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# Dynamic Investigation of Aqueous Solutions of 2-*t*-Butoxyethanol and 3-Methoxy-3-methyl-1-butanol by Ultrasonic Methods

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Ultrasonic absorption in the frequency range of 6.5 to 220 MHz has been measured in aqueous solutions of 3-methoxy-3-methyl-1-butanol and 2-*t*-butoxyethanol as a function of the concentration along with the measurement of sound velocity at 1.92 and 2.5 MHz at 25 °C. A single relaxational ultrasonic absorption has been found in both solutions and it is interpreted by a reaction kinetics associated with the interaction between solute and solvent, $AB \rightleftharpoons A+B$ where AB is the complex, A the solute and B the solvent. The forward and backward rate constants for the interaction have been determined from the concentration dependence of the relaxation frequencies to be $k_f=1.4\times10^8\ s^{-1}$ and $k_b=1.1\times10^8\ mol^{-1}\ dm^3\ s^{-1}$ for 3-methoxy-3-methyl-1-butanol solution and $k_f=9.0\times10^7\ s^{-1}$ and $k_b=1.3\times10^8\ mol^{-1}\ dm^3\ s^{-1}$ for 2-*t*-butoxyethanol solution. The water structure has also been estimated from the absorption data and it has been clarified for the water structure promoted by additions of such solutes. Correlations between the structures of the solutes and the ultrasonic properties of the solutions are discussed in terms of the hydrophobicity of the solutes.

The molecular structure of a self-associating liquid solvent is well known to be changed by the addition of solutes.[1] It is interesting and important to examine experimentally how much the change would be induced in relatively concentrated solutions. Ultrasonic techniques are very suitable to investigate such questions and they have been used extensively. They also give the dynamic information about the solutions and liquids. Rao and Verrall[2] have reported that in an aqueous micellar solution of 2-butoxyethanol (Butyl Cellosolve) the relaxation observed in the MHz frequency range is associated with the exchange reaction of the alcohol between the mixed micelles and the surrounding bulk solution. This has considerable interest in relation to microemulsions. However, clear relaxational absorptions are observed at concentrations below 1 mol dm$^{-3}$ even if surfactant are not added.[3,4] Without some clarification of the mechanism, it is difficult to discuss such ternary systems. By means of ultrasonic absorption and velocity measurements, we have been studying the effects on water structure when nonelectrolytes, e.g. alcohols or ethers, are added.[3–7] It has been found, so far, that the ultrasonic relaxations observed in the MHz frequency range are closely related to the balance of the hydrophobicity and hydrophilicity of the solute molecules.

To clarify the relation between the solute structures and the ultrasonic properties, we have chosen two isomeric solutes viz. 3-methoxy-3-methyl-1-butanol and 2-*t*-butoxyethanol. We consider that the structural effect of the solutes on the solvent water may shed light on the ultrasonic properties when they are examined in the solutions with isomeric solutes.

## Experimental

The chemicals used were commercial samples obtained from Tokyo Kasei Co., Ltd. and distilled once under reduced pressure. Solvent water was doubly distilled. The desired concentrations of the solutions were made by weighing the solutes.

The ultrasonic absorption coefficient, $\alpha$, was measured by the improved pulse apparatus in the frequency range from 6.5 MHz to 220 MHz; the principle and the detailed procedure of the measurement are described elsewhere.[4] The sound velocity was measured by an interferometer opperated at 2.5 MHz and a sing around meter at 1.92 MHz. The accuracy of both apparatuses is less than 1 m s$^{-1}$. The cells for the absorption and velocity measurements were immersed in a water bath which was controlled within ±0.005 °C and the measurements were performed at 25 °C.

The densities were measured at various temperatures by a standard pycnometer the volume of which was about 4.8 cm$^3$ and the thermal expansibility at 25 °C was determined. The viscosity coefficients of the solutions were measured by a Ubbelohde type viscometer at 25.0±0.1 °C.

