Self-Diffusion in Supercritical Water and Benzene in High-Temperature High-Pressure Conditions Studied by NMR and Dynamic Solvation-Shell Model

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Abstract. The self-diffusion coefficients of water and organic solvents in the high-temperature high-pressure conditions are studied by using high-temperature NMR and MD simulation methods. The experimental results are analyzed using a scheme based on the solvation shell relaxation time obtained by MD simulation. The dynamic effect of hydrogen bonding is discussed through the comparison between water and a nonpolar organic solvent, benzene, over a wide range of density and temperature. The hydrogen-bonding effects are as follows: (1) the self-diffusion coefficient of water depends on density more weakly than that of benzene, (2) the self-diffusion coefficient of water at the ambient density depends on temperature more strongly than that of benzene at the density, (3) the turnover from the mobile-shell type to the in-shell type with increasing density does not occur in supercritical water up to the ambient density, whereas such turnover is observed in benzene. These contrasts are reflecting the dynamic effect of the anisotropic attractive interactions.

1. Introduction
Supercritical fluids are fascinating solvents alternative to organic ones [1-9]. It is of great importance to obtain the molecular picture of dynamic modes in supercritical fluids, such as rotation, self-diffusion, and the relaxation of the solvation shell. Even at high temperatures, the translational and rotational dynamics of a solute molecule are essentially controlled by the dynamic interaction with the neighboring molecules in the solvation shell. For a better understanding of the role of solvation, it is of great importance to focus on the type and strength of dynamic intermolecular interactions. Here we investigate the self-diffusion of water and a nonpolar organic solvent, benzene, in high-temperature, less-packed (expanded) conditions. We have studied the unique effect of hydrogen bonding in sub- and supercritical water on the translational dynamics [10-12] as well as the structure [13] and the rotational dynamics [14]. Comparison to the organic solvent provides us with insights into the effect of strength and anisotropy of interaction. In this study, we examine the molecular picture of the dynamics over a wide range of temperature and density by utilizing the high-temperature high-pressure NMR and the dynamic solvation-shell model combined with molecular dynamics (MD) simulation.

In recent works [10-12,15,16], we investigated the self-diffusion of sub- and supercritical water using the high-temperature NMR method. The effect of the hydrogen bonding on the self-diffusion has
been elucidated using the simple gas kinetic model and the simple hydrodynamic model [17,18]. The experimental results alone cannot give a full account for the self-diffusion mechanism on the molecular level, however, since the microscopic details are averaged out in the integral of the relevant time correlation function. The MD method is a complementary, powerful tool to analyze the dynamics at the atomic spatial and femto- to picosecond time resolution. Its numerical results can be combined with an analytical formulation to provide a realistic, physical picture, which is often missed in widely used models such as the binary collision and Brownian dynamics. The purpose of the present work is to pursue the solvation shell picture in connection to the dynamics of supercritical water. We aim at acquiring a deeper understanding of the molecular mechanism of the translational dynamics based on the time correlation functions obtained by computer simulation.

Since the time profiles of the velocity and the orientation in fluids are controlled by the forces and torques exerted by solvating molecules, it is of great interest to establish the relationship between the dynamics and the solvating shell structures over a wide range of density. One of our purposes is to see whether the supercritical water dynamics is of the “in-shell” type in the sense that a water molecule diffuses or rotates within the “shell” or “cage” of solvating molecules clustering around it, or is categorized into the opposite case, the “mobile-shell type” in the sense that the solvation shell structure relaxes faster than the translational diffusion of a solute. For this purpose, the dynamic aspect of the shell structure as well as the static one is necessary to be explored. In this study, we investigate the observable translational and rotational dynamics and establish the relationship among the relaxations of collective shell structure, velocity, and orientation over a wide range of density.

2. Methods

The experimental scheme for NMR determination of the diffusion coefficient of high-temperature water is described elsewhere [10,11,15,16]. The TIP4P and the OPLS-AA models for water and benzene, respectively, are adopted in the MD simulation using model potentials [19,20].

