A New High-Temperature Multinuclear-Magnetic-Resonance Probe for Structure, Dynamics, and Reaction in Supercritical Water

Ken Yoshida†, Nobuyuki Matubayasi†, Masaru Nakahara†, Takeyoshi Ikeda‡+ and Takahiro Anai††

† Institute for Chemical Research, Kyoto University
‡+ Analytical Instruments Division, JEOL Ltd.

Introduction

Recently, super- and subcritical water attracts much attention as a green solvent alternative to harmful organic solvents. Various kinds of new organic reactions have been found to be induced in super- and subcritical water [1], [2], [3], [4], [5]. Actually, nature has known the power of supercritical water since long before human beings have begun to learn it. Hot water is naturally abundant in the hydrothermal vents in the deep ocean [6]. Supercritical water was much more widely spread in the hot ancient ocean and thus chemical evolution is believed to have proceeded in hot water. Recently hydrothermal synthesis of a precursor of an amino acid has been demonstrated in a test tube [7]. Thus supercritical water is a novel, green, and natural solvent for the next generation.

In order to understand, utilize, and control supercritical reactions, we need to elucidate the supercritical hydration from a dynamic viewpoint. NMR is a most suitable, promising method for the purpose. Previously, proton NMR [8], [9], [10], neutron scattering [11], x-ray diffractometry [12], infrared (IR) [13], and Raman spectroscopies [14] have been used to study the structure of supercritical water. NMR data can be analyzed more simply and clearly than IR and Raman data because of the information about the hydrogen-bonding structure due to the motional narrowing. According to the state-of-the-art, modern NMR apparatus is much more powerful than the neutron scattering and x-ray diffractometry. Using the first-generation NMR probe, we have elucidated the existence of the static hydrogen bonding [8], [9] and the timescale of the rotational dynamics (several tens of fs) in supercritical water [15].

We have developed a second-generation high-temperature NMR probe that can be applied to the translational, as well as rotational, diffusion measurements [16]. The translational dynamics is important since diffusion controls the rate of collision between reactive species. So far, the method applicable for supercritical conditions has been limited to the electric conductivity measurement [17], [18], [19], [20]. However, the conductivity method cannot be used for neutral species. The limitations should be overcome because some of interesting chemical reactions in such neutral molecules as H$_2$, CO, CO$_2$, HCOOH, and H$_2$O are known to play a key role in controlling supercritical water reactions. Using NMR, such neutral molecules are observable. The difficulty in measuring the high-temperature diffusion is the temperature inhomogeneity that can affect the diffusion measurement to a large extent. We have overcome this difficulty by introducing a new heating system that can regulate the temperature with precision. In the newly developed system, the sample is symmetrically heated from the upper and lower sides by using a solid-state material of high thermal conductivity. The new probe has been applied to the self-diffusion measurements on supercritical water over wide temperature and density ranges of 30-400 ºC and 0.0041-1.0 g cm$^{-3}$, respectively.

High-Temperature Probe

The following limitations of the first-generation probe [8], [9] have been improved by the second-generation high-temperature NMR probe: (i) The field strength of the superconductor magnet was 6.35 T (270 MHz for ¹H, wide-bore). (ii) The probe was not for multinuclear use (a different probe for each nucleus). (iii) The temperature homogeneity was insufficient for diffusion measurements because of the one-way flow of heated nitrogen gas from the bottom. The new probe was cooperatively developed by the Kyoto University group and JEOL; patent application, No.WO2005/022183. The probe is built into a 500 MHz system (JEOL JNM-ECA500) with a wide-bore superconductor magnet (11.3 T). The new high-temperature probe is multinuclear and can cover a wide range of resonance frequencies of 36-500 MHz; $^{19}$N, $^{35}$Cl, $^{133}$Cs, $^{17}$O, $^2$H, $^{29}$Si, $^{13}$C, $^{23}$Na, $^{31}$P, $^{19}$F, and $^1$H can be measured with a single
probe, irrespective of the charge of the monitored species. We have succeeded in determining the self-diffusion coefficient of the sodium ion in supercritical aqueous electrolyte solution [22].

