Dynamical Characterization in Aqueous Solutions of 3-Methoxy- and 3-Ethoxy-1-propanol by Ultrasonic Methods

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3-Methoxy-1-propanol and 3-ethoxy-1-propanol were synthesized through potassium propoxide from 1,3-propanediol. Ultrasonic absorptions in their aqueous solutions were measured in the frequency range from 8.5 to 220 MHz as functions of their concentrations along with the sound velocity and density. In a solution of 3-ethoxy-1-propanol, a single relaxational absorption was observed; the cause was attributed to a perturbation of an equilibrium as $AB \leftrightarrow A + B$, where AB represents the solute-solvent complex, A the solute and B the solvent molecules. On the other hand, no relaxational absorption was observed in a 3-methoxy-1-propanol solution up to 4 mol dm^{-3}. The thermodynamic and the kinetic parameters were evaluated for the above-mentioned process from the concentration dependences of the ultrasonic parameters in a 3-ethoxy-1-propanol solution. From evidence concerning the appearance and disappearance of ultrasonic relaxational absorption and comparisons of the rate and thermodynamic constants in aqueous solutions of various alcohols, the alternation of the water structure affected by the addition of the solutes is discussed in connection with the solute structures. The methoxyl group was explicitly found to act as a water structure breaker and the ethoxyl group to do so slightly.

It has been well-known that the addition of a nonelectrolyte into water leads to a water structural change.[1] Recent small-angle X-ray scattering studies[2] in aqueous solutions of nonelectrolytes have provided information about the microscopic properties, and it has been reported that quite large changes of the water structure are caused by the addition of such alcohols, as 2-methyl-2-propanol and 1-propanol and 2-propanol. However, the structural and dynamical properties in the solutions still seem to be beyond our understanding, especially in the concentrated solutions. Ultrasonic absorption methods[3] which provide rather macroscopic or phenomenological properties have been widely used to investigate such concentrated solution properties. From the results of sound absorption in some nonelectrolyte aqueous solutions, the solutes of which have hydroxyl groups,[4,5] we have shown that the cause of ultrasonic absorption is due to a solute-solvent interaction, and have speculated that the methoxyl group acts as a water structure breaker and that the propoxyl group acts as a promoter. Through an investigation of aqueous solutions concerning alcohols with an oxyethylene group,[6] we have predicted that the group has a small breaking effect on the water structure. In 1-propanol aqueous solutions, furthermore, another relaxation process was observed, which was responsible for the hydrophobic interaction of solute molecules. Under these circumstances, it is desired to determine how the ethoxyl group affects the water structure. Another purpose of this study is to observe dynamically whether the methoxyl group causes the hydrophobicity of the molecule to decrease when it is introduced to a molecule with quite high hydrophobicity.

Experimental

The chemicals for 3-methoxy-1-propanol and 3-ethoxy-1-propanol synthesis, 1,3-propanediol, anhydrous potassium carbonate, methyl iodide, and ethyl bromide were purchased from Wako Pure Chemical Co. The desired alcohols were obtained through potassium propoxide. The boiling points were 152 °C for 3-methoxy-1-propanol and 161 °C for 3-ethoxy-1-propanol. Identifications of the synthesized compounds were confirmed by their ^{1}H NMR spectra; the purities were verified by a gas chromatographic method to be more than 96% and the water contents in the synthesized compounds were checked by Karl Fischer method to be less than 2.5%.

The ultrasonic absorption coefficient was measured by a pulse method in the frequency range from 8.5 to 220 MHz. The detail procedure for the absorption measurement is described elsewhere.[7] The sound velocity was measured using an interferometer operated at 2.5 MHz. The cells for the absorption coefficient and the sound velocity measurements were immersed in a water bath controlled within ±0.002 °C. The density was measured by a standard pycnometer, the volume of which was about 5.5 cm^3. All measurements were carried out at 25 °C.

