset{C_1}{\mathrm{AB}} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{C_2}{\mathrm{A}} + \underset{C_3}{\mathrm{B}}, \tag{2}$$

where AB stands for the complex; A, the Allyl Cellosolve and B, the water which has ability of hydrogen-bonding. The C_i's indicate the equilibrium concentrations of the individual components. It is assumed that the liquid water consists of two states, that is, the hydrogen-bonded water and the nonhydrogen-bonded water, and that the rates between these states are too fast to be observed in our frequency range. Only nonhydrogen-bonded water may participate in the reaction considered here. The relation between the relaxation frequency and the concentrations is derived as follows:

$$2\pi f_r = k_b[(C_e-\beta C_w+K)^2+4\beta C_w K]^{1/2}, \tag{3}$$

where β is the mole fraction of the nonhydrogen-bonded water and C_w the analytical concentration of water, and where K is defined as $K=k_f/k_b$. The parameters, k_b, β, and K in Eq. 3 could be determined so as to get a reasonable curve which satisfied the experimental data to the relaxation frequency. The detail of the method for the determination have been shown elsewhere.[4] Similar experiments and calculations were performed at 20 and 30 °C. Figure 2 shows the concentration dependence of the relaxation frequency at various temperatures. The solid lines were calculated using the obtained parameters. The minimum position of the relaxation frequency shifts to a higher concentration with an increase in the temperature. This means that the fraction of the nonhydrogen-bonded water increases with the temperature. This is also clear from the temperature dependence of the β value. The obtained rate and the thermodynamic constants are listed in Table 2.

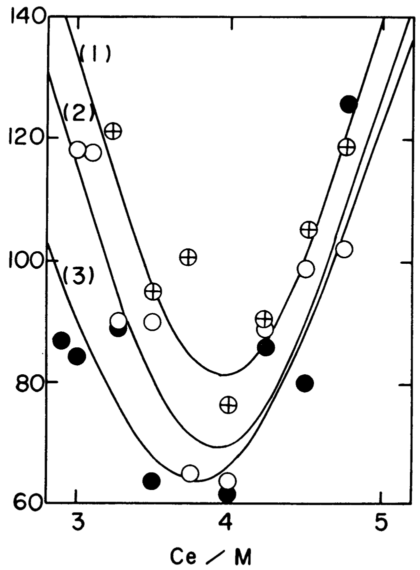

Fig. 2. Concentration dependence of the relaxation frequencies at various temperature. ⊕; 30 °C, ○; 25 °C, and ●; 20 °C.

TABLE 2. RATE AND THERMODYNAMIC CONSTANTS FOR INTERACTION BETWEEN WATER AND ALLYL CELLOSOLVE

T / °C	β	$10^{-}k_b$ / M^{-1} s^{-1}	10^2K / M
20	0.113±0.002	3.3±0.3	8.9±0.8
25	0.121±0.001	3.7±0.2	9.0±0.7
30	0.123±0.002	4.0±0.2	10.0±0.6

Now, it is possible to estimate the activation enthalpy for the backward reaction, $\Delta H^{\ddagger}_{b}$, from the plots of $\ln(k_b)$ *vs.* $1/T$, and the enthalpy change of the reaction, ΔH, from those of $\ln(K)$ *vs.* $1/T$. Using the most probable values of the rate and equilibrium constants, they are calculated to be $\Delta H^{\ddagger}_{b}=14\pm3$ kJ mol^{-1} and $\Delta H=8\pm2$ kJ mol^{-1}. The forward rate constants in Table 3 are obtained from the relation of $K=k_f/k_b$. The forward activation enthalpy, $\Delta H^{\ddagger}_{f}$ is found to be 22 ± 4 kJ mol^{-1} from the relation of $\Delta H=\Delta H^{\ddagger}_{f}-\Delta H^{\ddagger}_{b}$. The entropy change of the reaction, ΔS, is also estimated to be approximately 13 J mol^{-1} deg^{-1} from $\Delta G=\Delta H-T\Delta S$, where ΔG is defined as $-\Delta G=RT\ln(K)$.