In Fig. 1, we illustrate the new high-temperature probe. To minimize the temperature gradient in the sample, two electric heaters are placed symmetrically on the upper and lower sides of the sample. The sample holder is made of a good heat conductor, aluminum nitride; the thermal conductivity is as high as 200 W m$^{-1}$ K$^{-1}$, which is close to that of aluminum (240 W m$^{-1}$ K$^{-1}$). The rf coils are made of gold and can resist high-temperatures up to 450 °C. A large magnetic field gradient of 270 G cm$^{-1}$ can be generated at maximum. Hence the probe can be applied to measure the self-diffusion for various molecular species with low frequency and/or slow motion. To cancel the leaking of the gradient pulses, the shielding coil is incorporated. The heated nitrogen gas used in the previous probe is no longer necessary, and thus the new probe can be handled almost as safely as a normal solution-state probe. The gas-flow system is composed of materials of a wide range of magnetic susceptibility. This influenced the internal magnetic field and limited the shim conditioning to a high level.

The present measurements are carried out under isochoric conditions. The high-temperature and high-pressure conditions are controlled by the sealed tube method as shown in Fig. 2 [7], [8], [15], [16], [21]. The sealed quartz tube was positioned at the rf center to attain a high level of resolution.

**Temperature Homogeneity**

Homogeneous temperature distribution is indispensable for accurate NMR diffusion measurements at high temperatures. The temperature distribution within the new probe system is shown in Fig. 2 as a function of the height $z$ from the bottom of the sample holder.

![Fig. 1. The cross-section view of the high-temperature multinuclear diffusion NMR probe.](image1)

![Fig. 2. The temperature distribution in the sample holder as a function of the height $z$ (mm) from the bottom; the temperature monitored by the probe thermocouple is 250 (blue) and 400 °C (red). The sample settings for (a) subcritical and (b) supercritical conditions are shown on the scale corresponding to the longitudinal axis of the graph.](image2)
The sample is positioned close to the temperature minimum so that the temperature inhomogeneity can be minimized.

The currents of upper and lower heaters are adjustable independently to avoid the convection. The upper and lower heater currents are optimized to make the temperature gradient slightly upward with increasing z. In the previous probe, the temperature gradient was inevitably downward because of the heated gas flow from the bottom of the sample. We can confirm the absence of the convection effect by optimizing the parameters involved in the pulse sequence. When the diffusion coefficient is reliable in the optimized conditions, it should be independent of the time required for a molecule to diffuse in the pulsed field gradient spin-echo experiment.

The sample temperature was stable over time within ±0.2 °C due to the feedback temperature control. The sample temperature was controlled using a pulsed direct current applied at an on/off interval of 2.4 s as illustrated in Fig. 3. In order to avoid noises from the current on/off, the heater switches were left untouched during the acquisition of each free induction decay (FID). The current value during FID acquisition is optimized at each temperature.

Density Measurement

A precise density measurement is essential for the diffusion measurement in the low-density region. The sealed tube method employed in this study is suitable for the purpose. We have proposed two methods, the chemical shift method and the mass-volume method, which are used in the extremely low-density region [21] and medium to high-density region, [16] respectively.

In the chemical shift method, the density is determined by making use of the transition temperature $T_t$ and the $PVT$ data on the liquid-gas coexistence curve. The density in a supercritical state is equal to that of the gas branch of the coexistence curve at $T_t$ when the density is lower than the critical value. The $PVT$ data for water are released by the International Association for the Properties of Water and Steam (IAPWS) [23]. The $T_t$ can be determined according to the temperature dependence of the proton chemical shift $\delta$ of the gas phase. In Fig. 4, the temperature dependence of $\delta$ is shown for a water sample at 0.0041 g cm$^{-3}$ in the vicinity of $T_t$. As can be seen, $\delta$ has a maximum. The temperature of the maximum $\delta$ is $T_t$ because the temperature dependence of the hydrogen-bond strength, which is in positive correlation with $\delta$, turns over at $T_t$ in a closed system. $T_t$ and the density could be then determined with a precision of ±1 °C and ±1%, respectively. This method can be applied to determine for aqueous electrolyte systems in supercritical conditions.

It becomes difficult to apply the chemical shift method when the density approaches the critical value. For such a density region, we propose another method called the mass-volume method, in which the bore volume of the tube and the mass of the sample are precisely determined. The density is given by the solution volume in a sample tube divided by the bore volume of the tube determined by the inner diameter. The volume of solution was obtained by the masses of the tube with and without the sample. The bore volume of the tube is the difference between the total volume of the tube and the volume of the quartz itself; the total volume of the tube was determined by the outer diameter and is equal to the sum of the bore volume and the volume of the quartz itself. The total volume of the tube was determined by the change in the position of the meniscus when it was immersed into a liquid. The volume of the quartz itself was determined by its mass and density data. The masses were measured to an accuracy of 0.1% using an ultramicrobalance (Mettler Toledo UMX-2). When the sample is water, this method can be applied at 0.07 g cm$^{-3}$ and above.

