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NMR Study on the Reorientational Relaxation in Supercritical Alcohols

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The single-molecular reorientational relaxation of supercritical deuterated methanol and ethanol is studied by the ^{2}H nuclear magnetic resonance spin−lattice relaxation measurement, and the results are compared with the corresponding study on supercritical water (Matubayasi, N.; Nakao, N.; Nakahara, M. *J. Chem. Phys.* **2001**, *114*, 4107). The relaxation times of the OD deuterons of both alcohols show significant increase when they are transferred from liquid to supercritical phases. The reorientational relaxation of the OD vector is thus largely enhanced in the supercritical phase, as is the case of water. The relative increase in the reorientational relaxation rates of alcohols with density is larger than that of water. It indicates that the reorientational motion of supercritical alcohols is more diffusive than that of water. The molecular dynamics simulation of the supercritical methanol is also performed, and the results are consistent with experimental ones. The reorientational relaxation of two deuterated solute molecules, benzene (C_6D_6) and pyrazine ($C_4D_4N_2$), is studied in supercritical methanol in addition to the neat fluid. The density dependence of the ^{2}H spin−lattice relaxation rates of methanol, benzene, and pyrazine in supercritical methanol show a minimum. The density of the minimum relaxation rate decreases with increasing solute−solvent interaction, which can be explained in terms of the angular-momentum relaxation time.

I. Introduction

Supercritical fluids have been regarded as one of the promising solvents for industrial use for the past decades.[1] Some of the supercritical fluid technologies are currently in use, such as the supercritical fluid synthesis, treatment, extraction, and chromatography. We consider, however, that further development of the supercritical technology will require detailed knowledge on how the intermolecular interaction behaves in the supercritical phase to reveal itself as macroscopic quantities.

The reorientational relaxation is one of the sensitive probes of the intermolecular interaction, which can be measured by Raman, depolarized scattering, NMR, and so on. So far, a number of studies on the reorientational relaxation of neat supercritical fluids have been performed.[2−6] In most cases, the time-integrated reorientational relaxation time (τ_{2R} in the case of NMR and Raman spectroscopy) is weakly dependent on density, having a shallow minimum around the critical density. On the other hand, the relaxation time of the angular momentum (τ_J) is a strong function of density, in accordance with that of the time dependence of the reorientational correlation function. Therefore, it has already been revealed that the apparent insensitiveness of τ_{2R} to density is the result of the transition between diffusive and inertial regimes.[3,4,6]

Recently, Matubayasi et al. reported the single-molecular reorientational relaxation time of heavy water (D_2O) by the ^{2}H NMR spin−lattice relaxation measurement.[2] They demonstrated that τ_{2R} is greatly reduced in the supercritical phase (several tens of fs) compared with that in ambient condition (∼1 ps). Moreover, they also showed that τ_{2R} is a weakly increasing

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function of density in the medium- and high-density regions, and it has a minimum below the one-third of the critical density, which is smaller than those for other fluids.

Since alcohols have the same characteristics with water in that the strong hydrogen bonding exists between molecules, the study on supercritical alcohols is useful in order to realize how the intermolecular hydrogen-bonding interaction appears in the supercritical phase. In addition, supercritical alcohols are currently of certain industrial importance in themselves. The equilibrium structures of supercritical alcohols have therefore been studied extensively by NMR, Raman, infrared, X-ray, and neutron spectroscopies.[7−14]

In this work, we will present our experimental data on the ^{2}H NMR relaxation rates of two alcohols, methanol (CD_3OD) and ethanol (C_2D_5OD), in the supercritical phase. Although the ^{1}H NMR relaxation rates of supercritical alcohols have already been reported,[7,15] their analysis is not easy due to the complicated relaxation mechanisms of the proton. On the other hand, the relaxation mechanism of deuteron is usually simpler because of the dominance of the nuclear quadrupolar mechanism. Since the reorientational relaxation is considered to be a good probe of the intermolecular hydrogen-bonding interaction, it is interesting to investigate how the reorientational relaxation of supercritical alcohols differs from that of supercritical water.

