Solute Dependence of Mobility of Solvent Molecules in Solvophobic Solute Solutions: Dielectric Relaxation of Nonpolar Solute/Alcohol Mixtures

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The dielectric relaxation spectra of alcohol/nonpolar solute mixtures are measured at several temperatures (-15 °C $\leq T \leq 25$ °C) and for several molar fractions of solute ($0 \leq X_s \leq 0.114$) in the frequency range of 200 MHz $\leq \nu \leq$ 20 GHz. The double-Debye-type function is used for fitting of the spectra of mixtures, and the mean dielectric relaxation times (τ_{mean}) of alcohol molecules are determined. In the systems having strong interaction between alcohol and nonpolar solutes, τ_{mean} becomes shorter with an increase in the concentration of the solutes. On the other hand, τ_{mean} becomes longer in the system having weak interaction between alcohol and nonpolar solutes. These results contradict with our intuitive predictions, do not correspond to mixing enthalpy, and are not explained by the hydrodynamic theory. They are attributed to the mechanism of the coupling between long-range electrostatic interactions and concentration fluctuation caused by the addition of solutes, which is suggested by Yamaguchi et al. based on the mode-coupling theory (Yamaguchi, T.; Matsuoka, T.; Koda, S. *J. Chem. Phys.* **2004**, *120*, 7590).

Introduction

Water is the most abundant liquid on earth, and it is of great importance in industry, biology, and so on. In addition, there are several properties of water that are rarely found in other liquids. For example, the specific volume of water is largest at 4 °C, whereas the volume of most liquids is an increasing function of temperature. Therefore, water has long attracted many researchers in chemistry and physics, and a lot of studies have ever been performed on water. In addition to pure water, aqueous solutions, especially those of hydrophobic solutes, have ever been investigated. In biology, for example, membranes and proteins have many hydrophobic groups, so studies on hydrophobic solute solutions are important to understand the structures and functions of biological molecules in water.

The dynamics of water in many hydrophobic solute solutions has been measured so far, and it has been reported that the mobility of a water molecule slows down in comparison with pure water.[1,2] It contradicts with our intuition that the mobility of water molecules is decreased by solutes having weak interaction with water. The reduction of the mobility of water molecules in hydrophobic solute solutions has been elucidated by the formation of the hydrophobic hydration shell like the clathrate structure around the solutes in which hydrogen-bondings between solvents are enforced, which prevents the rotational motion of the solvent.[3,4] The clathrate-like structure was in fact originally proposed to elucidated the thermodynamic properties of hydration,[5] where the dissolution of hydrophobic molecules into water is accompanied by both the enthalpic and entropic loss.[2]

On the other hand, in the case of mixtures of alcohol solvents and nonpolar solutes, several examples for the decrease of the mobility of alcohol molecules in solvophobic solute solutions are reported.[6−10] Alcohol molecules do not form a tetrahedral hydrogen-bond network like water, and a chain-type hydrogen-bonding is suggested in some literatures.[11−18] Therefore, it is impossible to attribute the decrease in the mobility of solvent alcohol molecules with the addition of solvophobic solutes to the formation of a clathrate-like solvophobic-shell-like aqueous solution. In addition, if the variation of the mobility of the alcohol molecules in solvophobic solute solutions was explained by structure formation as water, then the tendency similar to water would appear in the thermodynamic quantity.

As for the hydrophobic solute solutions, Yamaguchi et al. revealed that the coupling between the density fluctuation arising from cavity formation by the solute and the electrostatic interactions between solvent molecules leads to the decrease in the mobility of water molecules based on the analysis using mode-coupling theory.[19] This mechanism does not require a tetrahedral hydrogen-bonding network. Therefore, we consider that the same mechanism can also be applied to the decrease in the mobility of solvent molecules in a solvophobic solute solution of alcohols.

In this work, we measure the dielectric relaxation of the mixtures of alcohols and nonpolar solutes. The alcohols we use are methanol and ethanol, and the solute−solvent interaction is varied in a systematic way, so as to clarify its effect on the mobility of solvent molecules. The temperature is varied from −15 to 25 °C for typical solutions in order to deduce the activation energy. The researches on hydrophobic solute solutions have been performed with some experimental methods as NMR,[20−22] X-ray analysis,[22] calorimetry,[5,23] and dielectric relaxation measurement.[1,24] Dielectric relaxation is one of the most fundamental methods for measuring dynamics of polar solutions and is a suitable method for the measurement of the collective reorientation of polar molecules.