## Results and Interpretation

The quantity $\alpha/f^2$ where $f$ is the frequency has been found to be frequency dependent for aqueous solutions of 3-methoxy-3-methyl-1-butanol (from 2.2 mol dm$^{-3}$ to 5.5 mol dm$^{-3}$) and 2-*t*-butoxyethanol (from 1.3 mol dm$^{-3}$ to 5.0 mol dm$^{-3}$). The experimental values of $\alpha/f^2$ for the 2-*t*-butoxyethanol solution are shown in Fig. 1 at various frequencies as a function of the analytical concentration, $C_e$. A peak sound absorption concentration has been observed though it is dependent on the measurement frequency. A similar dependence has also been observed for the 3-methoxy-3-methyl-1-butanol solution. No frequency dependence of $\alpha/f^2$ is found in either liquid solutes.

In general, the frequency dependence of the sound absorption coefficient can be well described by the next equation if it is due to a single relaxation process.

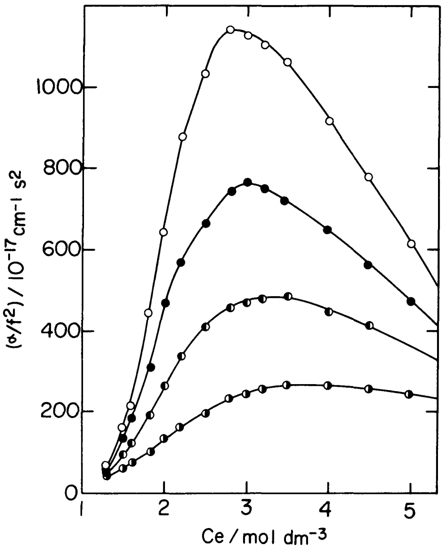

Fig. 1. The plots of $\alpha/f^2$ vs. concentration for aqueous solution of 2-*t*-butoxyethanol at 25 °C. —○—: 15 MHz, —●—: 45 MHz, —◐—: 95 MHz, —◑—: 220 MHz.

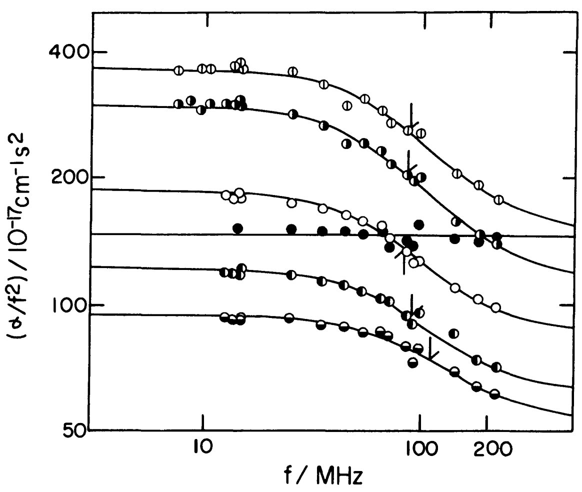

Fig. 2. The representative ultrasonic absorption spectra in aqueous solution of 3-methoxy-3-methyl-1-butanol at 25 °C. —⊖—: 2.2 mol dm$^{-3}$, —◐—: 2.4 mol dm$^{-3}$, —○—: 2.8 mol dm$^{-3}$, —◑—: 3.5 mol dm$^{-3}$, —⦶—: 4.5 mol dm$^{-3}$, —●—: liquid solute.

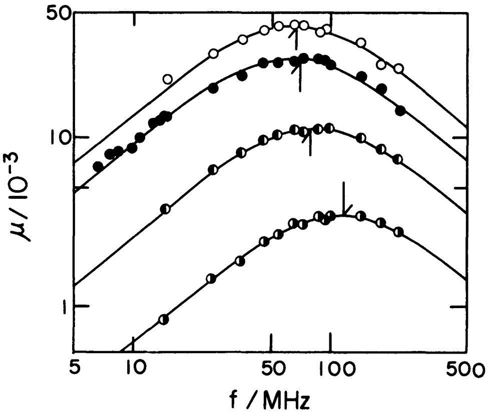

Fig. 3. The representaive ultrasonic absorption spectra in aqueous solution of 2-*t*-butoxyethanol at 25 °C. —◑—: 1.3 mol dm$^{-3}$, —◐—: 1.6 mol dm$^{-3}$, —●—: 2.0 mol dm$^{-3}$, —○—: 3.0 mol dm$^{-3}$.

