Effect of Ether Oxygen in Isomeric Alcohols on Water Structure Estimated from Ultrasonic Absorption and Velocity Data

Sadakatsu NISHIKAWA,* Kenichi MATSUMURA, and Masayuki UEDA
Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840
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4-Methoxy-1-butanol was synthesized form 1,4-butanediol through potassium 4-hydroxy-1-butoxide. The ultrasonic absorption coefficients in the frequency range from 9.5 to 220 MHz and the sound velocity at 2.5 and 1.92 MHz were measured in aqueous solutions as a function of the concentration. A single relaxational absorption was observed, the cause of which was attributed to the perturbation of an equlibrium associated with a solute–solvent interaction. The rate and thermodynamic parameters associated with the interacion were determined from the concentration dependence of the relaxation frequency. The results were compared with those for other isomeric alcohol solutions, and the effect of the alcohols on the water structure was considered in relation to the molecular structures of the solutes. It has been found that the position of the ether oxygen in the alcohol molecules gives rise to a considerable change in the solution properties.

In our series of ultrasonic experiments in aqueous solutions of alcohols,[1—4] investigations were carried out in order to obtain information concerning quantitative relations between the solute structures and the effects of alcohols on the water structure from absorption and velocity data. Actually, quite different characteristics of the sound absorption and velocity were observed when the hydrophobicities of the alcohols were clearly different.[5—7] It is well known that sound absorption in aqueous solutions of alcohols shows a maximum at a certain concentration (Peak Sound Absorption Concentration).[8] It is dependent on the frequency and the alcohol structure. Some theoretical treatments have been proposed to analyze the frequency dependence as well as the concentration dependence of the absorption. One is based on a fluctuation model in solutions and it has been applied to a system in which a large absorption is observed and the spectra are not described by a single relaxational equation[9] or to that in which the relaxational absorption is not observed.[10] Another is a treatment as one of the chemical relaxation methods.[11—13] When the hydrophobicity of alcohol is not very high, the observed absorption coefficient as a function of the frequency is well described by a single Debye-type relaxational equation.[1—3,11,14] The experimental condition for our aqueous solutions of alcohols is far from the critical points. Also, it has been shown that the obtained ultrasonic relaxation parameters can be interpreted in terms of a chemical reaction taking place in the solutions.[1—4]

A slight difference in the chemical structure of alcohol may give rise to the different absorption characteristics in an aqueous solution. In order to understand the effect of alcohol on the water structure, it seems to be necessary to find any differences in the ultrasonic characteristics in the solutions, the solutes of which comprise similar chemical formulas, e.g. those of isomers. The isomeric effect on the sound velocity has been studied by Murthy et al.[15] for butanol solutions. However, because of the limited solubility in water, any experimental study is restricted to be within a relatively low concentration range.

Under these situations, we previously reported the ultrasonic absorption results for aqueous solutions of some isomeric alcohols,[1] and found that the ultrasonic absorption characteristics depend on the solute structures. Based on this information, the effect of the position of ether oxygen in alcohol molecules on the solution properties is considered to provide significant contributions to aqueous solutions of alcohols. 4-Methoxy-1-butanol is another isomer with five carbons and one ether oxygen; this alcohol seems to be appropriate for determining the effect of the ether oxygen when the ultrasonic characteristics are compared with those for solutions of 3-ethoxy-1-propanol[2] and 2-propoxyethanol.[3] In this paper, the ultrasonic absorption and velocity data for aqueous solutions of various isomeric alcohols are compared and the effect of the structural differences of alcohols on the water structure is considered.

Experimental

4-Methoxy-1-butanol was synthesized from 1,4-butanediol through potassium 4-hydroxy-1-butoxide using potassium carbonate and methyl iodide purchased from Wako Chemicals Ltd. Purifucation of the synthesized alcohol was carried out several times by distillation. The alcohol, boiling point of which was 165°C, was identified by ^{1}H NMR; the purity was confirmed by a gaschromatographic method to be greater than 99.8%. The sample aqueous solutions were prepared by weighing using doubly distilled water. The aqueous solution was warmed, and phase separation could not be found up to 70°C.