Experiment

Cyclohexane, carbon tetrachloride (CCl_4), benzene, 1,4-dioxane, and pyrazine are chosen for solutes to vary solute−solvent interaction in a systematic way by keeping the sizes of

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the solutes close to each other. Methanol and ethanol are employed as solvents. All the solute molecules are nonpolar, to exclude the contribution of the dipole moment of the solute to the dielectric spectrum. Methanol, ethanol, cyclohexane, benzene, and *N*,*N*-dimethylformamide (DMF) (spectroscopic grade except for DMF (granted grade)) are purchased from Wako Chemicals. CCl_4 (99.9%), 1,4-dioxane (99.8%, anhydrous), pyrazine (99%), and propylene carbonate (PC, 99.7%, anhydrous) are obtained from Sigma-Aldrich. Methanol, ethanol, and DMF are dried by molecular sieves 3A (Wako Chemicals) before use, and other chemicals are used as received. We have confirmed by Karl Fischer titration that the water concentrations of methanol, ethanol, benzene, DMF, and PC are less than 0.1 wt %. The concentration of the solutes in the sample is $0 \leq X_s \leq 0.114$, where X_s stands for the molar fraction of solute.

The microwave equipment used in this work is described elsewhere,[25] which is composed of a vector network analyzer (Hewlett-Packard HP8720D, whose nominal bandwidth is from 50 MHz to 20 GHz) and a dielectric probe kit (Hewlett-Packard HP85070B, whose recommended bandwidth is from 200 MHz to 20 GHz). The dielectric spectra are measured from 200 MHz to 20 GHz. The temperature of the system is varied from −15 to 25 °C. The sample solution is contained in a glass cell with a water jacket through which the thermostated coolant liquid flows. The temperature of the solution is measured by a thermistor, and it is confirmed that the temperature is controlled within ±0.1 °C. A sealed cell is used for the measurement at the temperature lower than the ambient one, and dry nitrogen gas is purged into the cell, to avoid the absorption of moisture in the air. For the standard samples for the calibration of the dielectric measurement, we employ air, water, and methanol at $T > 0$ °C and air, PC, and methanol at $T < 0$ °C. The calibration data of methanol at 25 °C is taken from literature,[26] and those at other temperatures are determined by ourselves, with the standard samples of air, PC, and water at $T > 0$ °C and air, PC, and DMF at $T < 0$ °C. The data of water, PC, and DMF are taken from refs 27, 28, and 29, respectively. The viscosities of the mixtures are measured with a Ubbelohde viscometer at 25 ± 0.1 °C.

Results and Discussion

A. Spectra and Relaxation Times of the Mixtures. The complex dielectric spectra of pure methanol and methanol/nonpolar solute mixtures, $\epsilon^*(\nu)$, at 25 °C and $X_s = 0.06$ are displayed in Figure 1, where ν stands for the frequency. $\epsilon'(\nu)$ and $\epsilon''(\nu)$ represent the real and imaginary parts of $\epsilon^*(\nu)$, respectively. The peak of $\epsilon''(\nu)$ shifts to lower frequency with the addition of cyclohexane, whereas it shifts to the other direction when 1,4-dioxane is added. The variation of the relaxation time by solutes is qualitatively recognized in Figure 1, since the inverse of the peak frequency of $\epsilon''(\nu)$ corresponds to the relaxation time. The dielectric relaxation time of methanol is increased by cyclohexane, while it is decreased by 1,4-dioxane.