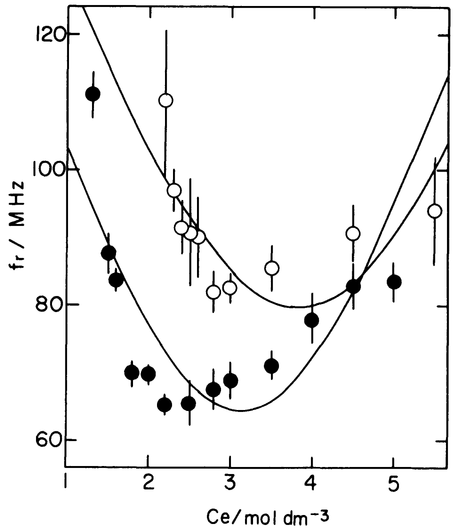

Fig. 4. The concentration dependence of the relaxation frequency for aqueous solutions of 3-methoxy-3-methyl-1-butanol(—○—) and 2-*t*-butoxyethanol (—●—) at 25 °C. The solid curves are the calculated ones.

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

or

$$\mu = (\alpha/f^2 - B)fc = Afc/[1+(f/f_r)^2], \tag{1'}$$

where $\mu$ is the excess absorption per wavelength, $A$ the amplitude of the excess absorption, $B$ the back ground absorption, $f_r$ the relaxation frequency and $c$ the sound velocity. Figures 2 and 3 show the representative ultrasonic absorption spectra for both solutions and they are shown with different formula, that is, with Eq. 1 and Eq. 1′. The ultrasonic parameters, $A$, $B$, and $f_r$ have been determined by a nonlinear least mean square method using microcomputer. The spectrum which is represented by both Eqs. 1 and 1′ can be seen on a computer display in order to check how the experimental data fit the theoretical curves. The ultrasonic results are listed in Table 1 along with some thermodynamic quantities. The solid curves in Figs. 2 and 3 are those calculated using these parameters. It is seen that a clear single relaxation process has been observed in both solutions. Figure 4 represents the concentration dependences of the relaxation frequencies and they

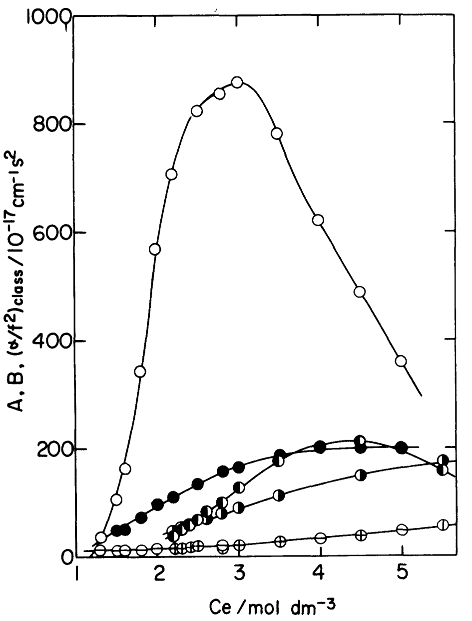

Fig. 5. The concentration dependences of the amplitude of the excess absorption. the background absorption and the classical absorption for aqueous solutions of 3-methoxy-3-methyl-1-butanol and 2-t-butoxyethanol. —◐—: *A*, —◑—: *B* and —⦶—: $(\alpha/f^2)_{class}$ for 3-methoxy-3-methyl-1-butanol, —○—: *A*, —●—: *B* and —⊖—: $(\alpha/f^2)_{class}$ for 2-*t*-butoxyethanol.

show a minimum. Figure 5 shows the dependence of the amplitude of the excess absorption and the back ground absorption. The classical absorption which is mainly due to shear viscosity is obtained by the next equation.[8]

$$(\alpha/f^2)_{class} = 8\pi^2\eta/3c^3\rho, \tag{2}$$

where $\eta$ is the viscosity coefficient and $\rho$ the solution density. The results for both solutions are also shown in Fig. 5 and are smaller than those of the back ground absorptions. This means that the observed relaxational absorptions are not due to the shear viscosity and another relaxation may be predicted at more than 200 MHz in both solutions which we will not consider further.