In addition, we perform experiments on the reorientational relaxation of two solute molecules, benzene (C_6D_6) and pyrazine ($C_4D_4N_2$), in supercritical methanol; the former does not have a hydrogen-bonding ability, while the latter does. By comparison of the density dependence of τ_{2R} of the three molecules involving different solute−solvent interaction, we can show how the hydrogen bonding appears in the reorientational relaxation in the supercritical fluids.

II. Experiment

The measurement of the ^{2}H NMR spin−lattice relaxation rate in the high-temperature, high-pressure fluid is described elsewhere.[2] Briefly, the sample alcohol is sealed into a quartz capillary at ambient condition, and the capillary is placed in a NMR sample tube. The size of the quartz capillary is typically i.d. 0.7 mm and o.d. 1.5 mm. The larger capillary, i.d. 1.5 mm and o.d. 2.5 mm, is also used in the low-density region, and it is confirmed that the effect of the capillary size is negligible at the intermediate density. The NMR tube is heated by hot nitrogen gas, and the temperature is controlled within ±5 K. All the measurements in the supercritical phase are performed at 543 K, well above the critical temperatures of methanol (513 K)[16] and ethanol (516 K).[17] The relaxation time of the neat fluid is also measured on the liquid branch of the liquid−gas coexistence line (saturation line). The density of the fluid in the supercritical phase is determined from the packing fraction at the ambient condition, and that on the saturation line is taken from the literature.[16,17] To measure the relaxation rates of the solutes, the methanol solution of 0.55 and 0.50 mol/dm^3 for benzene and pyrazine, respectively, is prepared at the ambient condition and then sealed into the capillary. The mole fraction of the solute is fixed, and the effect of solute−solute interaction is not taken into account in the discussion. The ^{2}H signal is measured by the multipurpose NMR spectrometer (JEOL EX-270 wide bore type), and the spin−lattice relaxation time is determined by the inversion−recovery method.

The deuterated alcohols for the measurements of pure alcohols, methanol-d_4 (CD_3OD, 99% D) and ethanol-d_6 (C_2D_5OD, 99% D), are purchased from CEA and used as received. Benzene solution is prepared by dissolving benzene-d_6 (C_6D_6, 99.9% D, CEA) into the light methanol (CH_3OH, Nacalai Tesque, spectroscopic grade). The former is used as received, and the latter is dried by the molecular sieves. Pyrazine-d_4 ($C_4D_4N_2$, 99.6% D, CDN) solution is prepared from the pyrazine and methanol-d_1 (CH_3OD, 99% D, CEA) in order to avoid the H−D exchange reaction of the pyrazine. In this case, both reagents are used without further purification or drying. The NMR spectrum of the sample does not change before and after the measurement of the spin−lattice relaxation rate, which ensures that the slight thermal decomposition of pyrazine under the high-temperature condition does not affect the NMR measurement.