To analyze the solute dependence of the relaxation time quantitatively, the measured spectra are fitted into the double-Debye-type relaxation function represented by eq 1. From the optimized values of τ_1 and τ_2, the mean dielectric relaxation time, $\tau_{\rm mean}$, is determined by eq 2.

$$\epsilon^*(\nu) = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_1)}{1 + 2\pi i\nu\tau_1} + \frac{(\epsilon_1 - \epsilon_\infty)}{1 + 2\pi i\nu\tau_2} \qquad (1)$$

$$\tau_{\rm mean} = \frac{\{\tau_1(\epsilon_0 - \epsilon_1) + \tau_2(\epsilon_1 - \epsilon_\infty)\}}{\epsilon_0 - \epsilon_\infty} \qquad (2)$$

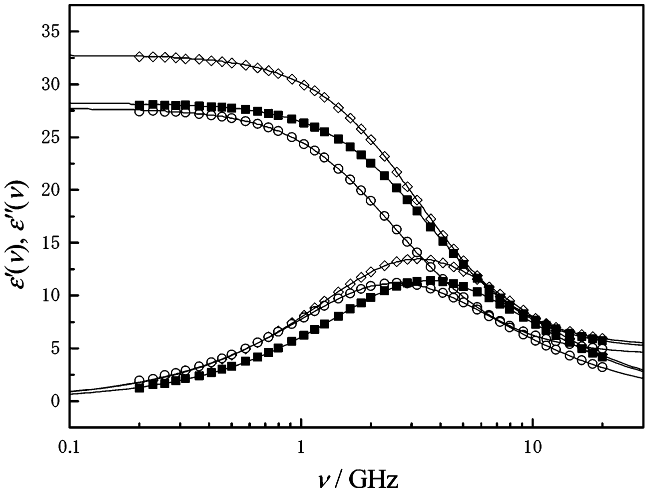

Figure 1. Dielectric dispersion [$\epsilon'(\nu)$] and loss [$\epsilon''(\nu)$] spectra of methanol/nonpolar solute ($X_s = 0.06$) mixtures at 25 °C. The solutes are cyclohexane (○) and 1,4-dioxane (■). The spectrum of pure methanol is also plotted as diamonds (◇) for comparison. The solid curves represent the fitting by eq 1.

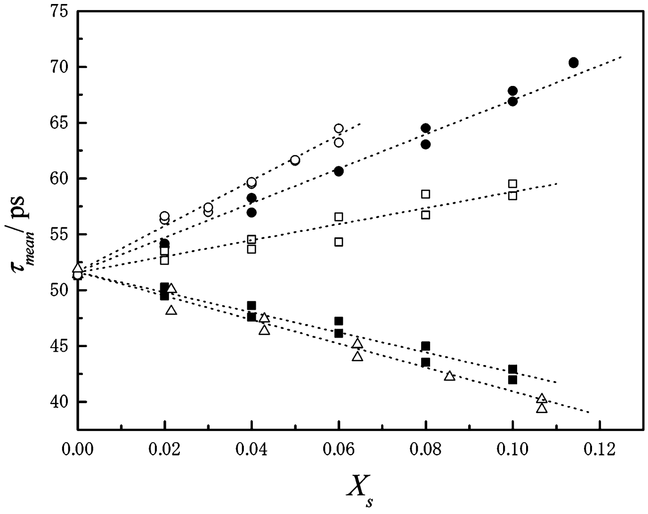

Figure 2. Mean relaxation time [$\tau_{\rm mean}$] of the methanol/nonpolar solute mixtures against the molar fraction of solute [X_s] at 25 °C. The solutes are cyclohexane (○), CCl_4 (●), benzene (□), 1,4-dioxane (■), and pyrazine (△). The dotted lines represent the fitting by the linear function, from the slope of which B_X coefficients are determined.

ϵ_0 and ϵ_∞ are the dielectric constants at low- and high-frequency limits, respectively. $\epsilon_0 - \epsilon_1$ and $\epsilon_1 - \epsilon_\infty$ are the relaxation amplitudes of the slower and faster steps, respectively. They are treated as free parameters in the fitting procedure. The estimation of ϵ_∞ is essential for the detailed discussion of the relaxation processes in the high-frequency range. However, we consider that it has little effect on the mean relaxation time defined by eq 2. As is observed in Figure 1, curves and symbols are in good agreement with each other, which indicates that the fitting procedure is adequately performed.