The sound velocity shows a maximum as is seen in Table 1. The adiabatic compressibility, $\kappa_s$, of the solution is obtained with the help of the next equation.

$$\kappa_s = (\rho c^2)^{-1} \tag{3}$$

The concentration dependences of the compressibility are shown in Fig. 6 along with some other solutions in order to compare where the concentra-

Table 1. Ultrasonic and Thermodynamic Parameters for Aqueous Solutions of 2-*t*-Butoxyethanol and 3-Methoxy-3-Methyl-1-Butanol at 25 °C

| $C_e$ | $f_r$ | $A$ | $B$ | $c$ | $\rho$ | $\eta$ | $\alpha_p^\circ$ |
|---|---|---|---|---|---|---|---|
| mol dm$^{-3}$ | MHz | $10^{-17}$ s$^2$ cm$^{-1}$ | | m s$^{-1}$ | g cm$^{-3}$ | $10^{-2}$ g cm$^{-1}$ s$^{-1}$ | $10^{-4}$ deg$^{-1}$ |
| | | | (3-Methoxy-3-methyl-1-butanol) | | | | |
| 2.20 | 111 | 41.9 | 52.8 | 1622 | 0.9927 | 2.37 | 5.4 |
| 2.30 | 96.9 | 52.8 | 55.9 | 1623 | 0.9926 | 2.45 | 5.4 |
| 2.40 | 91.5 | 60.5 | 61.8 | 1624 | 0.9923 | 2.57 | 5.4 |
| 2.50 | 90.8 | 68.5 | 68.3 | 1625 | 0.9920 | 2.68 | 5.6 |
| 2.60 | 90.3 | 86.7 | 68.6 | 1625 | 0.9916 | 2.80 | 5.7 |
| 2.80 | 82.0 | 102 | 85.2 | 1629 | 0.9907 | 3.01 | 6.1 |
| 3.00 | 82.4 | 129 | 92.4 | 1624 | 0.9895 | 3.33 | 6.2 |
| 3.50 | 85.7 | 179 | 114 | 1615 | 0.9866 | 4.17 | 6.8 |
| 4.50 | 88.6 | 214 | 149 | 1586 | 0.9791 | 6.09 | 7.7 |
| 5.50 | 94.1 | 161 | 175 | 1546 | 0.9691 | 8.26 | 8.1 |
| | | | (2-*t*-Butoxyethanol) | | | | |
| 1.30 | 114 | 38.2 | 35.3 | 1598 | 0.9953 | 1.61 | 4.4 |
| 1.50 | 87.4 | 112 | 48.8 | 1603 | 0.9943 | 1.77 | 4.6 |
| 1.60 | 83.8 | 166 | 52.1 | 1604 | 0.9938 | 1.84 | — |
| 1.80 | 69.5 | 346 | 72.5 | 1601 | 0.9929 | 2.02 | 5.4 |
| 2.01 | 69.2 | 531 | 90.6 | 1593 | 0.9916 | 2.24 | 6.1 |
| 2.20 | 65.1 | 708 | 110 | 1585 | 0.9901 | 2.39 | 6.5 |
| 2.50 | 65.3 | 824 | 135 | 1571 | 0.9878 | 2.79 | 6.8 |
| 2.80 | 67.5 | 856 | 166 | 1553 | 0.9845 | 2.99 | 7.1 |
| 3.00 | 68.8 | 876 | 163 | 1546 | 0.9827 | 3.14 | 7.6 |
| 3.50 | 71.3 | 784 | 189 | 1519 | 0.9758 | 3.76 | 7.6 |
| 4.00 | 77.9 | 618 | 201 | 1495 | 0.9694 | 4.31 | 7.9 |
| 4.50 | 83.2 | 485 | 198 | 1482 | 0.9623 | 4.86 | 8.3 |
| 5.00 | 83.4 | 359 | 198 | 1447 | 0.9546 | 5.49 | 8.7 |

tion is converted to the molar fraction, $n_e$.