Results and Discussion

There are several procedures to interpret the ultrasonic absorption: analysis of the concentration dependence, frequency dependence, and temperature dependence of the absorption.[8] The experimental absorption coefficients in this study were obtained as functions of the solute concentration and the frequency. In order to obtain the dynamic characteristics in solutions, the analysis of the frequency dependence may provide useful information. A Debye-type equation is well used and is associated with a perturbation of chemical equilibrium, although an analytical equation for the absorption spectra was still developed.[9] For a single relaxational process, the absorption spectrum is fitted by the following equation:

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

Here, α is the absorption coefficient, f the frequency, A the amplitude of the relaxational absorption, B the background absorption and f_r the relaxation frequency. The procedures for determining the ultrasonic parameters and for judging whether the spectrum is due to single relaxational absorption or not are described elsewhere.[7,10] Figure 1 shows representative ultrasonic absorption spectra in aqueous solutions of 3-methoxy-1-propanol and 3-ethoxy-1-propanol. A clear frequency dependence of α/f^2 was found for the latter solution, but no dependence was found for the former solution. The frequency-dependent experimental data were analyzed in terms of Eq. 1 by using a nonlinear least-mean-squares method. As can be seen in the figure, the experimental data are well-fitted to the single relaxational curves. The values of $[(\alpha/f^2)_{exp}-(\alpha/f^2)_{cal})]/(\alpha/f^2)_{exp}$ at all frequencies measured were less than ±0.1, where subscripts *exp* and *cal* indicate those of the experiment and calculation, respectively. The calculated ultrasonic parameters are listed in Table 1 along with the solution density and sound velocity values. Complete sets of the absorption coefficient as functions of the concentration and frequency are available upon request to one of authors (S. N.). Figure 2 shows the concentration dependence of the relaxation frequency for the 3-ethoxy-1-propanol solution. Figure 3 represents the results regarding the amplitude of the relaxational absorption and the background absorption. Because no relaxational absorption was

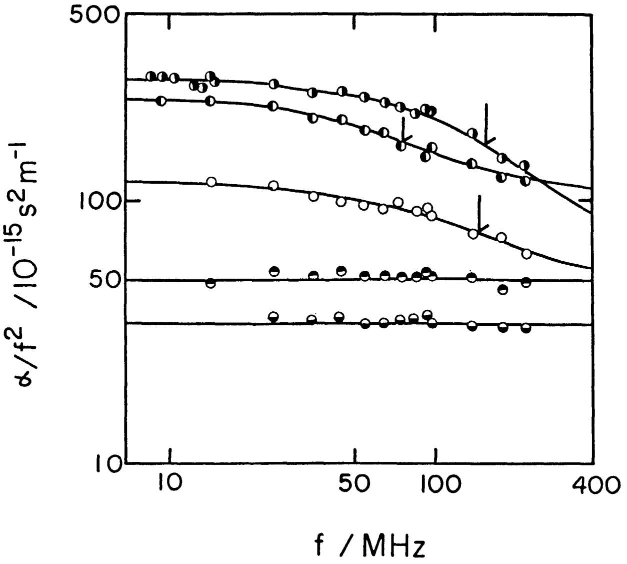

Fig. 1. The representative ultrasonic absorption spectra in aqueous solutions of 3-methoxy-1-propanol and 3-ethoxy-1-propanol at 25 °C. ◓: 3.91 mol dm^{-3} and ◒: 3.00 mol dm^{-3} 3-methoxy-1-propanol, ○: 3.00 mol dm^{-3}, ◐: 4.01 mol dm^{-3} and ◑: 6.00 mol dm^{-3} 3-ethoxy-1-propanol.