The values of $\tau_{\rm mean}$ of methanol/nonpolar solute mixtures at 25 °C are displayed in Figure 2. All mixtures are measured twice at each concentration, and both values are plotted. The data of CCl_4 (●) and 1,4-dioxane (■) are in good agreement with those of Buchner and Barthel[6] and Mashimo et al.,[30] respectively. According to a chemical intuition, the order of strength of interaction with alcohol is thought to be cyclohexane < CCl_4 < benzene < 1,4-dioxane < pyrazine. In Figure 2, the relaxation times become shorter in the same order, which represents that the decrease in the mobility of solvent molecules by the solute having a weak solute−solvent interaction is observed not only in aqueous solution of organic solutes but also in methanol/

TABLE 1: B_x Coefficient of the Dielectric Relaxation Time of Methanol/Nonpolar Solute Mixtures at 25 and −15 °C

solute	25 °C	−15 °C
cyclohexane	3.8	5.3
CCl_4	3.0	3.6
benzene	1.4	1.7
1,4-dioxane	−1.7	−3.4
pyrazine	−2.2	−4.4

nonpolar solute mixtures. The relaxation time of mixtures is shorter than that of pure methanol, when the solute has a strong interaction with the solvent in the case of methanol/nonpolar solute mixtures. In the case of aqueous solutions, the retardation effect on the relaxation time becomes smaller when the solute−solvent interaction is stronger,[1] as is observed in methanolic mixtures, but it is rarely found for neutral organic solute molecules that the relaxation time of mixtures becomes faster than that of pure water. Our results mean that the mobility of methanol molecules becomes larger when solutes have a stronger solute−solvent interaction, in contradiction with our intuitive prediction. For subsequent discussion, we evaluate B_X coefficients of mixtures defined by the following equation from the slope of the plots in Figure 2.

$$\tau_{\mathrm{mixture}}/\tau_{\mathrm{methanol}} = 1 + B_X \cdot X_S + \cdots\cdots \qquad (3)$$

Analyzing Figure 2, the solute dependence of the dielectric relaxation time is linear on each solute. It means that τ_{mean} is described by the B_X coefficient well and the effect of the correlation among the solutes is not observed. The estimated B_X coefficients at 25 °C are shown in the central column of Table 1.

The values of τ_{mean} of ethanol/nonpolar solute mixtures at 25 °C are shown in Figure 3. Cyclohexane has the weakest solute−solvent interaction, while pyrazine has the strongest one in a similar way to methanol/nonpolar solute mixtures. Figure 3 indicates the variation of the relaxation time similar to that of methanol. Comparing Figure 2 with Figure 3, we found that the solute dependence of τ_{mean} in ethanol/nonpolar solute mixtures is weaker than that in methanol/nonpolar solute mixtures when the solutes have a weak interaction with solvent and the opposite trend is observed when the solute−solvent interaction is strong. From Figures 2 and 3, we found that the decrease in the mobility of solvent molecules caused by the solutes having a weak solute−solvent interaction is not limited to water but found in hydrogen-bonding solvents as water or alcohol in general.

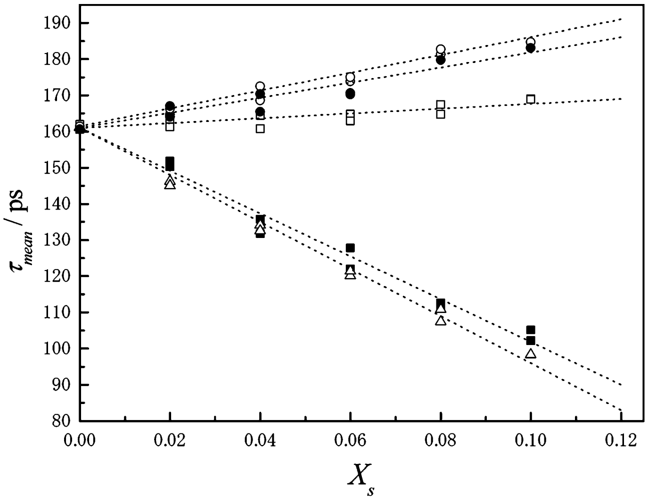

Figure 3. Mean relaxation time [τ_{mean}] of ethanol/nonpolar solute mixtures against the molar fraction of solute [X_s] at 25 °C. The symbols and lines are the same as those in Figure 2.