These concentration dependences of the ultrasonic properties, e.g. peak sound absorption concentration and peak sound velocity concentration are characteristic of aqueous solutions of nonelectrolytes with hydroxyl groups. In order to analyze such dependences, various models have been proposed.[9,10] The present authors have also been studying such phenomena on the bases of the experimental facts and only one reasonable mechanism is possible.[3–7] This is expressed by the following reaction.

$$\mathrm{AB} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{A} + \mathrm{B}, \tag{4}$$

where A is the solute, B the solvent and AB a solute solvent complex; $k_f$ and $k_b$ are the forward and backward rate constant respectively. In our model, it is assumed that the solvent water exists in hydrogen bonded and non-hydrogen bonded states, and the latter can participate in the above reaction. The model is similar to that proposed by Andreae et al. (model IV in Ref. 9). Under this assumption, the relation between the analytical concentrations and the relaxation frequency is derived as follows.[5]

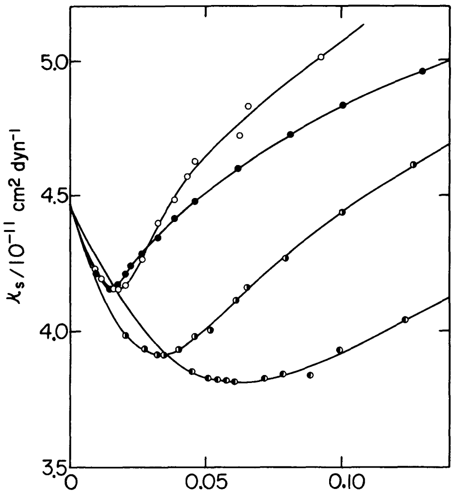

Fig. 6. The concentration dependence of the the adiabatic compressibility for four aqueous solutions. —●—: 2-butoxyethanol, —○—: 2-isobutoxyethanol, —◑—: 2-*t*-butoxyethanol, —○—: 3-methoxy-3-methyl-1-butanol.

$$2\pi f_r = k_b[(C_e - \beta C_w + K_{12})^2 + 4\beta C_w K_{12}]^{1/2}, \tag{5}$$

where $C_w$ the analytical concentration of the solvent, $K_{12}$ the equilibrium constant defined as $K_{12}=k_f/k_b$ and $\beta$ the molar fraction of the non-hydrogen bonded water. It is a good assumption that the parameters, $k_b$, $K_{12}$, and $\beta$ are concentration independent and they are determined so as to obtain the best fit of the experimental relaxation frequencies to Eq. 5. The solid curves in Fig. 4 are those calculated using these parameters and they seem to fit reasonably for both solutions. The $\beta$ parameter is a good measure to estimate the effect of the solute on water structure. These calculated rate and thermodynamic constants are tabulated in Table 2.

The excess absorption amplitude A is related to the volume and enthalpy change of the reaction by the next equation.[11]

$$\mu_{\max} = Af_r c/2 = \pi(\rho c^2\Gamma/2RT)(\Delta V - \alpha_p^\infty \Delta H/\rho C_p^\infty)^2(C_p^\infty/C_p^\circ) \tag{6}$$

where $\mu_{\max}$ is the maximum excess absorption perwave length, $R$ the gas constant, $T$ the absolute temperature, $\Delta H$ the standard enthalpy change of the reaction, $\Delta V$ the standard volume change of the reaction, $\alpha_p^\infty$ the thermal expansibility at high frequency limit, $C_p^\circ$ the specific heat at low frequency, $C_p^\infty$ that at high frequency limit and $\Gamma$ the concentration term which is given by $\Gamma=(1/[\mathrm{AB}]+1/[\mathrm{A}]+1/[\mathrm{B}]-1/[\mathrm{AB}]+[\mathrm{A}]+[\mathrm{B}]))^{-1}$. The most effective terms to control the concentration dependence of the maximum excess absorption per wavelength may be $\rho c^2\Gamma$. Once the equilibrium constant, $K_{12}$, and the $\beta$ value are determined, it is possible to calculate the concentration of the reactants and then the term is obtainable. In Fig. 7, the calculated values of $\rho c^2\Gamma$ for aqueous solution of 3-methoxy-3-methyl-1-butanol are plotted against the concentration along with the experimental results of the maximum excess absorption per wavelength. A similar dependence has also been observed in the solution of 2-*t*-butoxy-