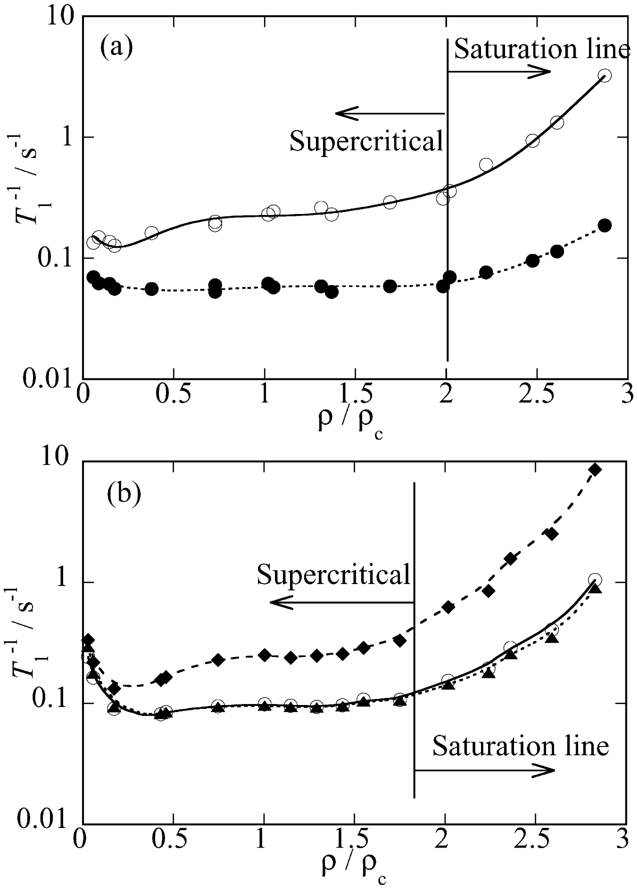

Figure 1. ^{2}H NMR spin−lattice relaxation rates (T_1^{-1}) of (a) methanol (CD_3OD) and (b) ethanol (C_2D_5OD) plotted against density (ρ) divided by their respective critical density (ρ_c). The symbols at the left side of the vertical lines denote the relaxation rates in the supercritical phase at 270 °C, and those at the right side show the relaxation rates on the liquid branch of the coexistence line. In (a), the open and filled circles stand for the relaxation rates of the deuterons of the OD and CD_3 groups, respectively. The temperature on the saturation line is, from right to left, 30, 100, 130, 175, and 200 °C, respectively. In (b), the relaxation rates of the deuterons of CD_3, CD_2, and OD groups are shown as the open circles, filled triangles, and filled diamonds, respectively. The temperature on the saturation line is, from right to left, 30, 100, 150, 170, and 200 °C, respectively. The curves in both figures are drawn simply for eye guides.

III. Results

III.A. Neat Alcohols. The ^{2}H NMR spin−lattice relaxation rates, T_1^{-1}, of CD_3OD and C_2D_5OD are shown in parts a and b of Figure 1, respectively, as functions of the density divided by their respective critical densities, ρ_c.[16,17] The effect of deuteration on the number-density-based equation-of-state is neglected. The relaxation rates of all the nuclei are reduced in the supercritical region compared with those under the ambient conditions. The relaxation rates increase with decreasing density at the density below $0.2\rho_c$. Such a behavior resembles that reported by Matubayasi et al. for supercritical water.[2] By comparison of the relaxation rates of the deuterons of hydroxyl and alkyl groups, the density dependence of the former is much larger than that of the latter. The relaxation rates of the hydroxyl deuterons agree well with previous literatures at 30 °C.[18,19]

Since the deuteron nucleus has a quadrupole moment, the spin−lattice relaxation of the deuteron is usually dominated by the nuclear quadrupolar mechanism. Indeed, the dominance of the quadrupolar mechanism is proven in ref 2 for supercritical water and is expected to be valid for the hydroxyl deuterons of alcohols since they have larger relaxation rates. In the nuclear quadrupolar mechanism, the nucleus with the quadrupolar moment interacts with the electric field gradient produced by the asymmetry of the electronic distribution due to chemical bonds. Since the nuclear quadrupolar moment is dependent on the nuclear spin state, the latter is also coupled to the electric field gradient, which fluctuates according to the thermal reorientational motion of the molecule. The reorientational motion of the molecule therefore causes the spin−lattice relaxation, and its relaxation rates (T_1^{-1}) are then described as follows

$$T_1^{-1} = \frac{3\pi^2}{2}\chi_D{}^2\tau_{2R} \tag{1}$$

where χ_D is the nuclear quadrupolar coupling constant (QCC) and τ_{2R} denotes the reorientational relaxation time of the gradient of the electric field on the nucleus. The gradient of the electric field on the deuteron can be approximated to be axially symmetric around the bond vector (C−D or O−D), denoted as **u**, and its reorientational relaxation time, τ_{2R}, is given by

$$\tau_{2R} = \int_0^\infty C_{2R}(t)\,\mathrm{d}t \tag{2}$$

where the rank-2 reorientational correlation function $C_{2R}(t)$ is defined as

$$C_{2R}(t) = \left\langle \frac{3}{2}\left[\frac{\mathbf{u}(0)\cdot\mathbf{u}(t)}{|\mathbf{u}|^2}\right]^2 - \frac{1}{2}\right\rangle \tag{3}$$

According to eq 1, the variation of T_1^{-1} essentially stands for that of τ_{2R} when the variation of QCC is not so strong. The faster spin−lattice relaxation in liquids can thus be read as the slower reorientational relaxation there. In particular, the reorientations of the O−D vectors of both alcohols are more than 10 times enhanced in the supercritical phase compared with those in the liquid phase. The value of τ_{2R} is a weakly increasing function of density in the supercritical region, and it increases with density reduction below $0.2\rho_c$.

