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Ultrasonic Relaxation Associated with Solute–Solvent Interaction in an Aqueous Solution of 5-Methoxy-1-pentanol

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Synopsis. After 5-methoxy-1-pentanol was synthesized, the sound velocity, density, and ultrasonic absorption coefficients in the frequency range from 7.5 to 220 MHz were measured in aqueous solutions at 25 °C. The sound velocity and density were reported in terms of the polynomials as a function of the analytical concentration. The absorption could be described approximately by a single Debye-type relaxational equation in the 2.00 and 5.00 mol dm^{-3} range. The cause of the relaxation was attributed to a perturbation of an equilibrium associated with an interaction between the solute and the solvent; the rate and thermodynamic constants were determined. The results are discussed by comparing them with those previously reported in relation to the water structure.

Ultrasonic methods have been extensively used to study the dynamic properties of aqueous solutions of nonelectrolytes.[1—5] In our previous reports[6—8] for aqueous solutions of some alcohols, we showed that the hydrophobic and hydrophilic balance of alcohols has an important role in ultrasonic relaxations. In a 4-methoxy-1-butanol solution, only a single relaxational absorption is observed; the cause of the relaxation is attributed to a perturbation of an equilibrium associated with the solute–solvent interaction.[7] In that of 3-methoxy-1-propanol, no relaxational absorption has been found up to 220 MHz.[8] The methoxyl group makes the hydrophobicity decrease, and has an ability as a water structure breaker.[6] Thus, the addition of the methoxyl group to an alcohol molecule with a relatively large hydrocarbon group may shed light on the dynamical properties associated with the balance between the hydrophobicity and hydrophilicity of alcohols.

In order to investigate the above speculation, 5-methoxy-1-pentanol was chosen in this study, and the ultrasonic relaxational characteristics were examined.

Experimental

5-Methoxy-1-pentanol has been synthesized from 1,5-pentanediol through potassium 5-hydroxy-1-pentoxide using potassium carbonate and methyl iodide. These chemicals used for the synthesis were all purchased from Wako Pure Chemical Industries Co. The boiling point of the synthesized 5-methoxy-1-pentanol was 239 °C, and was identified by proton NMR. The purity was checked by a gas-chromatographic method to be more than 98%. The ultrasonic absorption coefficients, α, were measured in the frequency range from 7.5 to 220 MHz by a pulse method.[9] The sound velocity data were obtained by a sing-around meter at 1.92 MHz and an interferometer at 2.5 MHz. The solution density measurement was carried out using Shibayama density meter. All of the measurements were performed in a water bath maintained at a constant temperature of 25 °C.

Results and Discussion

The solution density, ρ, and sound velocity, v, were measured as a function of the analytical concentration, C_0, as shown in Fig. 1. They are well approximated to a three-degree polynomial function in the concentration range from 0 to 6.00 mol dm^{-3}, as follows: $v=1496.5+91.715C_0-22.426C_0^2+1.3524C_0^3$ m s^{-1} ($r^2=0.99527$), and $\rho=0.99707-3.29093\times10^{-3}C_0-7.80424\times10^{-4}C_0^2+1.37075\times10^{-5}C_0^3$ kg dm^{-3} ($r^2=0.997126$). Here r^2 is the determination coefficient. The feature of the sound velocity is typical for aqueous solutions of alcohols, i.e., it goes through a maximum.

Figure 2 shows some representative ultrasonic absorption spectra for aqueous solutions of 5-methoxy-1-pentanol. The frequency dependence of the absorption coefficients was approximately fitted to a Debye-type relaxational equation as $\alpha/f^2=A/[1+(f/f_r)^2]+B$, where f is the frequency, A and B are the constants, and f_r is the relaxation frequency. The procedure for the determination of these parameters is also described elsewhere.[9] The solid curves represent the calculated ones. In Table 1, the obtained ultrasonic parameters are listed along with the density and sound velocity values. The concentration dependences of the relaxation fre-