Ultrasonic absorption coefficients were obtained by a pulse method over the frequency range from 9.5 to 220 MHz. Details concerning the measurement are described elsewhere.[4] The sound velocity was measured using an interferometer at 2.5 MHz (with an accuracy within ±50 cm s^{-1}) and a sing-around meter at 1.92 MHz, which provided a relative error of less than ±5 cm s^{-1}. Density measurements were carried out using a conventional Ostwald pycnometer the volume of which was around 4.5 cm^3, and Shibayama

density meter. The sing-around meter and density meter were connected to a 16-bit microcomputer; values of both the sound velocity and the density were obtained concurrently. All of the measurement cells were immersed in a water bath which was controlled to within ±0.002°C. The measured temperature was at 25°C.

Results and Discussion

The adiabatic compressibility, κ_s, of solutions is related to the sound velocity and the density through the Laplace equation, as

$$\kappa_s = (\rho c^2)^{-1}, \quad (1)$$

where ρ is the solution density and c the sound velocity. Figure 1 shows the concentration dependence of the compressibility for aqueous solutions of five isomeric alcohols. Clear differences are observed in these solutions, even if the solutes are all isomers.

We next present the results of ultrasonic absorption data in an aqueous solution of 4-methoxy-1-butanol. The representative spectra are shown in Fig. 2. All of the absorption coefficients, α as a function of the measured frequency, f, are well satisfied with a Debye-type single relaxational equation, expressed as

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

where f_r is the relaxation frequency, and A the relaxational part of the absorption and B the part of the residual absorption that includes classical absorptions. The detail procedure for determining the ultrasonic parameters is described elsewhere.[4] The obtained parameters are listed in Table 1 along with the solution density and sound velocity data. The characteristic trends of the relaxational absorption as a function of the alcohol concentration are that the relaxation frequency goes through a minimum and that constant A tends to show a maximum. Such dependencies are also observed in many aqueous solutions of alcohols.[1,2,7,10] Figure 3 shows the concentration dependence of the relaxation frequency. As has been reported so far,[1—3,14] the most plausible cause of the observed relaxational mechanism is a perturbation of the equilibrium associated with the solute–solvent interaction, represented by

$$AB \underset{k_b}{\overset{k_f}{\rightleftharpoons}} A + B, \quad (3)$$

where A is the solute molecule, B the solvent molecule with hydrogen-bonding abilities, AB the complex and k_f and k_b are the forward and backward rate constants, respectively. Solvent water is assumed to exist in two states (hydrogen-bonded water and nonhydrogen-bonded water) ; it is also assumed that the rates of the transition between them are too fast.[16] The relation between the relaxation frequency and the analytical concentrations of the solute and the solvent is derived as[17]

$$2\pi f_r = k_b\{(C_e - \beta C_w + K_{12})^2 + 4\beta C_w K_{12}\}^{1/2}, \quad (4)$$

where K_{12} is defined as $K_{12}=k_f/k_b$, C_e and C_w are the analytical concentrations of the solute and solvent, respectively, and β the fraction of water having a less structured molecule. This parameter may also be expressed as the fraction of water which has the ability to interact with alcohol. The rate and thermodynamic