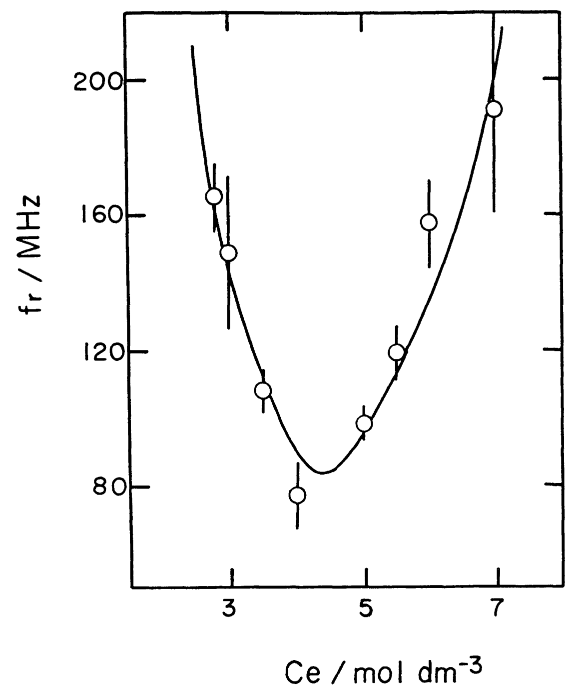

Fig. 2. The concentration dependence of the relaxation frequency for 3-ethoxy-1-propanol solution at 25 °C.

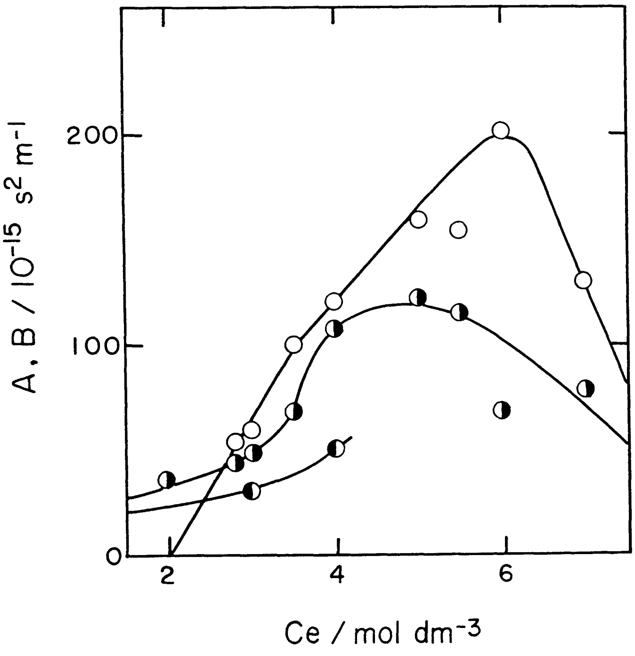

Fig. 3. The concentration dependences of the amplitude of the relaxational absorption and back ground absorption. ○: A for 3-ethoxy-1-propanol, ◑: B for 3-ethoxy-1-propanol ◐: B for 3-methoxy-1-propanol solutions.

Table 1. Ultrasonic Parameters and Density for Aqueous Solution of 3-Ethoxy-1-propanol at 25 °C

C_e	A	B	f_r	c	ρ
$\mathrm{mol\,dm^{-3}}$	$10^{-15}\,\mathrm{s^2\,m^{-1}}$		MHz	$\mathrm{m\,s^{-1}}$	$\mathrm{kg\,dm^{-3}}$
1.00	—	—	—	1562.3	0.9951
2.00	—	—	—	1608.4	0.9933
2.50	—	—	—	1624.5	0.9927
2.80	54.6±1.8	43.1±2.4	165.8±10.9	1629.7	0.9925
3.00	58.1±3.9	47.9±5.5	149.3±24.0	1631.7	0.9923
3.50	100.5±2.5	67.8±2.5	108.9±7.0	1627.6	0.9915
4.01	119.0±9.8	108.4±3.5	76.6±10.0	1612.0	0.9843
5.00	159.6±4.0	123.8±3.0	98.8±5.5	1588.5	0.9814
5.50	154.8±3.8	115.2±4.6	119.8±8.1	1568.7	0.9765
6.00	201.3±8.0	69.6±10.7	157.9±13.1	1547.5	0.9716
7.00	131.2±18.1	79.5±20.3	191.3±30.2	1491.3	0.9601