The density dependence of T_1^{-1} of the alkyl deuterons is smaller than that of the hydroxyl one. Since τ_{2R} of the C−D bond of alcohol is affected by the internal motion of the alkyl group, it is quite reasonable that the effect of intermolecular interaction on the reorientation of the C−D bond is smaller than that on the O−D. In addition, the relaxation mechanism other than the quadrupolar one may also be operative in the case of alkyl deuteron. The quadrupolar mechanism is usually dominant for deuteron due to its high efficiency. However, considering that the absolute values of T_1^{-1} for the alkyl deuteron are very small, the quadrupolar mechanism for alkyl deuterons may not be efficient enough to dominate other relaxation mechanisms. Anyway, since the hydrogen bonding is the characteristic interaction of alcohols, the intermolecular interaction around the hydroxyl group is the most important to understand the properties of alcohols. Therefore we will focus only on the reorientational relaxation of the O−D bond hereafter in this work.

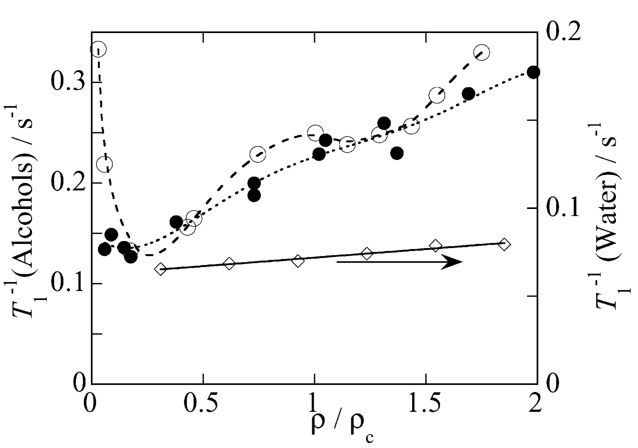

Figure 2. The ^{2}H spin−lattice relaxation rates of the OD groups of supercritical water (open diamonds with solid curve), methanol (filled circles with dotted curve), and ethanol (open circles with dashed curve). The temperature of the fluid is 270 °C for alcohols and 400 °C for water. The rates of water are drawn from the literature reported by Matubayasi et al.[2] Note here that the rates of alcohols and water are plotted in the different scales. The curves stand for nothing more than the guide for eyes.

Figure 2 compares the density dependence of T_1^{-1} of supercritical alcohols with that of supercritical water.[2] The temperature is 543 K for alcohols and 673 K for water. The density is reduced by their respective critical density in the plot. The values of T_1^{-1} of all the fluids are increasing functions of density above $0.2\rho_c$. The amounts of the relative increase for methanol and ethanol are similar, whereas it is twice as large as that of water. The values of T_1^{-1} of all fluids increase with decreasing density below $0.2\rho_c$, although the value is not shown for water since the lowest density examined could be only roughly specified.

Equation 1 relates the ^{2}H NMR spin−lattice relaxation rate, T_1^{-1}, to the reorientational relaxation time, τ_{2R}. However, the value of χ_D is dependent on the environment of the molecule, as is the O−D bond polarization. Therefore we have to take the density dependence of the QCC into account in order to discuss that of τ_{2R}. In addition, we need the absolute value of the QCC to obtain the absolute value.