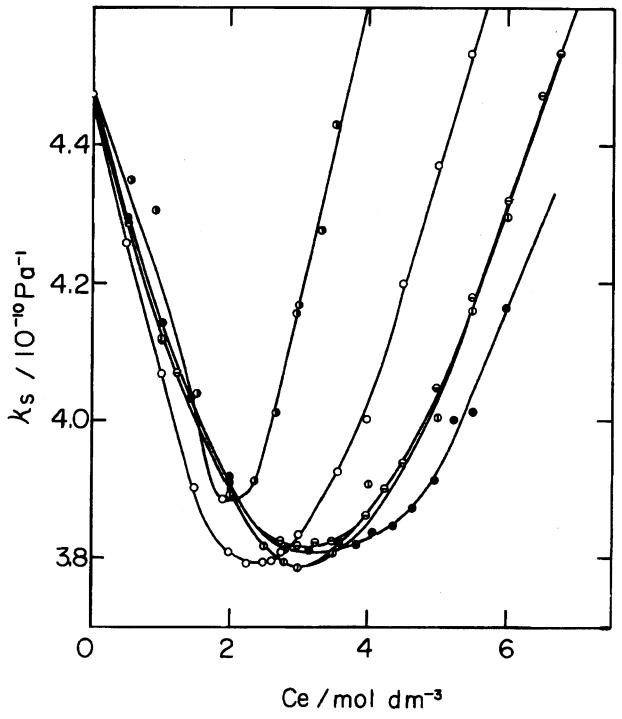

Fig. 1. Concentration dependence of the adiabatic compressibility for five isomeric alcohol solutions at 25°C. ○ : 1-methoxy-2-butanol, ⊖ : 3-methoxy-1-butanol, ⊙ : 3-ethoxy-1-propanol, ● : 4-methoxy-1-butanol, ◑ : 2-propoxyethanol.

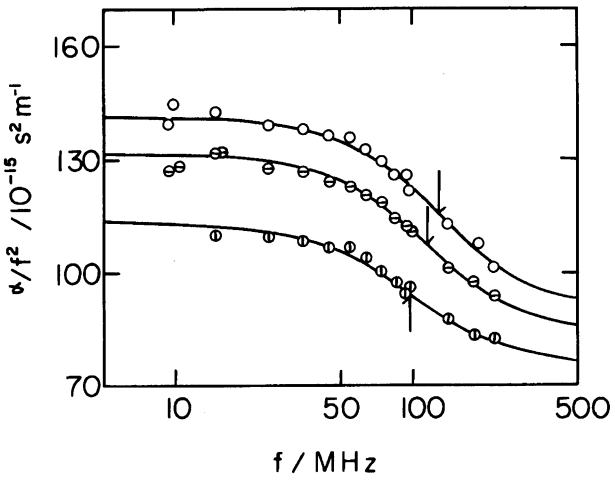

Fig. 2. Representative ultrasonic absorption spectra in an aqueous solution of 4-methoxy-1-butanol at 25°C. The arrows indicate the position of the relaxation frequency. ⊙ : 4.37 mol dm^{-3}, ⊖ : 4.97 mol dm^{-3}, ○ : 5.52 mol dm^{-3}.

Table 1. Ultrasonic Parameters for an Aqueous Solution of 4-Methoxy-1-butanol at 25°C

Concn	f_r	A	B	c	ρ
mol dm^{-3}	MHz	10^{-15}s^2 m^{-1}		m s^{-1}	kg dm^{-3}
0.202	—	—	—	1509.9	0.9966
0.505	—	—	—	1529.0	0.9956
1.01	—	—	—	1558.4	0.9944
1.44	—	—	—	1580.2	0.9931
2.00	—	—	—	1603.9	0.9917
2.79	140.1±15.1	12.9±0.5	42.8±0.7	1627.5	0.9895
3.17	123.8±9.6	18.1±0.5	49.0±0.6	1629.7	0.9882
3.60	104.2±7.4	25.7±0.8	60.1±0.6	1628.3	0.9864
3.85	116.7±4.8	27.7±0.4	62.0±0.5	1630.3	0.9851
4.09	103.7±8.9	35.3±1.3	70.3±1.0	1627.0	0.9846
4.37	98.1±4.7	37.5±0.8	75.6±0.6	1626.8	0.9827
4.65	118.9±6.2	45.7±0.8	77.2±1.0	1622.2	0.9816
4.97	113.8±4.2	48.2±0.7	83.5±0.7	1615.5	0.9790
5.24	120.8±7.9	48.7±1.1	92.1±1.4	1599.8	0.9758
5.52	131.7±7.1	52.4±1.0	88.9±1.4	1598.2	0.9756
6.00	131.6±6.8	52.0±0.9	93.8±1.3	1573.8	0.9694
8.00	—	—	—	1457.8	0.9431