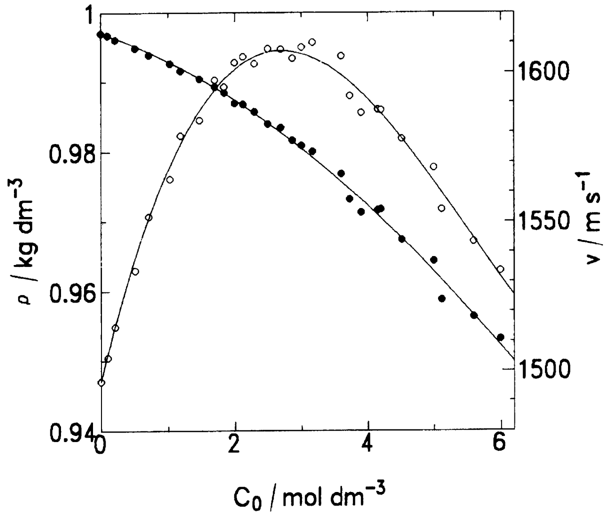

Fig. 1. Concentration dependence of the sound velocity and density for aqueous solution of 5-methoxy-1-pentanol at 25 °C. ○: sound velocity for the right scale, ●: density for the left scale.

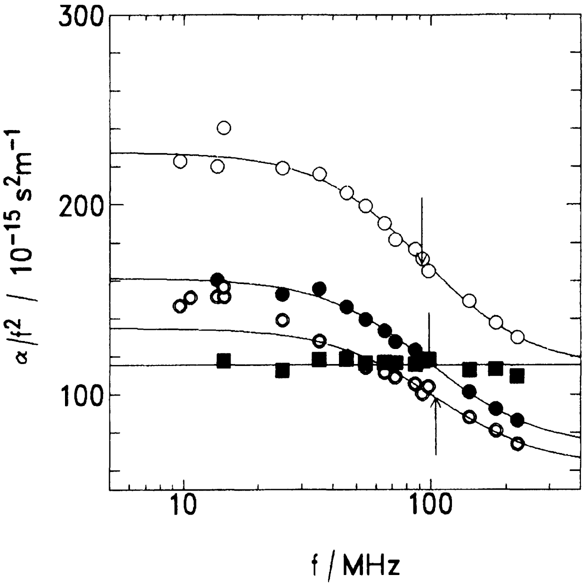

Fig. 2. Representative ultrasonic absorption spectra in aqueous solutions of 5-methoxy-1-pentanol at 25 °C. ◎: 2.50 $\mathrm{mol\,dm^{-3}}$, ○: 3.00 $\mathrm{mol\,dm^{-3}}$, ●: 5.00 $\mathrm{mol\,dm^{-3}}$, ■: liquid 5-methoxy-1-pentanol. The arrow indicates the position of the relaxation frequency.

Table 1. Ultrasonic Relaxation Parameters, Sound Velocity and Density for Aqueous Solutions of 5-Methoxy-1-pentanol at 25 °C

Concn	f_r	A	B	v	ρ
$\mathrm{mol\,dm^{-3}}$	MHz	$10^{-15}\ \mathrm{s^2m^{-1}}$		$\mathrm{m\,s^{-1}}$	$\mathrm{kg\,dm^{-3}}$
2.00	111±11	42±2	49±2	1603.4	0.9870
2.50	104±8	73±2	62±2	1607.9	0.9840
2.70	93±6	83±3	72±2	1607.8	0.9835
3.00	99±3	88±1	72±1	1608.4	0.9809
3.17	95±4	94±2	77±1	1610.0	0.9801
3.60	92±5	108±3	90±2	1605.4	0.9769
3.73	91±7	124±5	92±3	1592.1	0.9732
3.90	91±5	123±3	98±2	1586.4	0.9713
4.15	94±7	125±5	103±3	1587.5	0.9716
4.20	89±5	116±3	109±2	1587.3	0.9718
4.51	89±4	118±3	109±2	1577.8	0.9674
5.00	93±3	114±2	114±1	1568.2	0.9643
5.15	92±5	115±3	117±2	1554.1	0.9588
5.60	95±3	88±2	118±1	1543.4	0.9563
6.00	105±6	72±2	119±1	1533.6	0.9531