In the previous work on supercritical water by Matubayasi et al., they estimated the QCC of the water molecule from the dipole moment of water obtained by their molecular dynamics (MD) simulation.[2] In this work, we employed another method to estimate the QCC of methanol and ethanol proposed by Farrar et al.[19,20] In their study, they performed the ab initio calculation of the clusters of methanol or ethanol and found that the chemical shift and the QCC of hydroxyl deuteron are linearly correlated. By utilization of this linear relationship, they estimated the QCC of methanol in carbon tetrachloride[20] or neat ethanol at various temperatures.[19] According to their procedure, we evaluate the QCC of supercritical alcohols from the chemical shift of the OD deuteron. The chemical shift is determined by using that of methyl deuteron as the internal standard. The relative chemical shifts are consistent with those reported by Hoffmann and Conradi for protons.[7] In the case of methanol, for instance, the value of the QCC changes from 288 kHz at the lowest density to 258 kHz at $2\rho_c$, while that at ambient condition is 210 kHz. The proportionality coefficient of eq 1 in

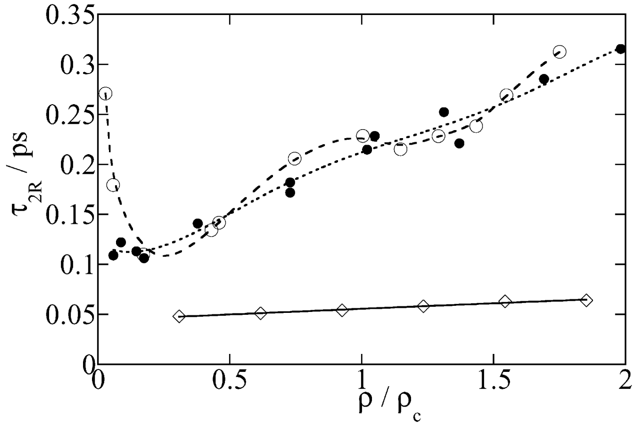

Figure 3. The reorientational relaxation times (τ_{2R}) of the OD vectors of supercritical water, methanol, and ethanol plotted against the reduced density (ρ/ρ_c). The symbols are the same as those in Figure 2. Note that the relaxation times of alcohols and water are compared in the same scale here.

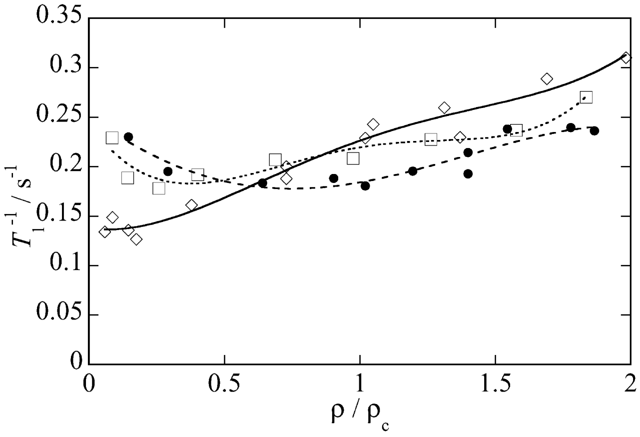

Figure 4. The ^{2}H spin−lattice relaxation rates of the solute molecules in supercritical methanol at 270 °C. The filled circles with a dashed curve, open squares with a dotted curve, and open diamonds with a solid curve represent the relaxation rates of benzene (C_6D_6), pyrazine ($C_4D_4N_2$), and the OD group of methanol (CD_3OD), respectively. The curves are drawn for the guides for eyes.

ambient liquid is twice as large as that of low-density gas, and the change within the supercritical region is about 25%. Therefore, the variation in T_1^{-1} shown in Figure 1 comes in most parts from that in τ_{2R}.

Figure 3 exhibits τ_{2R} of the O−D bond of supercritical alcohols obtained by the above method. The relaxation time of water estimated by the variable QCC scheme of Matubayasi et al. is shown together.[2] Although there are small modifications, the relative density dependence of τ_{2R} is similar to that of T_1^{-1} shown in Figure 2. The reorientational relaxation times of both alcohols are similar and the increasing functions of the density above $0.2\rho_c$. The absolute value of τ_{2R} is typically several hundreds of fs, and it has a minimum value of 100 fs around $0.2\rho_c$. The reorientational relaxation of supercritical alcohols is slower, and its density dependence is larger than that of water.