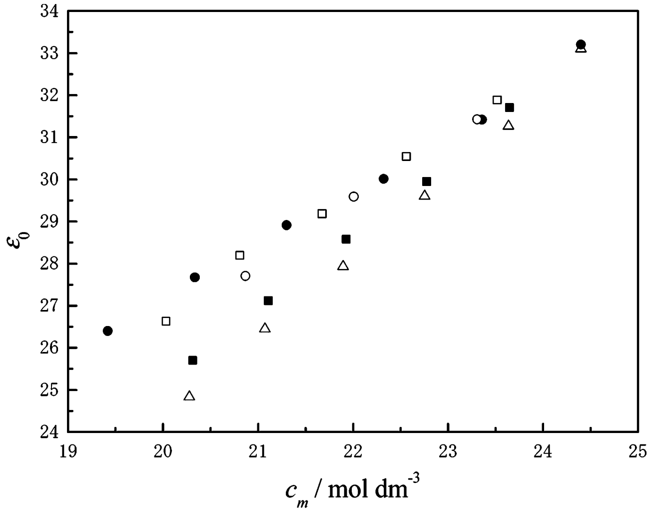

Figure 4. Static dielectric permittivity [ϵ_0] of methanol/nonpolar solute mixtures against methanol concentration [c_m] at 25 °C. The symbols are the same as those in Figure 2. The points at $c_m = 24.4$ mol dm^{-3} represent the neat methanol.

B. Static Permittivity. As discussed in the Introduction, the mechanism of the decrease in the mobility of solvent molecules in water/hydrophobic solute mixtures with the addition of hydrophobic solutes has been elucidated by the formation of the hydrophobic hydration shell like the clathrate structure around the solutes. However, since alcohol molecules do not form a tetrahedral structure such as water, the same discussion cannot explain the decrease in the mobility of solvent molecules in alcoholic mixtures. Moreover, it cannot explain the increase in the mobility of solvent molecules with the addition of solutes having a strong solute−solvent interaction, either.

Since the dielectric relaxation expresses the relaxation of collective electric polarization, the dielectric relaxation time is influenced by the following two factors. One is the static contribution which means the correlation of the equilibrium fluctuation between the dipole moments of individual molecules. The other is the dynamic contribution which represents the friction on molecular reorientation. The former is expressed by a g factor, which is reflected in ϵ_0. The relaxation time becomes longer as the g factor becomes larger according to the theory of Madden and Kivelson.[31] Therefore, the variation of ϵ_0 is a good measure of the static factor.

Figure 4 indicates ϵ_0 of methanol/nonpolar solute mixtures at 25 °C. There are three contributions in ϵ_0, that is, the strength of the dipole moment of individual molecules, the number density of the molecules having the dipole moment, and the g factor. Under the assumption that the dipole moment of alcohol molecules do not change with the addition of solutes, the difference in the static permittivity at the same concentration of methanol can be identified as the difference in the g factor that represents the static correlation among the dipole moments of methanol, because only methanol molecules have a dipole moment in the system. In Figure 4, the values of ϵ_0 have the solute dependence, that is, the values of ϵ_0 of 1,4-dioxane and pyrazine are a little smaller. However, the difference is not so large as to explain that of the dielectric relaxation time. Therefore, the factor dominating the solute dependence of the dielectric relaxation time is not the static but the dynamic one.

C. Viscosity of Mixtures. According to the Stokes−Einstein−Debye equation derived from hydrodynamic consider-

TABLE 2: Viscosity B_X Coefficient of the Alcoholic Mixtures at 25 °C[a]

solute	B_X
cyclohexane[b]	0.8
CCl_4[c]	0.9
benzene[d]	0.1
1,4-dioxane[e]	0.2
pyrazine	0.3

[a] The viscosity of the pyrazine solution is determined in our present work, and all the others are determined by refs 32, 33, 34, and 35. [b] Determined from the data in ref 32. [c] From ref 33. [d] From ref 34. [e] From ref 35.

ation, the variation of the viscosity of mixed liquid corresponds to that of the dielectric relaxation time if the reorientation of methanol is treated in a hydrodynamic manner. Therefore, the viscosities of solutions are focused in this subsection. Combining the data of our work with the literatures,[32−35] we determine the solute concentration dependence of the viscosity of methanol/nonpolar solute mixtures, which is linear in this concentration range, and converted into the B_X coefficient defined by the following equation.

$$\eta_{\text{mixture}}/\eta_{\text{methanol}} = 1 + B_X \cdot X_S + \cdots\cdots \qquad (4)$$

η_{mixture} and η_{methanol} denote the viscosities of mixed solutions and neat methanol, respectively. The results are summarized in Table 2. If the dielectric relaxation time can be treated hydrodynamically, then the viscosities decrease with the addition of the solute in the strong solute−solvent interaction system and vice versa. That is, the values of the B_X coefficient of Tables 1 and 2 have to correspond with each other. However, the correspondence between the viscosity and the dielectric relaxation time we expected is not observed at all. Therefore, we consider that the hydrodynamic treatment expressed by the Stokes−Einstein-Debye equation is not suitable for the present systems.