3. Dynamic solvation-shell model

Using the dynamic solvation shell scheme [12], we analyze the molecular mechanism of the self-diffusion process in supercritical fluids in terms of the ratio of the relaxation time of the translational velocity to the lifetime of the solvation shell. The relaxation time of the translational velocity \( \tau_D \) is defined by the time integral of the normalized velocity autocorrelation function expressed as

\[
\tau_D = \int_0^\infty dt \left\langle \frac{\langle v(0) \cdot v(t) \rangle}{\langle v(0) \rangle} \right\rangle,
\]

(1)

and the \( \tau_D \) determines the self-diffusion coefficient \( D \) through \( \tau_D = MD/RT \) with the molecular weight \( M \).

The relaxation time of the solvation shell \( \tau_s \) is the one for the solvation number \( n \). The solvation number \( n \) is defined by the number of neighboring molecules within the cutoff distance \( r_c \), which is determined by the inertia center of a molecule. We took \( r_c = 5.0 \) and 9.0 Å for water and benzene, respectively, whose distances correspond approximately to the first minimum positions in the radial distribution functions of these molecular centers. The time scale \( \tau_s \) is the relaxation time corresponding to the autocorrelation function, \( C_s(t) \), of the solvation shell state given by

\[
C_s(t) = \sum_n \left\langle \Theta_n(t) \Theta_n(0) \right\rangle.
\]

(2)

Here \( \Theta_n(t) \) is a characteristic function that is unity when the solvation number is equal to \( n \) at time \( t \), and \( \Theta_n(t) \) is zero otherwise.

The \( \tau_D \) depending on the solvation number \( n \) is examined using the autocorrelation function defined by eq.(3);
First, we discuss the dynamics of the solvation shell. In Figure 1(a), we show the shell relaxation time, \( \tau^D_n \), for water conditioned by the solvation number \( n \). \( \tau^D_n \) at fixed \( n \) increases with decreasing density \( \rho \) and \( \tau^D_n \) at fixed \( \rho \) increases with decreasing \( n \). The more crowded the shell is, the faster it relaxes due to the more frequent exchange of the solvating molecules. In order to scrutinize the effect of hydrogen bonding, we compare \( \tau^S_n \) for water with that for benzene that has no hydrogen bonding. As shown in Figure 1(b), the shell relaxation of benzene is more directly related to the density effect continuously in sub- and supercritical states.

It should be noted that this scheme is general and can be applied to any dynamic mode of interest. For example, similarly to \( \tau^D_n \), \( \tau^S_n \) can be defined as

\[
\tau^S_n = \sum_n P_n \tau^S_n.
\]

The results on the rotational dynamics are also reported elsewhere [12].

On the basis of \( \tau^D \) and \( \tau^S \), the mechanism of the translational diffusion at a certain thermodynamic state can be classified into the “mobile-shell” type and the “in-shell” type. The mobile-shell type is the low-density behavior in which the velocity relaxes slower than the shell structure with \( n \) does (\( \tau^D_n/\tau^S_n > 1 \)); the solvation time \( \tau^S_n \) is used as the reference. The in-shell type is the high-density behavior in which the velocity relaxes within the solvation shell (\( \tau^D_n/\tau^S_n < 1 \)). Our solvation-shell scheme is valid over an arbitrary density range from the gaseous to the liquid states and thus can be applied to analyze the density effect continuously in sub- and supercritical states.

4. Results and Discussion

First, we discuss the dynamics of the solvation shell. In Figure 1(a), we show the shell relaxation time, \( \tau^S_n \), for water conditioned by the solvation number \( n \). \( \tau^S_n \) at fixed \( n \) increases with decreasing density \( \rho \) and \( \tau^S_n \) at fixed \( \rho \) increases with decreasing \( n \). The more crowded the shell is, the faster it relaxes due to the more frequent exchange of the solvating molecules. In order to scrutinize the effect of hydrogen bonding, we compare \( \tau^S_n \) for water with that for benzene that has no hydrogen bonding. As shown in Figure 1(b), the shell relaxation of benzene is more directly related to \( \rho \) and less to \( n \) than that of water. A similar tendency was observed also in the case of translational and rotational dynamics, as an indication of the effect of attractive interaction [12]. The tendency is especially remarkable in the case of rotation because the rotational dynamics is sensitive to the anisotropic effect and also because rotational dynamics proceeds within the shell (i.e. in-shell type) [12]. To explore the attractive hydrogen-bonding effect, it is informative to examine the solvation-shell relaxation time conditioned by the number of hydrogen bonding. In Figure 1(c), we show \( \tau^S_n \) (HB) conditioned by the number \( n_{HB} \) of hydrogen bonding. Here a hydrogen bond is defined by an intermolecular O–H pair whose distance is less than 2.4 Å. In comparison to \( \tau^S_n \) conditioned by the distance of the inertia center, the shell characterization by hydrogen bonding leads to the stronger control by the shell state and less by the hydrogen bonding.