III.B. Solute Molecules in Methanol. Figure 4 shows the ^{2}H NMR spin−lattice relaxation rates of benzene-*d*$_6$ (C_6D_6) and pyrazine-*d*$_4$ ($C_4D_4N_2$) in supercritical methanol. The results on neat methanol-*d*$_4$ are plotted together. So long as the density dependence of the QCC of benzene-*d*$_6$ and pyrazine-*d*$_4$ is not available at present, our discussion below is based on the density dependence of T_1^{-1}, considering that it essentially represents the density dependence of τ_{2R}.

Contrary to that of methanol, the solvent density dependence of T_1^{-1} of benzene is small, and it has a shallow minimum around the critical density of the solvent. Such a behavior resembles that reported for the nonassociated neat supercritical fluids. The characteristic density dependence of τ_{2R} of supercritical water and alcohols as compared with other fluids is thus not due to the properties of the solvent, but to the solute−solvent interaction. The result on pyrazine-*d*$_4$ lies between those of benzene-*d*$_6$ and methanol-*d*$_4$. The value of T_1^{-1} for pyrazine-*d*$_4$ is a weakly increasing function of density above $0.3\rho_c$, and it increases with decreasing density below there. The minimum value of T_1^{-1} is close to that of benzene, which means that the minimum values of τ_{2R} are similar between benzene and pyrazine if the QCCs of deuterons are assumed to be similar.

IV. Discussion

The reorientational relaxation of a molecule in liquid is usually diffusive, that is, τ_J is much smaller than the free rotation time. In such a case, τ_{2R} is inversely proportional to τ_J, and the large value of the former means that the frictional force on the molecule is large.[21]

On the other hand, the relationship between the free rotation time and τ_J can be inverted in the gaslike low-density region of a supercritical fluid. In such a case, the reorientational relaxation is not completed before the relaxation of the angular momentum due to the conservation of the rotational axis. Therefore, τ_{2R} correlates positively with τ_J, and the large value of the former stands for the small friction on the rotation of the molecule.

This relationship between the rotational friction and the reorientational relaxation is more complicated than that between the translational friction and the diffusion coefficient. In the latter case, the diffusion coefficient is proportional to the relaxation time of the linear momentum in both gas and liquid, and the larger the diffusion coefficient always means the smaller the friction.

Supercritical fluid is the fluid that can continuously connect the dense liquid and the sparse gas without any phase transition. Therefore, the transition between the diffusive and inertial regimes of the reorientational relaxation should be observed in the supercritical region.

There have been many studies on the reorientational relaxation of neat supercritical fluids by experiments, computer simulations, and theories.[2,3,4,5,6,22−24] The reorientational relaxation time of neat supercritical fluids is weakly dependent on density in most cases, having a shallow minimum around the critical density. The reorientational relaxation function is diffusive in the high-density region, that is, the function relaxes in the exponential way. On the other hand, the reorientational correlation function, defined by eq 3 and obtained by the Raman line-shape analysis or the MD simulation, changes strongly with density.[2−5] In the low-density region, the function shows an oscillatory behavior and has a slow tail, as is expected from the angular-momentum conservation.

There are also some theoretical models, such as the extended *J*-diffusion or the Fokker−Plank−Langevin ones, to describe the transition from the diffusive to the inertial regimes.[23,24] In these theories, it has been revealed that the reorientational relaxation time has its minimum value when the relaxation time of the angular momentum is close to the free rotation time and the minimum value is also comparable to the free rotation time.

In the previous work on supercritical water by Matubayasi et al., they performed MD simulations and showed that the above statement also holds in the case of supercritical water,