Table 2. Rate and Thermodynamic Parameters in Aqueous Solutions of 3-Ethoxy-1-propanol and 1-Propanol at 25 °C

Alcohol	k_{21}	K_{12}	β
	$10^8\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$	$\mathrm{mol\,dm^{-3}}$	
1-Propanol	0.51±0.05	4.5±1.0	0.141±0.013
3-Ethoxy-1-propanol	2.41±0.12	0.27±0.07	0.159±0.004

observed in the 3-methoxy-1-propanol solution within the measured frequency range, the background absorption is only indicated in the same figure.

The sound velocity also goes through a maximum, as can be seen in Table 1. The phenomenon of the peak sound velocity as being a function of the concentration is also a characteristic of aqueous solutions of alcohols, along with the peak sound absorption concentration.

The characteristic phenomena associated with the observed relaxation are that the relaxation frequency goes through a minimum and that the amplitude of the relaxational absorption goes through a maximum. These trends are not interpreted by reaction models only associated with the solutes in the solution. Under these experimental facts, we have proposed the following reaction mechanism for interpreting the relaxational absorption.[4] That is, the solute may interact with solvent water and they form the complex, presumably, due to their hydrogen-bonding ability.

$$\mathrm{AB} \underset{k_{21}}{\overset{k_{12}}{\longleftrightarrow}} \mathrm{A}+\mathrm{B} \qquad (2)$$

where AB is the complex formed by alcohol and water and A the solute molecules. Attention should be paid to the notation, B, which represents non-hydrogen-bonded water molecules, or less-structured water molecules; we assume that such reactants, B, can only participate in the reaction described by Eq 2. Under this assumption, the relation between the analytical concentrations and the relaxation frequency is derived as[5]

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

where k_{ij} is the rate constant, C_e and C_w the analytical concentration of alcohol and water, respectively, and β the fraction of non-hydrogen-bonded water; K_{12} is defined as $K_{12}=k_{12}/k_{21}$. The three parameters, k_{21}, β and K_{12}, in Eq. 3 are determined in order to give the best agreement with the experimental data, by means of a nonlinear least-mean-squares. The solid curve in Fig. 2 was calculated from the variation of the concentration. The determined rate and thermodynamic constants are listed in Table 2, along with those for a 1-propanol solution for a comparison.

In order to confirm the cause of relaxational absorption, the concentration dependence of the amplitude of the relaxational absorption should also be analyzed. In ultrasonic studies, the maximum excess absorption per wave length, $\mu_{\max}$, is usually considered. For the reaction under consideration, it is given

$$\mu_{\max} = 0.5\,Af_r c = (\pi\rho c^2\Gamma/2RT)(\Delta V - \alpha_p \Delta H/\rho C_p)^2, \qquad (4)$$

where ρ is the solution density, ΔV the standard volume change of the reaction, ΔH the standard enthalpy change of the reaction, C_p the specific heat at the constant pressure, α_p the thermal expansion coefficient, and Γ the concentration term given by $\Gamma=\{[\mathrm{AB}]^{-1}+[\mathrm{A}]^{-1}+[\mathrm{B}]^{-1}-([\mathrm{AB}]+[\mathrm{A}]+[\mathrm{B}])^{-1}\}^{-1}$. In order to grasp the precise variation of $\mu_{\max}$ on the analytical concentration, the values of the specific heat and the thermal expansion coefficient are desired. Without these values, we reluctantly compare the experimental values of $\mu_{\max}$ with $\rho c^2\Gamma$, which is the most controlling term to $\mu_{\max}$. Figure 4 indicates the concentration dependences of $\mu_{\max}$ and $\rho c^2\Gamma$.