D. Temperature Dependence. When nonpolar solutes are dissolved into water, the mixing enthalpy is positive, the mobility of water decreases, and its activation energy increases.[1,5] It has long been considered that we can explain these observations based on the idea of “structure formation” such as the formation of a hydrophobic hydration shell in a consistent manner.

For alcohol, the heat of dissolution with the addition of CCl_4 to methanol is slightly positive,[36] so that a similar idea may be applicable. However, the mixing of methanol with cyclohexane, benzene, or 1,4-dioxane is endothermic.[10,37−40] As we have shown above, the dielectric relaxation time increases with the addition of solvophobic solutes into methanol. It indicates that the consistency between the thermodynamics and the dielectric relaxation time claimed for the hydrophobic hydration is not observed in alcoholic solutions. Therefore, we measure the temperature dependence of the dielectric relaxation time for methanol/nonpolar solute mixtures to know how the activation energies for alcohol systems behave.

The Arrhenius plots of the ratio of the dielectric relaxation time against the temperatures for methanol/cyclohexane or 1,4-dioxane mixtures are shown in Figure 5. τ_{mixture} is the value of τ_{mean} of mixtures at each temperature and τ_{methanol} is the value of τ_{mean} of pure methanol at the corresponding temperature. Cyclohexane is chosen as the example of the systems for which τ_{mean} increases with the addition of solute at 25 °C and 1,4-dioxane is chosen as that for other trends. From Figure 5, it is found that the ratio of $\tau_{\text{mixture}}/\tau_{\text{methanol}}$ increases with the decrease of the temperature for cyclohexane mixtures and it decreases for 1,4-dioxane. In other words, the temperature dependence of $\tau_{\text{mixture}}/\tau_{\text{methanol}}$, irrespective of its sign, becomes strong with the addition of the solute in the case of both 1,4-dioxane and cyclohexane.

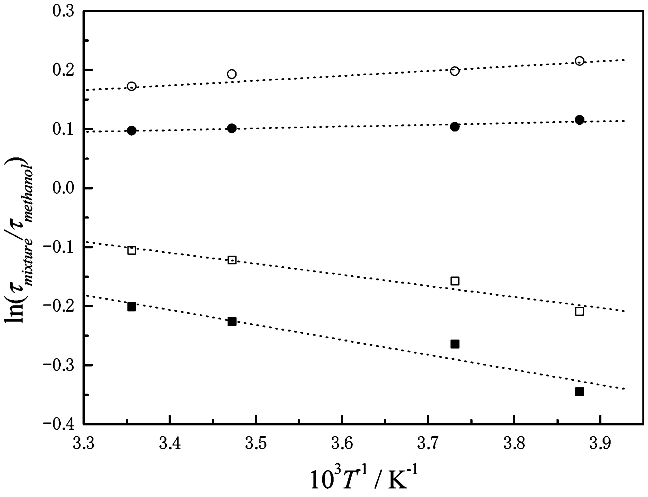

Figure 5. Plots of $\ln(\tau_{\text{mixtures}}/\tau_{\text{methanol}})$ against T^{-1}. The symbols represent experimental values: (○) cyclohexane, $X_s = 0.06$; (●) cyclohexane, $X_s = 0.03$; (□) 1,4-dioxane, $X_s = 0.06$; (■) 1,4-dioxane, $X_s = 0.10$. The dotted lines represent the slope of the Arrhenius plot of each mixture.