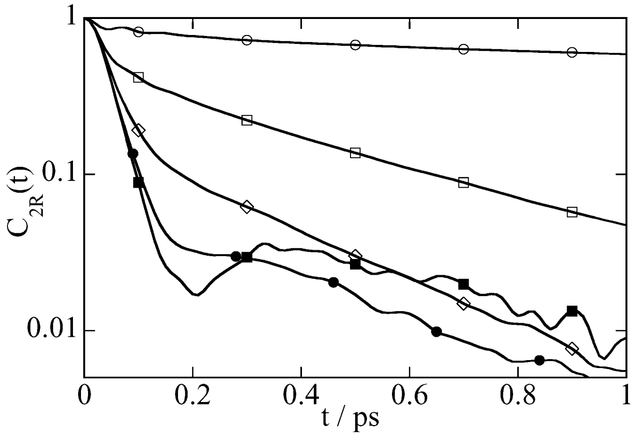

Figure 5. The rank-2 reorientational correlation function, defined by eq 3, of the O−D vector of methanol-d_4 calculated by MD simulations. (○) 298 K and 0.887 g/cm^3 (ambient condition), (□) 543 K and 1.8ρ_c, (◊) 543 K and 0.3ρ_c, (●) 543 K and 0.1ρ_c, and (■) 543 K and 0.03ρ_c.

although the reduced density of the minimum τ_{2R} of water is different from that of other nonassociated supercritical fluids.[2]

To obtain some insight into the reorientational relaxation of supercritical alcohols, we perform the MD simulation on the supercritical methanol-d_4. The simulation on the methanol at the ambient condition is also performed for comparison. The intermolecular interaction used in the simulation is derived from the OPLS model.[25] All the simulation runs are performed at 543 K except for that at the ambient condition. Since the critical temperature of OPLS methanol is reported to be 493 K,[26] 543 K is well above the critical temperature. One simulation run is performed for each state point. In each run, after the equilibration run of 100 ps, the run is continued for 100 ps to calculate the correlation function. The length of the time step is 1 fs. The long-range Coulombic interaction is treated by the Ewald method, and the short-range one is cut off at the half length of the simulation cell. In the equilibration run, the linear and the angular velocities of molecules are scaled to adjust the temperature, and the averaged temperature is controlled within ±2%.

In Figure 5, we show the rank-2 reorientational correlation functions, $C_{2R}(t)$ defined by eq 3, of the O−D vector of methanol-d_4 obtained by MD simulations. In contrast to the slow reorientational relaxation at the ambient condition, the relaxation time is shortened in the supercritical condition up to several hundreds of fs, which is consistent with our estimate from the NMR experiment (Figure 3). The correlation function relaxes in a monotonic way above 0.3ρ_c, indicating that the reorientational relaxation is diffusive in this region. The oscillatory behavior appears below 0.1ρ_c, and the very slow component develops with decreasing density, leading to the increase in the reorientational relaxation time. Although we could not determine the relaxation time precisely due to the slow convergence of the correlation function, we confirmed from the running integral that the value of τ_{2R} at 0.03ρ_c is larger than those at 0.1ρ_c and 0.3ρ_c. All these features in the simulation are consistent with our present experiment. In addition, the free rotation time is estimated to be about 100 fs in Figure 5, which is close to the minimum τ_{2R} estimated in Figure 3. Although the absolute time scale of the relaxation is different, Yoshii et al. already reported similar density dependence of the reorientational correlation function in their MD simulation of supercritical water.[5]

On the basis of the pictures above, we can explain the difference in the density dependence of τ_{2R} of supercritical water and alcohols as follows. The relaxation of the angular momentum of supercritical water is faster than that of alcohols, probably due to the stronger intermolecular interaction, large number density, large collision frequency due to the small mass, and so on. However, since the free rotation time of water is very small due to its small inertia moment, it can be smaller than τ_J even if the latter is also small, and the reorientational relaxation of water can easily get into the inertial regime. Therefore, the reorientational relaxation of supercritical water is more inertial than those of supercritical alcohols, leading to the small density dependence of τ_{2R} in the high-density region compared with those of alcohols.

The discussion above considers the isotropic rotation, not taking the anisotropy of the inertia moment and the friction into account. The water and alcohol molecules are not spherical tops, and their reorientational relaxation is also strongly anisotropic. However, we believe that the difference in the density dependence of τ_{2R} between water and alcohols is essentially explained by the difference in the inertia moment, although the anisotropy of the inertial and intermolecular interaction may also affect the results quantitatively.