quency and the amplitude of the ultrasonic relaxation, A, are very similar to those previously reported for solutions of other alcohols.[7,8] We therefore considered that the cause of the observed relaxational absorption was due to the solute–solvent interaction, $\mathrm{AB} \rightleftharpoons \mathrm{A}+\mathrm{B}$, where A is the solute, B the solvent, and AB the complex formed by hydrogen bonding, presumably. The relation between the relaxation frequency and the concentration is given for this mechanism as[10]

$$2\pi f_r = k_b\left\{(C_0 - \beta C_w + K_{12})^2 + 4\beta C_w K_{12}\right\}^{1/2}, \quad (1)$$

where k_b is the backward rate constant, C_w the analytical concentrations of the solvent, β the fraction of less-structured water, and K_{12} the equilibrium constant. The experimental relaxation frequency was fitted to Eq. 1 using a non-linear least-mean-square program. The solid curve in Fig. 3 is the calculated one. The obtained rate and thermodynamic constants are listed in Table 2 along with those for aqueous solutions of alcohols with a terminal methoxyl group. A confirmation of the cause of the relaxational absorption may also be obtained from an analysis of the concentration dependence of the maximum absorption per wavelength, $\mu_{\max}=0.5Af_rv$. As has been described in previous reports,[7,8] the most predominant term controlling the concentration dependence of $\mu_{\max}$ is $\rho v^2\Gamma$, where Γ is the concentration term, expressed as $\Gamma=\{1/[\mathrm{A}]+1/[\mathrm{B}]+1/[\mathrm{AB}]-1/([\mathrm{A}]+[\mathrm{B}]+[\mathrm{AB}])\}^{-1}$. Figure 4 represents the experimental $\mu_{\max}$ and the calculated $\rho v^2\Gamma$ values. The similar dependences indicate that the relaxational absorption is due to a perturbation of the equilibrium associated with the solute–solvent interaction.

No relaxational absorption has been observed in an aqueous solution of 1,5-pentanediol up to 4.85 $\mathrm{mol\,dm^{-3}}$ in a pulse frequency range.[11] A replacement of the hydroxyl group by a methoxyl one seems to cause the hydrophobicity of the molecule to slightly increase. It is thus expected that the ultrasonic relaxation process appears in the pulse frequency range. Along with an increase in the hydrophobicity of whole molecule, the frequency range of the relaxational absorption tends to decrease. As is indicated in Table 2, the relaxational phenomenon is not found in aqueous solutions of 3-methoxy-1-propanol, though it is observed in those of 4-methoxy-1-butanol and 5-methoxy-1-pentanol. Shindo

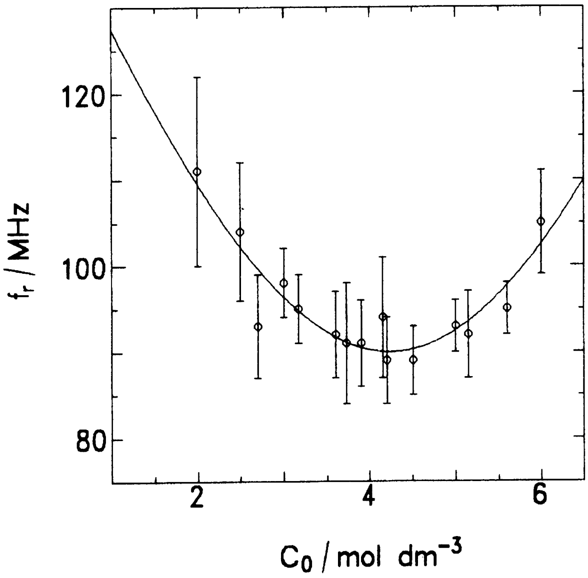

Fig. 3. Concentration dependence of the relaxation frequency. The solid curve is the calculated values following the solute–solvent interaction model.