Table 2. The Rate and Thermodynamic Constants for Aqueous Solutions of some Isomers at 25 °C

| Solute | $k_f$ / $10^8$ s$^{-1}$ | $k_b$ / $10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $\beta$ | Ref. |
|---|---|---|---|---|
| $CH_3OC(CH_3)_2CH_2CH_2OH$ | 1.4 ±0.1 | 1.1±0.1 | 0.135 | This work |
| $(CH_3)_3COCH_2CH_2OH$ | 0.90±0.09 | 1.3±0.1 | 0.0975 | This work |
| $CH_3CH_2CH_2CH_2OCH_2CH_2OH$ | 1.1 ±0.1 | 2.0±0.2 | 0.0270 | 4 |
| $(CH_3)_2CHCH_2OCH_2CH_2OH$ | 0.55±0.07 | 2.5±0.3 | 0.0428 | 6 |

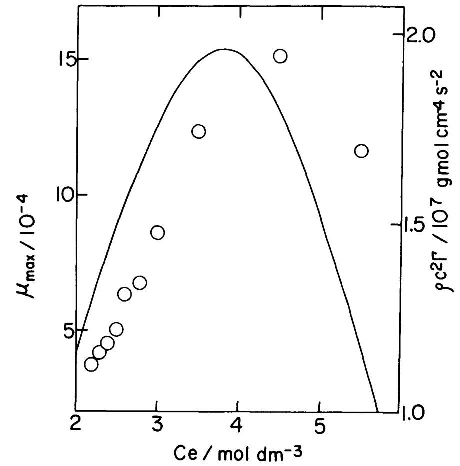

Fig. 7. The concentration dependences of the experimental maximum excess absorption per wave length (left scale) and the calculated $\rho c^2 \Gamma$ (right scale) for aqueous solution of 3-methoxy-3-methyl-1-butanol.

ethanol.

## Discussion

The observed ultrasonic absorption in aqueous solutions of 3-methoxy-3-methyl-1-butanol and 2-*t*-butoxyethanol are characteristic of a single relaxation in the frequency range from 6.5 to 220 MHz. However, in solutions of 2-butoxyethanol[3,4] and 2-isobutoxyethanol[6] which are also isomers, another relaxation has been observed at less than 10 MHz in addition to that observed from the range of 30 to 100 NHz. Such a process has also been predicted by Fanning and Kruus.[12] The slower relaxation has been attributed to the perturbation of the equilibrium associated with the molecular aggregates or microemulsions. Depending upon the structure of the solute or the property, which may be mainly due to the hydrophobicity, a single or double relaxations appear. This is the experimental fact obtained from the frequency dependence of the ultrasonic absorption.

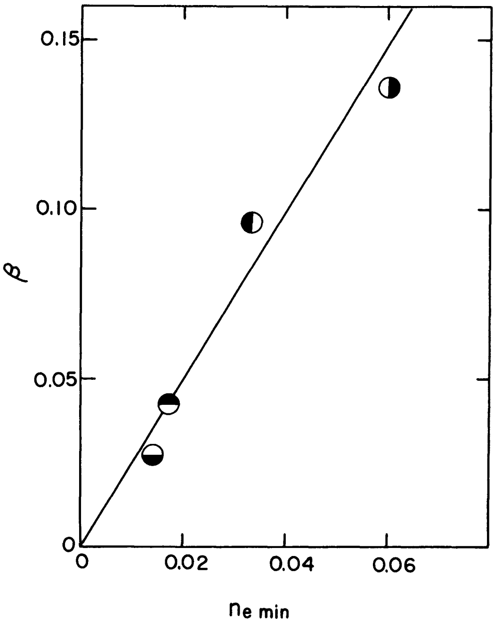

Fig. 8. The correlation between the $\beta$ value and the concentration where the compressibility minimum appears. ◑: 2-butoxyethanol, ◐: 2-isobutoxyethanol, ◓: 2-*t*-butoxyethanol, ◒: 3-methoy-3-methyl-1-butanol.