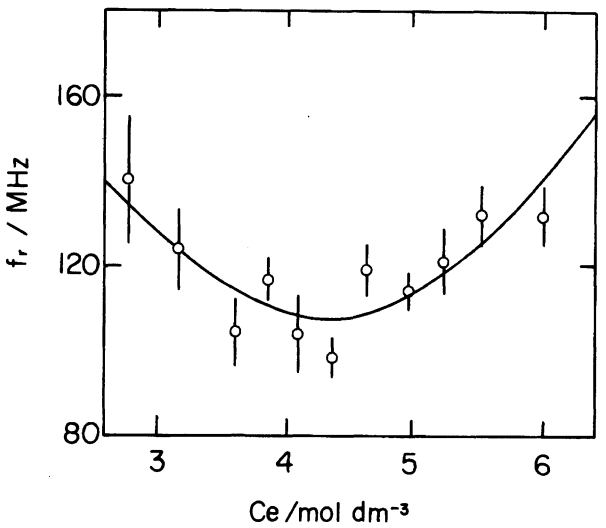

Fig. 3. Concentration dependence of the relaxation frequency for an aqueous solution of 4-methoxy-1-butanol.

constants were determined so as to obtain the best fit of the experimental relaxation frequency to Eq. 4 using a nonlinear least-mean squares method. The solid curve in Fig. 3 was drawn by using the determined k_b, K_{12}, and β values; it can be seen that the experimental values are well fitted to the calculated curve. A further confirmation of the cause of the ultrasonic relaxation may be performed by analyzing the concentration dependence of the maximum absorption per wave-length, μ_{max}, which was calculated from the absorption and velocity data as $\mu_{max}=0.5Af_rc$.[18]

$$\mu_{max} = \pi\rho c^2\Gamma(\Delta V - \alpha_p\Delta H/\rho C_p)^2/2RT, \quad (5)$$

where ΔV is the volume change of the reaction, ΔH the enthalpy change of the reaction, α_p the thermal expansion coefficient, C_p the heat capacity at constant pressure and Γ the concentration term expressed as $\Gamma=\{1/[A]+1/[B]+1/[AB]-1/([A]+[B]+[AB])\}^{-1}$ for the reaction under consideration. However, the dependence can not be very precisely analyzed because of a lack of the experimental data concerning the thermal expansion coefficient and the heat capacity for the aqueous solution. Therefore, a comparison between the μ_{max} and $\rho c^2\Gamma$ was carried out (in Fig. 4). The positions of both peaks are considerably different. This may

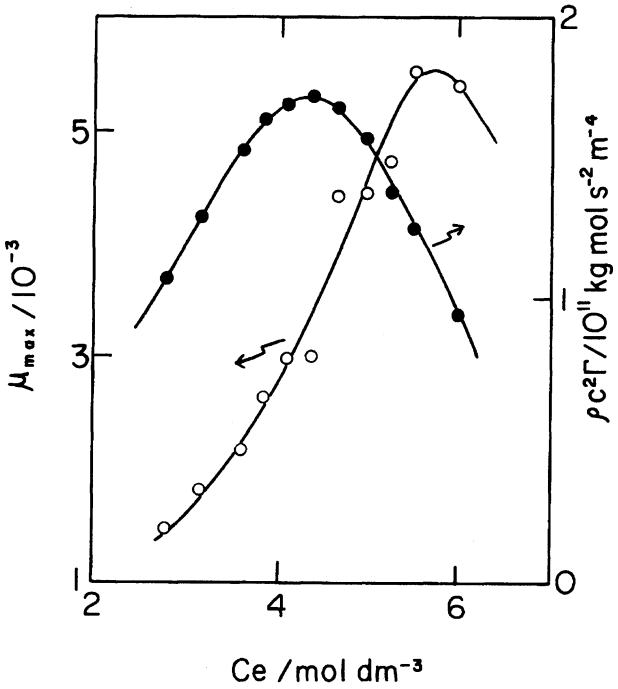

Fig. 4. Comparison of the maximum absorption per wavelength with the $\rho c^2\Gamma$ for an aqueous solution of 4-methoxy-1-butanol.