Table 2. Rate and Thermodynamic Constants for Aqueous Solutions of Normal Alcohols with a Terminal Methoxyl Group

Alcohol	$\frac{k_b}{10^8\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}}$	$\frac{K_{12}}{\mathrm{mol\,dm^{-3}}}$	β	Reference
3-Methoxy-1-propanol	No relaxation up to 220 MHz			(8)
4-Methoxy-1-butanol	1.76±0.2	0.81±0.15	0.147±0.004	(7)
5-Methoxy-1-pentanol	0.83±0.04	2.4±0.2	0.158±0.004	This work

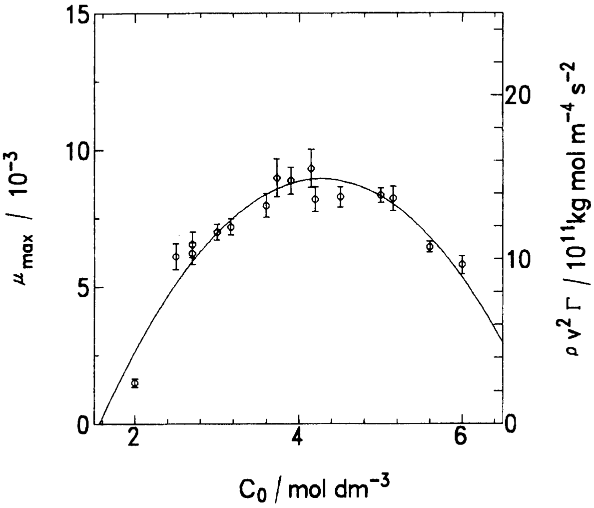

Fig. 4. Concentration dependences of the maximum absorption per wavelength (left scale) and the most dominant term for the maximum absorption per wavelength, $\rho v^2 \Gamma$ (right scale).

et al.[2)] have reported frequency-independent α/f^2 values up to 200 MHz in an aqueous solution of 2-methoxyethanol. This may be because of the relatively low hydrophobicity of this alcohol molecule. A recent study by Brai and Kaatze[1)] has indicated that the ultrasonic absorptions in aqueous solutions of popular alcohols are the sum of Debye-type relaxational absorptions and fluctuational absorptions. It is hard to conclude whether plural relaxations definitely exist in a 5-methoxy-1-pentanol solution, because our frequency range is not very wide compared with them. Actually, double relaxational absorptions are observed in the pulse frequency range when the alcohols have their relatively large hydrophobic group at the terminal.[6)] The ultrasonic absorptions are so dependent on the hydrophobicity of alcohols that a slight change of the molecular structure is reflected in the absorption.[7)] However, a slight deviation from the single relaxational equation in the lower frequency range has been observed for the spectra of an aqueous solution of 5-methoxy-1-pentanol in the concentration range less than 4 mol dm^{-3}. This might be the appearance of another relaxation in the lower frequency range.

The hydrophobicity of alcohols is estimated by considering the variation in the β values which are the fraction of nonhydrogen-bonded water. The larger is the value, the more hydrophilic is the alcohol molecule. The β value for a 5-methoxy-1-pentanol solution is approximately the same as that of 4-methoxy-1-butanol, as is shown in Table 2. This is an unexpected result, because the hydrophobicity of the former was thought to be higher than that of the latter based on their molecular structures. Since alcohol molecules are considered to exist in cages formed by water hydrogen-bond networks and the hydrogen bond of water around hydrocarbon chains of alcohols may be facilitated. Thus, the β value generally decrease when alcohols with a relatively large hydrocarbon coexist. One of the causes for the similar β values of the above two alcohol solutions might be the possibility of a bending of 5-methoxy-1-pentanol molecule in aqueous media; thus the effective number of water molecules influenced by the hydrophobic group of the alcohol might decrease. This molecular conformation might then be reflected in a decrease in the mobility of the alcohol; the backward rate constant which is the rate of formation of the complex, AB, becomes smaller than that of 4-methoxy-1-butanol solution, as can be seen in Table 2.

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