Another parameter which is obtained from the ultrasonic experiments is the maximum excess absorption per wave length, $\mu_{\max}$, which is expressed by this equation:

$$\mu_{\max} = Af_r c/2 = (\pi c^2\rho\Gamma/2RT)(\Delta V-\Delta H\alpha_p/\rho C_p)^2, \tag{4}$$

where ρ is the solution density; ΔV, the volume change of the reaction; C_p, the specific heat, and α_p the thermal expansion coefficient. The term Γ is derived as $\Gamma=[1/C_1+1/C_2+1/C_3-1/(C_1+C_2+C_3)]^{-1}$ for the reaction considered here.[1] In order to determine accurately the enthalpy and volume changes of the reaction from Eq. 4, the values of α_p and C_p as the each concentration are necessary. Many thermodynamic parameters, including α_p and C_p in aqueous solutions of nonelectrolytes may show anomalous characters at around or less than the concentration where the sound velocity exhibits the maximum. The concentration range where the sound excess absorption appears is more than that concentration and so we may expect that these thermodynamic parameters change gradually with the concentration. Therefore, it is assumed that the α_p and C_p for the Allyl Cellosolve solution are expressed as linear functions of the mole fraction of the solute, n, in our

TABLE 3. COMPARISON OF THE RATE AND THERMODYNAMIC CONSTANTS FOR THREE ETHERS AT 25 °C

Solute	β	$\frac{10^{-7}k_f}{\mathrm{s}^{-1}}$	$\frac{10^2K}{\mathrm{M}}$	Reference
Allyl Cellosolve	0.121	3.0	9.0	This work
Propyl Cellosolve	0.100	9.6	74	4
Butyl Cellosolve	0.029	4.2	25	3

limited concentration range. The values of a_p and C_p for Propyl Cellosolve are used for the estimation because the data for Allyl Cellosolve are unfortunately not available. They are $C_{p,\mathrm{soln}}=1.7n+4.2(1-n)$ [J g^{-1}] and $a_{p,\mathrm{soln}}=1.1\times10^{-3}n+2.6\times10^{-4}(1-n)$ [deg^{-1}]. The obtained enthalpy and volume change are $\Delta H=8\pm4$ kJ mol^{-1} and $\Delta V=0.6\pm0.4$ cm^3 mol^{-1}. It should be noticed that a serious error may be contained in both the determinations of the enthalpy change of the reaction; these two values seem to be almost the same in the experimental error also because of the uncorrect values of the thermal expansion coefficient and the specific heat for Allyl Cellosolve. The obtained enthalpy change is still quite small; this might be because the reaction sites are surrounded by extremely polar water molecules.[6)]

From these results in the present study, the following conclusions are derived. First, there are some aspects estimating the effects of solutes on the water structure.[7–10)] The β parameter is also useful for the estimation because it is the fraction of nonhydrogen-bonded water molecule. As may be seen in Table 3, Allyl Cellosolve acts as a water structure promoter when the β value is compared with that in pure water.[10)] However, its activity is not so much as that of the ether with a larger hydrophobic group. This dependence of the β parameter on the solute structure may reflect the effect of the hydrophobic group of the solute molecules or the hydrophobicity. With increasing the hydrophobicity, the fraction of the nonhydrogen-bonded water decreases.

Second, there might be various interactions between the solute and the solvent. The hydrogen bonding of water with the allyloxy group might also be possible. However, a similar concentration dependence of the ultrasonic absorption has been observed in alcohol solutions,[1,2,11)] and even if such interaction exists, the time range may be different from ours. It might be considered in quite low frequency range because the water molecules around the alkyl group may be tightly bound by themselves.

Finally, other reaction mechanisms, for example, the association reactions between ethers by hydrogen-bonding, are possible causes of the excess absorption. However, the concentration dependence of the relaxation frequency can not be interpreted in terms of such reaction mechanisms. The background absorption, B, is still high than those expected from the classical aboorptions. Other relaxational absorptions may also exist in the higher frequency range. Therefore, we may confirm that the excess absorption solution is due to the interaction between water and the hydroxyl group of the ether.

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