Table 2. Rate and Thermodynamic Constants for Five Isomeric Alcohol Solutions

Alcohol	k_b / 10^8 mol^{-1} dm^3 s^{-1}	K_{12} / mol dm^{-3}	β	Reference
1-Methoxy-2-butanol	0.94±0.06	1.7±0.3	0.190±0.007	(1)
3-Methoxy-1-butanol	2.24±0.20	0.57±0.14	0.159±0.007	(1)
3-Ethoxy-1-propanol	2.41±0.12	0.27±0.07	0.159±0.004	(2)
4-Methoxy-1-butanol	1.76±0.14	0.81±0.15	0.147±0.004	This work
2-Propoxy-ethanol	1.75±0.11	0.48±0.09	0.102±0.004	(3)

be because the contribution of the heat capacity and the thermal expansion coefficient to μ_{max} was ignored, and because the solute-solute interaction may exist in the solution.

The obtained rate and thermodynamic constants are listed in Table 2 for a comparison with those for other solutions of alcohols having similar structure. It can be clearly seen that the β values are dependent on the structure of the solute, even if they are all isomers. The increase in the β value means that number of less-structured or nonhydrogen-bonded water molecules increases. It is therefore considered that the smaller is the β, the more is the water structure promoted. It should be noticed that the values for 3-ethoxy-1-propanol and 3-methoxy-1-butanol solutions are almost the same and that the value for 4-methoxy-1-butanol solution is slightly lower than that for 3-methoxy-1-butanol. It is also interesting to note that the β value for 4-methoxy-1-butanol solution exists between those for 2-propoxy-ethanol and 3-ethoxy-1-propanol solutions, and that it is close to that for 1-propanol solution.[17] We have speculated from the absorption data for 3-methoxy-1-propanol, 3-ethoxypropanol and 1-propanol solutions that the methoxyl group may act as a water structure breaker and that the propoxyl group can promote the water structure.[1] These speculations were also confirmed by the present experimental study. A comparison of the data for 3-methoxy-1-butanol and 4-methoxy-1-butanol solutions indicates that the position of the methoxyl group has a considerable effect on the hydrophobic ability of alcohol molecules.

Clear differences have also been found in the concentration dependence of the relaxing part of the absorption, A, as can be seen in Fig. 5 for aqueous solutions of these five alcohols. Considering the magnitude for various alcohol solutions, it has been generally observed that it increases with an increase in the size of the hydrophobic group of alcohol. However, even if the hydrophobicity of 4-methoxy-1-butanol is considered to be less than 3-methoxy-1-butanol, the maximum value for the former alcohol is smaller than that of the latter. This means that the relaxing part of the absorption does not always reflect the hydrophobicity of alcohol.

Now, the solution characteristics estimated from the compressibility data are hopefully combined with those from the ultrasonic relaxation data. The adiabatic compressibility is widely used to obtain the information concerning the properties in liquids and solutions, since it is possible to determine the sound velocity and density values quite accurately.[19] The change in the adiabatic compressibility for the solutions of five isomeric alcohols can be clearly seen in Fig. 1. The concentration at which the compressibility shows a minimum is found to be dependent on the kind of alcohol. The ultrasonic relaxational absorption appears from a threshold concentration, as is shown in Fig. 5; it is also dependent on the solute structure. Such a trend is very remarkable when the hydrophobic ability is relatively high.[4] We consider that the solvent structure may be dramatically changed at such a concentration where relaxation appears. The concentration of the minimum compressibility is slightly larger than that at which the relaxational absorption appears. In order to find a correlation between the ultrasonic relaxation and the com-