Here we shall comment on the comparison between the reorientational relaxation times of supercritical methanol based on the NMR measurement and those reported by Hiejima et al. based on the microwave spectroscopy.[27] Although both reorientational relaxation times show qualitatively similar density dependence in that their density dependence is inverted in the low-density region, the inversion point appears near the critical density in the case of microwave spectroscopy. The same discrepancy is also found for supercritical water,[2,28] and there have been many MD simulation studies on the reorientational relaxation of supercritical water in order to resolve this problem.[29−32] In general, the simulation results are consistent with the NMR experiment and disagree with the microwave spectroscopy. In the case of methanol, our MD simulation is also consistent with our NMR experiment. Since only the time-integrated relaxation times are observed in both the microwave and NMR spectroscopy, we consider it will be the best method for clarifying the reason for the discrepancy to measure the functional form of the reorientational correlation function by the THz spectroscopy.

The solute dependence of τ_{2R} in supercritical methanol (Figure 4) can also be explained in terms of the transition between the inertial and diffusive regimes. The molecular structure of benzene and pyrazine resemble each other so that they have similar inertia moments and free rotation times. On the other hand, the solute−solvent interaction is considered to be stronger for pyrazine due to the hydrogen bonding between the lone pairs on the nitrogen atoms of pyrazine and the hydroxyl group of methanol. The loss of the angular momentum of pyrazine is thus faster than that of benzene, and the τ_J value of the former is smaller than that of the latter. Since the competition between τ_J and τ_{2R} values determines whether the reorientational relaxation is diffusive, smaller τ_J and similar τ_{2R} values of pyrazine compared with benzene mean that the reorientational relaxation of the former is likely more diffusive. It is consistent with the fact that the inversion of the density dependence of the reorientational relaxation time of pyrazine occurs at a lower density than that of benzene. Since the free rotation times of these two solute molecules are quite similar, their minimum τ_{2R} are close to each other, which is also consistent with their similar minimum T_1^{-1} shown in Figure 4. By comparison of these two solute molecules with neat methanol, the free rotation time of methanol is smaller than those of benzene and pyrazine. Nonetheless, the density of the minimum T_1^{-1} is the smallest among the three in the case of methanol, which indicates that the effect of the enhanced dissipation of the angular momentum due to the hydrogen bonding is stronger than that of the reduced free rotation time.

The difference in the density dependence of the reorientational relaxation times of supercritical hydrogen-bonding fluids (water and alcohols) and nonassociating ones can be understood in the same way. Because of the strong anisotropy of the intermolecular interaction of water or alcohols, as is represented by the directional hydrogen bonding, the intermolecular transfer of the angular momentum is enhanced, which results in the shift of the reduced density of minimum τ_{2R} to the lower-density region.

V. Summary

The ^{2}H NMR spin−lattice relaxation rates of supercritical methanol-d_4 and ethanol-d_6 were determined as the function of density at 543 K. The data on the liquid branch of the liquid−gas coexistence line were also presented. The results were compared with the corresponding one for supercritical water reported by Matubayasi et al.[2]

The spin−lattice relaxation rates decrease by about 1 order of magnitude when the fluids are transferred from the ambient to the supercritical conditions, as is observed in the case of water. The degree of the reduction of the spin-relaxation is larger for the hydroxyl deuterons than for the alkyl ones, which can be ascribed partly to the effects of the internal motions of the alkyl groups.

The reorientational relaxation times of the O−D bonds increase with density above $0.2\rho_c$, which indicates that the reorientational relaxation is in the diffusive regime. On the other hand, the density dependence is inverted in the lower-density region due to the angular momentum conservation. This picture is consistent with the MD simulation in the case of methanol. Compared with water, the increase in τ_{2R} with density in the higher-density region is stronger for alcohols, which is explained by the larger inertia moments of alcohols.

We also compared the reorientational relaxation of the three solute molecules, methanol, benzene, and pyrazine, in supercritical methanol. All the relaxation times exhibit a minimum against the density variation. The density of the minimum reorientational relaxation time decreases with increasing strength of the solute−solvent interaction, that is, benzene shows a minimum at the highest density, and methanol does at the lowest. This behavior is elucidated in terms of the efficiency of the angular-momentum relaxation of the solute. The stronger solute−solvent interaction makes τ_J shorter, leading to the more diffusive behavior of the reorientational relaxation.

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