**Figure 1.** The relaxation time \( \tau^S_n \) of the solvation shell as a function of the solvation number \( n \) for (a) water and for (b) benzene. (c) \( \tau^S_n \) (HB) of water conditioned by the number \( n_{HB} \) of hydrogen bonding.
bulk density. Since the orientational preference in attraction is essential in water, the shell state is conditioned more strongly by the number of hydrogen bonding that can distinguish the solvating molecules in the bonding configuration from those which are not.

In Figure 2, we show the self-diffusion coefficients $D$ obtained by the high-temperature high-pressure NMR experiment and the MD simulation. The density-diffusivity product normalized by $\sqrt{T}$, $\rho D/\sqrt{T}$, for water and benzene is shown as a function of $\rho$ in Figure 2. In supercritical conditions, especially at extremely low densities, it is more convenient to examine $\rho D/\sqrt{T}$ rather than $D$ itself since $D$ rises steeply with density reduction. The quantity $\rho D/\sqrt{T}$ is independent of density in the case of supercritical fluids; cf., experimental results on methane, ethylene, xenon, and carbon dioxide [21-24]. Thus, the increase in the diffusivity with decreasing density is exceptionally small in the case of supercritical fluids; cf., experimental results on methane, ethylene, xenon, and carbon dioxide [21-24].

The two extremes, $\tau D/\tau S \rightarrow 1$ and $\tau D/\tau S \ll 1$, correspond to the dilute gas-like picture and the dense liquid-like, Brownian picture, respectively. $\tau D/\tau S$ for water in Figure 3(a) shows that the water diffusion is of the mobile-shell type over the density range of 0.01-1.0 g cm$^{-3}$ at 400 ºC; no turnover from the in-shell to the mobile-shell type up to the ambient density. At the ambient density of 1.0 g cm$^{-3}$, the packing fraction of water is still rather small and the shell is mobile due to weakened hydrogen bonding at 400 ºC. A large value of $\tau D/\tau S$ at 1.0 g cm$^{-3}$ and 400 ºC means the invalidity of the liquid-like, Brownian picture and in favor of the gas-like picture. The collision (interaction) is, however, not binary; $n \gg 1$ at densities of 0.05 g cm$^{-3}$ and higher [12]. The diffusing molecule is rather well solvated at densities of 0.05 g cm$^{-3}$ and higher, but the solvation shell is too soft to allow the complete relaxation of the velocity within a shell even at 1.0 g cm$^{-3}$. At ambient temperature, $\tau D/\tau S$ is much smaller than that at the same density at 400 ºC and is comparable to unity. The shell is less

![Figure 2](image-url)
mobile in ambient condition probably because the tetrabedral hydrogen-bonding network is formed and the self-diffusion is of the in-shell type, in accordance with the Brownian picture.

A remarkable contrast is seen between water and benzene in the density dependence of $\tau_D/\tau_S$ at medium to high densities. As shown in Figure 3(b), the ratio $\tau_D/\tau_S$ for benzene is ~6 at 0.05 g cm$^{-3}$ and decreases with density down to ~1 at the ambient density of 0.87 g cm$^{-3}$. In benzene, the diffusion at 400 °C is of the mobile-shell type only in the low-density region and is of the in-shell type at the ambient density of 0.87 g cm$^{-3}$. The density dependence of $\tau_D/\tau_S$ observed for benzene is in harmony with the common view of the transition from the collision to the Brownian picture with increasing density.