Diffusion Measurement

Our sample is pure light and heavy water ($\text{H}_2\text{O}$ and $\text{D}_2\text{O}$). The diffusion coefficients are obtained by the pulsed field gradient spin-echo method [24], [25]. The quality of our multinuclear spectra can be seen from those in Fig. 5(a) taken under extreme conditions. There is shown the $^2\text{H}$ spectrum for heavy water at a low density of 0.097 g cm$^{-3}$ at a supercritical temperature of 400 °C. This is a most difficult condition for the acquisition of the FID signals in this work. The FID signals were accumulated once for each duration time of a field gradient pulse $\delta$. The signal-to-noise
ratio for δ = 0 ms exceeds 40, resulting in accurate diffusion coefficients within ±1%. The intensities of spin-echo signals M(τ) are extracted from Fig. 5(a) and plotted in Fig. 5(b) in order to determine the diffusion coefficient. The total uncertainty of D at 400 °C is estimated as about ±5% by taking into account the error due to the sample resetting.

**Self-Diffusion Coefficients**

The self-diffusion coefficients D have been determined for light (H₂O) and heavy (D₂O) water along the coexisting curve. There have been carried out a few pulsed field gradient spin-echo (PGSE) experiments on the self-diffusion coefficients of water in sub- and supercritical water [26], [27], [28], [29]. The D values for H₂O by Hauser et al.[26] are in agreement with the present values over the entire temperature range. The D values for D₂O by Krinicki et al. [27] are slightly larger. The difference can be ascribed to the convection effect in their apparatus. Furthermore, our measurement was performed at resonance frequency one order of magnitude higher. For the case of H₂O, the D values by Jonas and co-workers [29] are in reasonable agreement with the present values.

The temperature and density effects are not separated when the temperature is varied along the saturation curve. In supercritical water, however, the density effect can be isolated by fixing the temperature; thus the kinetic and potential effects are more clearly differentiated. The self-diffusion coefficient D obtained for water including extremely low densities is shown in Fig. 6 in the form of \( \rho D/\sqrt{T} \). The slope of \( \rho D/\sqrt{T} \) against \( \rho \) is almost zero or slightly negative. This slope can be interpreted in terms of the lifetime of the supercritical hydration structure obtained through our recent molecular dynamics (MD) simulation [30]. The extrapolation of the experimental values to the zero density limit are much smaller than those predicted by the hard-sphere model, in which attractive interactions are neglected. This reflects the strong effect of attractive interaction on the self-diffusion in the low-density supercritical water.

**Isotope Effect**

At ambient conditions, the diffusion data of various isotopic species of water have yielded a rather detailed picture of the diffusion in water [31], [32]. In spite of the recent increase of interest in the dynamic isotope effect in water [33], [34], [35], reliable data are still awaited at high temperatures and high pressures, owing to experimental difficulties. The new high-temperature probe developed here is powerful enough to determine the isotope effect, which requires extremely high accuracy and precision.

In Fig. 7, we plot the isotope ratio \( D(D²H₂O)/D(H₂O) \) against the temperature along the coexisting curve. It is clearly shown that the isotope effect decreases with increasing temperature. The value \( D(D²H₂O)/D(H₂O) \), which is 1.23 in ambient water, becomes close to and slightly larger than unity at 350 °C. This slight increase has been beyond the precision of the previous studies [26], [27], [29]. Since D₂O is considered to be more structured than H₂O [36], [37], the isotope effect is a useful probe to intermolecular interaction, typically hydrogen bonding, apart from the density and the temperature dependencies. In ambient conditions, the effect of intermolecular interaction strength overwhelms the mass effect; the lower the temperature and/or the higher the density, the larger the isotope effect [38], [39]. It is of great interest to investigate the effect of weakened and distorted hydrogen bonding on the self-diffusion for super- and subcritical water from the classical and quantum mechanical points of view.

**Future Directions**

The high-temperature NMR method is now being proven to be useful in a broad range of areas including material, geological, and environmental sciences and technology. It is powerful in detecting reaction intermediates and identifying hydration effect on reactive species for environmentally benign, noncatalytic reactions in hot water [5], [7]. Application to ionic liquids, a new type of green solvent, is also subject to in-situ observation of a chemical process in it over a wide range of temperature [40]. A high-temperature condition is useful to characterize physical and chemical properties of polymers and organic complexes; a high-resolution, multinuclear
NMR can be conducted by melting or vaporizing them. It is thus expected in near future that the high-temperature NMR is a standard experimental procedure.

References