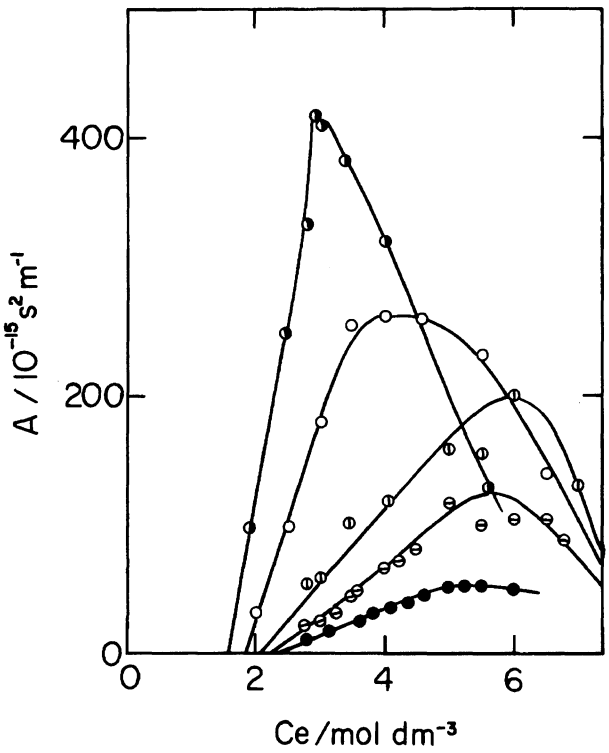

Fig. 5. Concentration dependence of the relaxational part of the absorption, A, for five isomeric alcohol solutions at 25°C. ○: 1-methoxy-2-butanol, ⊖: 3-methoxy-1-butanol, ⊕: 3-ethoxy-1-propanol, ●: 4-methoxy-1-butanol, ◑: 2-propoxyethanol.

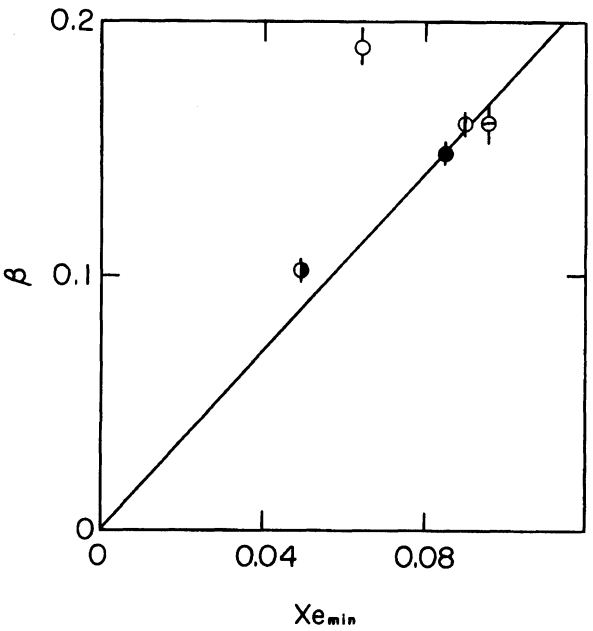

Fig. 6. Plots of the β values vs. the mole fraction, Xe_{min}, at which the minimum compressibility appears for five isomeric alcohol aqueous solutions. The deviation of the 1-methoxy-2-butanol data from the straight line is discussed in Ref. 1. ○: 1-methoxy-2-butanol, ⊖: 3-methoxy-1-butanol, ⓘ: 3-ethoxy-1-propanol, ●: 4-methoxy-1-butanol, ◑: 2-propoxyethanol.

pressibilty data, we plotted the fraction of the less structured water, β, vs. the mole fraction, Xe_{min}, where the compressibility minimum appears, finding a linear relation (Fig. 6). Such linear correlation was also found in other isomeric alcohol solutions.[14] At this stage, it is not yet well understand why such a relation holds for isomeric alcohol solutions. However, it is certain that the water structure is altered dramatically at a certain concentration of alcohol, and that the concentration is very dependent of the alcohol hydrophobicity. The concentration tends to become lower when the ability of the hydrophobicity increases.

In conclusion, the ultrasonic absorption and velocity in aqueous solutions of alcohols reflect the structural change of water; it is possible to estimate the ability of the hydrophobicity of alcohols from the relaxation parmeter and the adiabatic compressibility.

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