TABLE 3: Difference of Activation Energy [$\Delta H_m^{\ddagger E}$] of Methanol/Nonpolar Solute Mixtures with that of Neat Methanol from Figure 5

solute	mole fraction of solute	$\Delta H_m^{\ddagger E}$/kJ mol^{-1}
cyclohexane	$X_s = 0.06$	0.7
cyclohexane	$X_s = 0.03$	0.2
1,4-dioxane	$X_s = 0.06$	−1.5
1,4-dioxane	$X_s = 0.10$	−2.1

The value of the difference between the activation energy of mixture and that of pure methanol denoted as $\Delta H_m^{\ddagger E}$ is decided as the slopes of the Arrhenius plots in Figure 5, which is summarized in Table 3. The value of $\Delta H_m^{\ddagger E}$ is positive in cyclohexane mixtures and negative in 1,4-dioxane ones. On the other hand, the mixing of methanol with cyclohexane or 1,4-dioxane is endothermic within the concentration range studied here.[39,40] Therefore, the activation energy is not correlated with the heat of mixing, and the solute dependence of the dielectric relaxation time of mixtures is not explained in terms of the thermodynamics of mixing. It has been reported that the idea of “structure formation” has the consistency in the aqueous solution. However, the consistency claimed this does not extend to alcoholic solutions. The correlation among mixing enthalpy, activation energy, and dielectric relaxation time is quite different in water and alcohol. Therefore, we cannot give a unified explanation to the thermodynamic and dynamic quantities if we discuss water and alcohol at the same time.

We have discussed the solute dependence of the dielectric relaxation time of the mixtures in various ways so far, based on the static correlation of dipole moments, hydrodynamic theory, and the correlation with thermodynamic quantities, but none of them gives a good insight.

The values of τ_{mean} of methanol/nonpolar solute mixtures at −15 °C are shown in Figure 6. The observed solute dependence is similar to that in Figure 2. The ratios of τ_{mixture} and τ_{methanol} at 25 and −15 °C are shown in Figure 7. The effect of the addition of solutes at −15 °C is larger than that at 25 °C in Figure 7. For quantitative discussion, we evaluate the B_X coefficients of mixtures for −15 °C defined by eq 3 from the

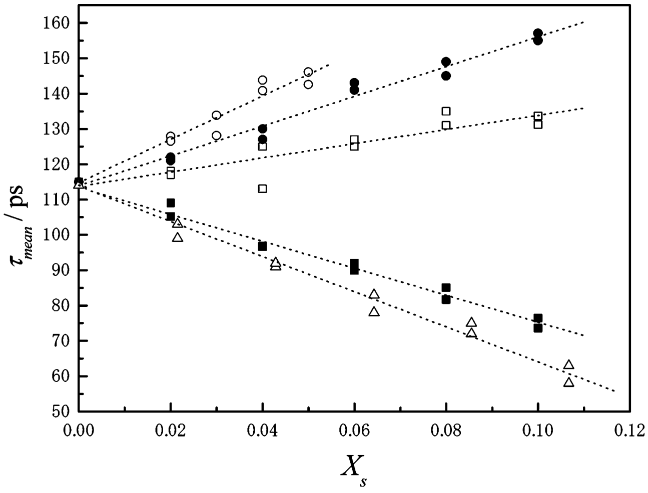

Figure 6. Mean relaxation time [τ_{mean}] of methanol/nonpolar solute mixtures against the molar fraction of solute [X_s] at −15 °C. The symbols and lines are the same as those in Figure 2.