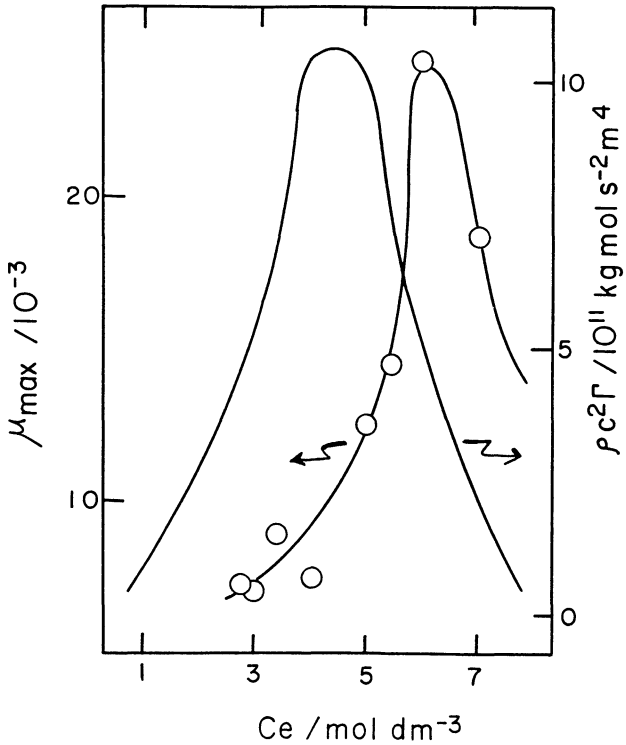

Fig. 4. The comparison of the μ_{max} and $\rho c^2\Gamma$ for 3-ethoxy-1-propanol solution.

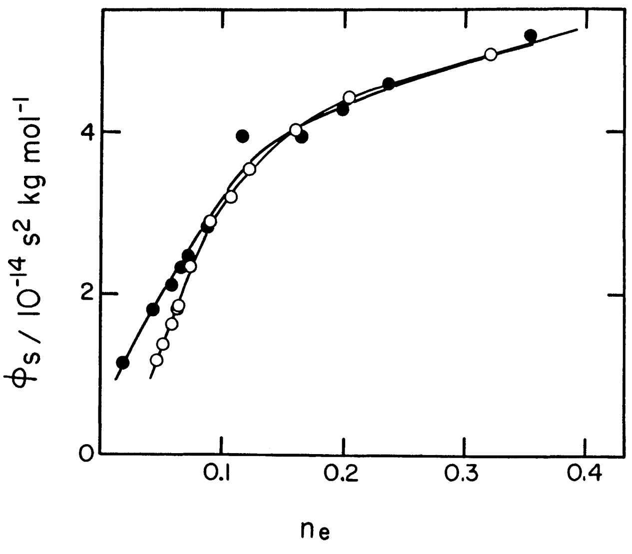

Fig. 5. The apparent molar compressibility for 3-ethoxy-1-propanol (○) and 1-propanol (●) solutions as a function of alcohol mole fraction, n_e at 25 °C.

Though the peak positions are slightly different, the trends seem to be similar, which supports our analysis.