It has been found that the $\beta$ values which are introduced to interpret the observed relaxation process increase with decreasing hydrophobicity of the solute molecules.[13] The $\beta$ values obtained increase in the series 2-butoxyethanol, 2-isobutoxyethanol, 2-*t*-butoxyethanol and 3-methoxy-3-methyl-1-butanol as is seen in Table 2. Therefore, this series is expected to indicate the order of the hydrophobicity of the solute. The $\beta$ value indicates the fraction of water which can interact with solute molecules or the fraction of the less structured water. The lower this value, the higher the water structure is promoted. Comparing with the $\beta$ value in liquid water,[14] the values obtained are still lower than that in liquid water. This means that the solutes used in this investigation act as the structure promoter to water within the seriese, 2-butyoxyethanol, 2-isobutoxyethanol, 2-*t*-butoxyethanol, 3-methyl-3-methoxy-1-butanol. This fact is also obtained from the analysis of the concentration dependence of the relaxation frequency.

The hydrophobicity of the solute may also influence the concentration dependence of the compressibility. As is seen in Fig. 6, $\kappa_s$ goes through a minimum. The minimum occurs at the lower concentration and the curve is sharper the more hydrophobic the solute. This kind behavior is also seen in the concentration dependence of an apparent molar volume.[15] The series of the concentration where the compressibility shows a minimum or the series of the sharpness of the curve seems to be the same as that of the $\beta$ values. This is the experimental fact obtained from the concentration dependences of the density and the sound velocity.

It is interesting to examine the correlation between these two independent results, that is, the value which is obtained from the absorption data and the behavior of the compressibility which is obtained from the velocity and density data. Figure 8 shows the plots of the $\beta$ values vs. the molar fraction at which the compressibility of the solution indicates a minimum ($n_{e\,\min}$). A linear relationship seems to hold. Comparing the results of the 2-*t*-butoxyethanol solution with that of 3-methoxy-3-methyl-1-butanol, it is seen that the position of the oxygen atom in the molecule may influence the hydrophobicity of the molecules because both the vertical and the horizontal values of the latter solution in Fig. 8 are lower than that of the former. This might be because the *t*-butyl group is bulky when the hydrophobic group of 3-methoxy-3-methyl-1-butanol is compared with that of 2-*t*-butoxyethanol. Murty and Subrahmanyan[16] have reported the structure enhancing efficiency of the isomeric butyl alcohols in the order, *t*-butyl>butyl alcohol from sound velocity studies. However, the present study indicated that 2-butoxyethanol has a more enhancing effect on water structure than 2-*t*-butoxyethanol. Lara and Desnoyers[17] have also investigated the solution properties of 2-butoxyethanol from the solution compressibility and they have found that microemulsions exist in the solution. Their result is consistent with ours which has been estimated from the ultrasonic absorption and velocity results. No previous reports of such a clear correlation between the results of the absorption and the compressibilities in the aqueous solutions are known to the authors.

It has been reported[4,7,13] that the standard volume and enthalpy changes of the reaction may be calculated using Eq. 6 on the assumption that $C_p^\infty/C_p^\circ \cong 1$ and $\alpha_p^\infty/\alpha_p^\circ \cong 1$. In order to estimate the reaction parameters, we have measured the thermal expansibility of both solutions and it is listed in Table 1. If such assumptions for the specific heat and the expansibility were satisfied, the plots of $(\mu_{max}/\rho c^2\Gamma)^{1/2}$ vs. $\alpha_p^\circ/\rho C_p^\circ$ might give a straight line. However, a linear plot has been obtained in a limited concentration range. We considered that the contribution of the relaxational specific heat, $\delta C_p = C_p^\circ - C_p^\infty$, may be important when the reaction parameters, $\Delta V$ and $\Delta H$ are determined simultaneously over such wide concentration ranges. However, it may be concluded that the dominant term which controls the concentration dependence of the maximum excess absorption is clearly $\rho c^2\Gamma$ as is seen in Fig. 6. In order to obtain the quantitative analysis of the concentration dependence of the maximum excess absorption per wavelength in the present two solutions, the experimental specific heat at a constant pressure is required but it is not available in our laboratory.

The effect of the second component, such as salts or surfactants, on the ultrasonic properties in aqueous solutions of nonelectrolytes are interesting in relation to the microemulsion in the solutions. They are now under investigation and the results will be reported in due course.

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