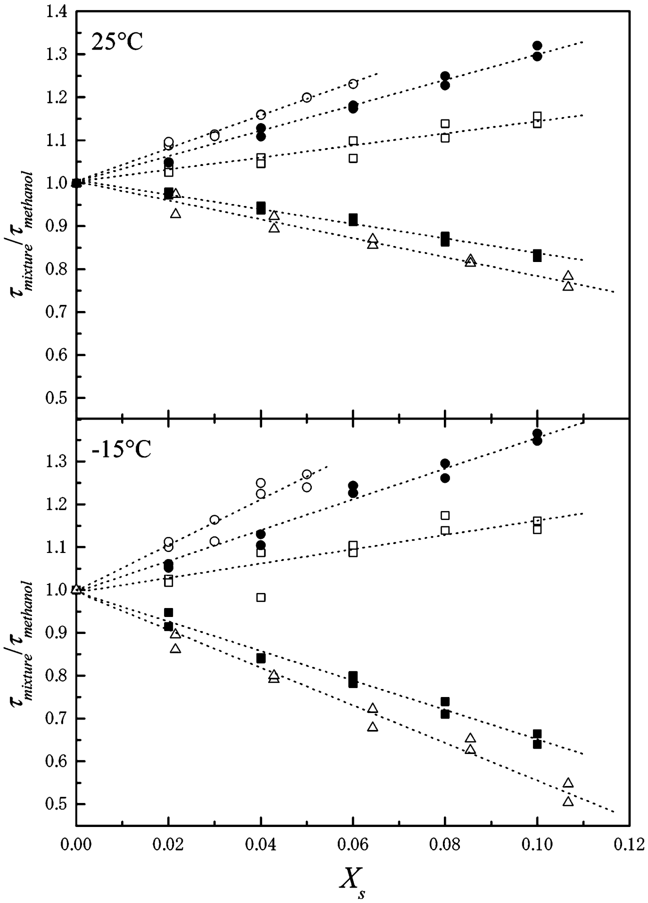

Figure 7. Plots of $\tau_{\mathrm{mixtures}}/\tau_{\mathrm{methanol}}$ against the molar fraction of solute [X_s]. The symbols and lines are the same as those in Figure 2.

slopes of the plots in Figure 7. The estimated B_X coefficients are shown in the right column of Table 1. These results indicate that the absolute values of the B_X coefficient become larger when the temperature becomes lower. In other words, the concentration dependence is amplified at low temperature. It suggests that the solute concentration dependence of the dielectric relaxation time of methanol/nonpolar solute mixtures is an energy-dominated phenomenon, that is, the change of the dielectric relaxation time is related to that of the activation energy, if we assume that the dielectric relaxations the activation process.

The energy dominance is in harmony with the mechanism of the dynamics of hydrodynamic hydration proposed by Yamaguchi et al.[19] In their mechanism, the increase in the fluctuation of the number density of solvents caused by the cavity formation due to the solute leads to the increase of electrostatic friction on the dielectric mode, which reduces the mobility of water molecules in the hydrophobic solution. Since the mechanism proposed by Yamaguchi et al. does not require the structure specific to aqueous solutions, it can be applied also to solvophobic solutions in general, and it explains the energy dominance as is demonstrated in Table 2, because the reduction of mobility of the solvent is caused by the electrostatic interaction. The dependence of the solvent mobility on the solute−solvent interaction in their mode-coupling theory of aqueous solutions also corresponds to that of the present experimental results for alcohols.

Conclusions

In alcohol/nonpolar solute mixtures, we found that the dielectric relaxation time of alcohol molecules becomes longer with the addition of the solute in a weak solute−solvent interaction system and becomes shorter in a strong interaction system. The solute dependence of the value of ϵ_0 is not like the dielectric relaxation time, which means that the variation of the dielectric relaxation time is caused not by the static contribution but by the dynamic one. In addition, the correlation between the viscosity and the dielectric B_X coefficients is not observed. This result indicates that we cannot explain the solute dependence of the dielectric relaxation time by the hydrodynamic theory.

The dielectric relaxation time, the activation energy, and the mixing enthalpy of alcohol/nonpolar solute mixtures are compared with those of aqueous solutions of hydrophobic solute. For alcohol solvent systems, the dielectric relaxation times are increased by the addition of solute with a weak solute−solvent interaction, the mixing enthalpy is positive in most cases, and the change in the activation energy is positive and negative for solvophobic and solvophilic solutes, respectively. For an aqueous system, on the other hand, the dielectric relaxation times increase with the addition of hydrophobic solutes, the heat of dissolution is negative, and the change of the activation energy is positive. Therefore, the simultaneous explanation of the thermodynamic and dynamic quantities is impossible, if we discuss water and alcohol at the same time.

The solute concentration dependence of the dielectric relaxation time is enhanced by decreasing temperature. This result indicates that the solute concentration dependence of the dielectric relaxation time of methanol/nonpolar solute mixtures is energy dominating, in harmony with the conclusion of theoretical calculation by Yamaguchi et al. that the increase in the fluctuation of the number density of solvents caused by the cavity formation due to the solute leads to the increase of electrostatic friction on the dielectric mode, which reduces the mobility of water molecules in the hydrophobic solution. The mechanism suggested by Yamaguchi et al. may apply not only to the hydrophobic solute solutions but also to solvophobic solute solutions in general.

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