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Nuclear magnetic resonance and molecular dynamics simulation study on the reorientational relaxation of solutes in supercritical methanol

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Abstract

The effect of solvent density on the single-molecular reorientational relaxation of deuterated methanol and benzene in supercritical methanol are investigated both by the nuclear magnetic resonance (NMR) experiment and the molecular dynamics (MD) simulation. In the NMR experiment, the rank-2 reorientational relaxation time is determined from the spin-lattice relaxation time of deuterons. The relaxation time of the **O**–**D** vector of methanol is an increasing function of density above 0.3 ρ_c, where ρ_c stands for the critical density, while that of the **C**–**D** vector of benzene shows a shallow minimum around ρ_c. To clarify the origin of the difference, MD simulations of both neat methanol and benzene in methanol are performed. The MD simulation revealed that the reorientational relaxation of the **O**–**D** vector of methanol is diffusive above 0.3 ρ_c, whereas the effect of the inertial motion is strong on the reorientational relaxation of benzene.

Keywords: Supercritical fluid; Methanol; Reorientational relaxation

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1. Introduction

The reorientational relaxation is one of the most sensitive probes of the intermolecular interaction in liquids, and it has been studied also in many neat supercritical fluids [1–4] and solutions [5–7]. In liquids, the reorientational relaxation is usually in the diffusive regime, and the large value of the reorientational relaxation time means the strong intermolecular interaction. On the other hand, the reorientational relaxation in supercritical fluids in the low-density region may not be diffusive. In the inertial regime, the large value of the reorientational relaxation time stands for the smaller friction on the molecule since the reorientational relaxation time of an isolated molecule is infinite due to the conservation of the rotational axis. It is therefore required to clarify the relationship between the reorientational relaxation time and the intermolecular interaction to utilize the former as a probe of the latter.

We have presented in our previous study the reorientational relaxation time of deuterated methanol, benzene, and pyrazine in supercritical methanol [8]. The density dependence of the relaxation time of all three solutes shows a minimum value, indicating the transition between the inertial and diffusive regimes. However, the density of the minimum relaxation time depends on the solute species; it is the lowest for methanol and the highest for benzene. We considered it is due to the difference in the efficiency of the angular momentum loss caused by the difference in the anisotropy of the solute–solvent interaction.

In this study, we perform the molecular dynamics (MD) simulation of the reorientational relaxation of both methanol and benzene in supercritical methanol. In contrast to the nuclear magnetic resonance (NMR) experiment where only the time-integrated value of the reorientational time-correlation function is determined, we can analyze the time evolution of the reorientational correlation functions in the MD simulation so that we can obtain a deeper insight into the detailed dynamics of the molecule.

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2. NMR experiment

The measurement of the ^{2}H-NMR spin-lattice relaxation time of solutes in supercritical methanol is described elsewhere [1,8]. The sample alcohol (methanol-d$_4$) or the alcoholic solution (benzene-d$_6$ in methanol-h$_4$) are sealed into a quartz capillary at ambient condition, and the capillary is placed in an NMR sample tube. In the measurement of the relaxation rates of the solute, the methanol-h$_4$ solution of 0.55 mol/dm^3 of benzene-d$_6$ is prepared at the ambient condition and then sealed into the capillary. The methanol-d$_4$ (CD_3OD, 99%D) is 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 methanol-h$_4$ (CH_3OH, Nacalai Tesque, spectroscopic grade). The former is used as received, and the latter is dried by molecular sieves. 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) [9]. The density of the fluid in the supercritical phase is determined from the packing fraction at the ambient condition. 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. From the measurements at same density on different days and with different samples, the error of T_1^{-1} is estimated to be 10% at most.

According to the nuclear quadrupolar coupling mechanism of the spin-lattice relaxation of the ^{2}H nucleus, its spin-lattice relaxation rates (T_1^{-1}) are described as

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

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 $\boldsymbol{u}$, 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

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

Although the methanol-d$_4$ has two different kinds of ^{2}H nuclei, those of methyl and hydroxyl groups, we analyzed the relaxation of only the latter since the former is likely affected by the internal motion of the methyl group. The QCC value of the **O**–**D** deuteron is determined based on the linear correlation between the chemical shift and QCC proposed by Wendt and Farrar [10]. The solvent effect on the QCC of benzene-d$_6$ is neglected, and the value used for the neat liquid, 192.5 kHz [11–13], is applied to the supercritical solution.

3. MD simulation

The NVE ensemble simulations on the neat methanol-d$_4$ or the benzene-d$_6$ in methanol-d$_4$ are performed. The temperature of the system is 543 K, and the simulation is carried out at four different densities, 0.3, 1.0, 1.8, and 2.9 ρ_c, where ρ_c stands for the critical density of the neat methanol, and 2.9 ρ_c is the density at the ambient condition. The systems consist of 256 methanol-d$_4$ (neat fluid) or 255 methanol-d$_4$ and 1 benzene-d$_6$ (solution), which are packed into the cubic cell with the periodic boundary condition. The long-range Coulombic interaction is treated by the Ewald method. The orientational degree of freedom is described by the quaternion, whose equation of motion is integrated by the time-reversible and area-preserving algorithm developed by Matubayasi and Nakahara [14]. The time step is chosen to be 1 fs. After the equilibration run of 100 ps, the run is continued for 100 ps (for neat fluid) or 1 ns (for solution) to obtain the correlation functions. The simulation run for the solution at 0.3 ρ_c is performed twice with different initial conditions, and results are averaged to improve the poor statistics. The linear and angular momenta are sometimes scaled during the equilibration run to adjust the temperature, and the average temperature is controlled within ±2%. We used the OPLS potential for methanol [15], where the methyl group is treated as the united atom. The masses of the methyl group and the hydrogen atom are increased to 15 and 2 in the atomic unit, respectively. The OPLS six-site model of benzene is employed here for the model of benzene [16]. The mass of the CD group is also increased to 14 in the atomic unit. The standard combination rule is used for the Lennard–Jones interaction between different kinds of interaction sites. Since there is no partial charge in the OPLS six-site model of benzene, there is no electrostatic interaction between benzene and methanol, so that the solute–solvent interaction is naturally expected to be weaker for benzene than methanol. Although there is a weak electrostatic interaction between the O–H group of methanol and the π-electron of benzene in the real system, we believe it does not change the qualitative nature of the present results.

4. Results and discussion

The values of the rank-2 reorientational correlation time from the NMR measurements, τ_{2R}, are plotted in Fig. 1 as