There are two factors contributing to the contrast between water and benzene pointed above; (1) the anisotropic attractive interactions and (2) the packing fraction. The role of the anisotropic effect (1) has been demonstrated through the comparison between all-atom model and spherical, Lennard-Jones (LJ) model for benzene. It was observed that the LJ model can reproduce the turnover behavior in supercritical benzene [12]. This indicates that the anisotropic effect on the translational dynamics in benzene is weak at such a high temperature, whereas the anisotropic effect persists in supercritical water [14,25]. The effect of packing (2) was demonstrated by investigating the water diffusion in extremely high-pressure high-density conditions [12]. The onset of the turnover from the mobile-shell to the in-shell type was observed at 1.2-1.5 g cm$^{-3}$ with 400 °C; the ratio $\tau_D/\tau_S$ decreases to 2-3. When water molecules are highly packed at such high densities, the attractive part in the pair potential is less important than that at lower densities. Actually, the packing fraction of water at the highest density of 1.5 g cm$^{-3}$ (0.48) is comparable to that for benzene at 0.87 g cm$^{-3}$ (0.51). The ambient density of 1.0 g cm$^{-3}$ is not high enough for water since liquid water is known to have an open structure at 1.0 g cm$^{-3}$ due to the hydrogen bond network. The temperature dependence of $D$ is much larger for water than for benzene when compared at their ambient densities. The water diffusion shows the in-shell/mobile-shell turnover with the temperature increment at the ambient density, unlike that for benzene. In water at room temperature with ambient density, a diffusing molecule is caged in the solvation shell structured by the tetrabedral hydrogen-bonding network, even though the packing fraction is not very high. Once the temperature is raised up to the supercritical, the network structure no longer exists and the density is not high enough to cause a large packing effect. Thus the shell is not structured enough to cage in the diffusing molecule.

![Figure 3](image-url). The ratio $\tau_D/\tau_S$ plotted against the density $\rho$ for (a) water and (b) benzene.
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References
[1] Seewald J S 1994 Nature (London) 370 285.
[2] Marrone P A, Arias T A, Peters W A and Tester J W 1998 J. Phys. Chem. A. 102 701.
[3] Miksa D, Li J and Brill T B 2002 J. Phys. Chem. A. 106 11107.
[4] DeSimone J M 2002 Science 297 799.
[5] Nagai Y, Morooka S, Matubayasi N and Nakahara M 2004 J. Phys. Chem. A. 108 11635.
[6] Weingärtner H and Franck E U 2005 Angew. Chem. Int. Ed. 44 2672.
[7] Yasaka Y, Yoshida K, Wakai C, Matubayasi N and Nakahara M 2006 J. Phys. Chem. A. 110 11082.
[8] Ibuki K and Ueno M 2006 J. Chem. Phys. 124 134506.
[9] Fujisawa T, Terazima M and Kimura Y 2008 J. Phys. Chem. A. 112 5515.
[10] Yoshida K, Wakai C, Matubayasi N and Nakahara M 2005 J. Chem. Phys. 123 164506.
[11] Yoshida K, Matubayasi N and Nakahara M 2006 J. Chem. Phys. 125 074307.
[12] Yoshida K, Matubayasi N and Nakahara M 2007 J. Chem. Phys. 127 174509.
[13] Matubayasi N, Wakai C and Nakahara M 1997 J. Chem. Phys. 107 9133.
[14] Matubayasi N, Nakao N and Nakahara M 2001 J. Chem. Phys. 114 4107.
[15] Yoshida K, Matubayasi N and Nakahara M 2008 J. Chem. Phys. 129 214501.
[16] Yoshida K, Matubayasi N and Nakahara M 2009 J. Mol. Liq. 147 96.
[17] Hirschfelder J O, Curtiss C F and Bird R B 1954 Molecular Theory of Gases and Liquids (Wiley: New York).
[18] Tyrrell H J V and Harris K R 1984 Diffusion in Liquids (Butterworths: London).
[19] Jorgensen W L, Chandrasekhar J, Madura J D, Impey R W and Klein M L 1983 J. Chem. Phys. 79 926.
[20] Jorgensen W L and Severance D L 1990 J. Am. Chem. Soc. 112 4768.
[21] Harris K R 1978 Physica A 94 448.
[22] Arends B, Prins K O and Trappeniers N J 1981 Physica A 107 307.
[23] Peereboom P W E, Luigjes H and Prins K O 1989 Physica A 156 260.
[24] Etesse P, Zega J A and Kobayashi R 1992 J. Chem. Phys. 97 2022.
[25] Matubayasi N, Wakai C and Nakahara M 1999 J. Chem. Phys. 110 8000.