The relaxational absorption in aqueous solutions of alcohols is very sensitive to the hydrophobicity of alcohol molecules. In a solution of methanol, relaxational absorption at room temperature is reported to be observed over a frequency range of more than 500 MHz;[11] in the solution of ethanol it is found at around 300 MHz[12,13] and in that of 1-propanol it exists in a range less than 100 MHz.[5,14,15] Madigosky and et al.[15] have reported the absorption coefficients far below 100 kHz in a solution of 1-propanol, and have preferred to analyze the absorption using fluctuation theories. In this type solution, the absorption coefficient divided by the square of the frequency increases upon decreasing the frequency far below the MHz frequency range. However, in a solution of 2-propanol, the values are almost frequency independent below 10 MHz.[16] As can be seen in Fig. 1, the dependence of α/f^2 in the solution of 3-ethoxy-1-propanol is too small below 10 MHz and the absorption spectrum can be well-analyzed by the Debye-type single relaxational equation. Following our experimental results, we have considered that the absorption is very dependent on the structure of the alcohols, especially on the hydrophobic group. Our analytical results also indicate that the water structure is considered to be altered, depending upon the change in the solute hydrophobicity. As is shown in the present study, no relaxational absorption is observed in the solution of 3-methoxy-1-propanol in the pulse frequency range, and the single relaxational absorption is found in the solution of 3-ethoxy-1-propanol. The cause of the relaxational absorption is reasonably analyzed by a model associated with the interaction between the solute and the solvent; the relaxation process also reflects a change in the ratio of the hydrogen-bonded water and non-hydrogen-bonded water. It is, therefore, interesting to compare the result for the aqueous solution of 3-ethoxy-1-propanol with that of the 1-propanol solution. As can be seen in Table 2, the β value for 1-propanol solution is slightly smaller than that for 3-ethoxy-1-propanol, which means that the introduction of the ethoxyl group makes the hydrophobicity of 1-propanol decrease. The same decreasing trend of the β value has been observed in solutions of alcohols with oxyethylene groups, although the magnitude of the β change is smaller than that for the ethoxyl group.[6] One way to estimate the strength of hydrophobicity is to determine the concentration dependence of the apparent molar compressibility, Φ_s. This method is used by Desnoyers and his co-worker,[17] and is calculated by

$$\Phi_s = \kappa_s \Phi_v + (\kappa_s - \kappa_w)/m\rho_0, \qquad (5)$$

where κ_s is the adiabatic compressibility of the solution, κ_w that of solvent, Φ_v the apparent molar volume, ρ_0 the solvent density and m the molality which is converted from the molarity using the solution density. The sharper is the profile of the dependence, the greater is the hydrophobicity. Figure 5 indicates a comparison of the two solutions of 1-propanol and 3-

ethoxy-1-propanol as a function of mole fraction. The latter solution shows a broader dependence than does the former, the result of which is consistent with that obtained from the above-mentioned absorption data. It should be noticed that another relaxation process associated with molecular aggregation through a hydrophobic interaction is observed in the solution of 1-propanol, in addition to absorption due to a solute–solvent interaction. The former absorption disappears when the ethoxyl group is involved. This is because the ether oxygen may prevent the formation of an aggregate in an aqueous solution, and because of a decrease in the hydrophobicity. The small change in the molecular structure of alcohols provides a quite large change in the structure of water. This is clearly seen by comparing the results for the 3-ethoxy-1-propanol solution with that for a 2-propoxyethanol solution,[18] in which the single relaxational absorption due to a solute solvent interaction is found and the β value is 0.10. In general, the ultrasonic relaxational absorption associated with the solute solvent interaction would appear in the MHz frequency region when the sizes of the alcohols are order of propanols or butanols. Upon decreasing the hydrophobicity, the relaxation frequency increases to more than 100 MHz. However, in the solution of 3-methoxy-1-propanol, no relaxational absorption is observed, although the relaxation is found in the solution of 1-methoxy-2-propanol.[3] According to the studies reported so far, 2-propanol has less hydrophobic activity than does 1-propanol. The introduction of a methoxyl group seems to cause the relaxation process to shift to a higher frequency range. It might then be considered that 1-methoxy-2-propanol is less hydrophobic than 3-methoxyl-1-propanol. However, the disappearance of relaxation in the latter solution is speculated since intramolecular hydrogen boning might be plausible in 3-methoxyl-1-propanol, and the total hydrophobic activity of the molecule might decrease. We expect that the hydrophobic and hydrophilic balance of 3-methoxy-1-propanol is close to or less than ethanol, and that the relaxational absorption may appear at more than 200 MHz.

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