NMR Study of Water Structure in Super- and Subcritical Conditions

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(Received 2 December 1996)

The proton chemical shift of water is measured at temperatures up to 400 °C and densities of 0.19, 0.41, 0.49, and 0.60 g/cm^3. The magnetic susceptibility correction is made in order to express the chemical shift relative to an isolated water molecule in dilute gas. Comparison of the chemical shifts of water in neat fluids at high temperatures to those in organic solvents at ambient conditions shows that the hydrogen bonding persists in supercritical water. At each density, the strength of the hydrogen bonding is found to reach a plateau value at high temperatures. [S0031-9007(97)02757-9]

PACS numbers: 61.25.Em, 76.60.Cq, 82.30.Nr

Water, which is an unusual solvent in ambient conditions, has recently been revealed to be a unique medium for chemical processes in super- and subcritical conditions [1]. In these extreme conditions, water loses its characteristics in ambient conditions and the solvation properties change drastically [1,2]. In order to understand and control the solvation properties on the molecular level, it is indispensable to characterize the microscopic structure of water in super- and subcritical conditions.

Typically, the microscopic structure of water is described in terms of the correlation functions between the intermolecular pairs of atoms O-H, O-O, and H-H. In particular, the O-H pair correlation function provides information on the hydrogen bonding between a pair of water molecules. An important observation on the hydrogen bonding of water in super- and subcritical conditions was presented by Mountain [3] in his computer simulation studies. He showed, using the TIP4P model, that the hydrogen bonding persists in super- and subcritical water over a wide density range 0.1–1 g/cm^3. This observation is supported by most of the later simulation studies [4–10] with an exception of an *ab initio* molecular dynamics simulation by Fois *et al.* [11] A markedly different conclusion was obtained, however, from neutron scattering studies by Postorino *et al.* [12–14]. They showed with their O-H pair correlation function that at a supercritical temperature 400 °C, the hydrogen bonding does not persist apparently even at a liquidlike density (0.66 g/cm^3). Although there seems no established conclusion concerning the hydrogen bonding between a neighboring pair of water molecules in a supercritical state, it is concluded from all of the computer simulations [3–11], the neutron scattering studies [12–14], and the x-ray diffractometry [15] that the hydrogen bond network involving more than two water molecules is destroyed at high temperatures. Thus, it is desirable to study supercritical water with an experimental method which sensitively probes the short-range order of water.

In this work, we study water in super- and subcritical conditions using proton NMR spectroscopy. The proton chemical shift is known to be sensitive to the hydrogen bonding of the observed proton with its environment, and we measure the proton chemical shifts of water up to a supercritical temperature 400 °C. Confining water in a capillary placed in an NMR sample tube, we can raise the temperature of water along the saturation curve and realize a supercritical state of water. The observed resonance frequency of proton is then corrected with the magnetic susceptibility, and the chemical shift is obtained which is free from ambiguities due to the use of a reference material. Our results show that the proton chemical shifts of water at supercritical conditions are on the downfield sides of those of water in nonpolar and weakly polar organic solvents at ambient conditions. In other words, the local environment of a water molecule in the supercritical region involves the hydrogen bonding.

In the capillary method, a capillary is placed in an NMR sample tube, standing up parallel to the external magnetic field. The content of water in the capillary uniquely determines the transition temperature T_t at which the distinction between the liquid and gas phases disappears (see Fig. 1), and the density of water remains constant

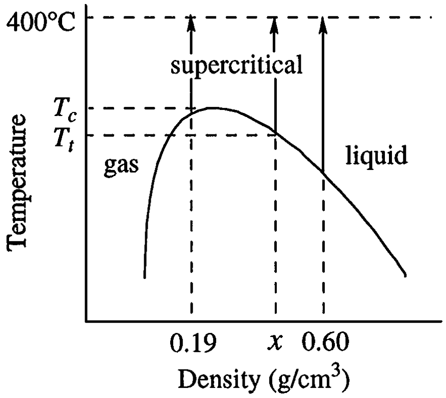

FIG. 1. Schematic phase diagram of water. Up to the transition temperature T_t, water is on the saturation curve, and beyond T_t, the density of water remains constant. The transition temperature T_t is uniquely determined by the water content x and is equal to or smaller than the critical temperature T_c.

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when the temperature is raised beyond T_t. When the ratio of the (liquid) water volume in the capillary to the total volume of the capillary is x at room temperature, the density of water at a temperature above T_t is x in the unit of g/cm^3, provided that the water density is 1 g/cm^3 at room temperature. Thus, at a temperature above T_t, the temperature and density can be controlled as independent variables in the capillary method. At a temperature below T_t, on the other hand, since the water in the capillary is in the two-phase region, only the temperature can be controlled as an independent variable and the densities of the liquid and gas phases are given by the saturation curve [16]. The water contents examined in this work are $x = 0.19$, 0.41, 0.49, and 0.60. At temperatures above T_t, the sample with $x = 0.19$ contains water in the gaslike region and the samples with $x = 0.41$, 0.49, and 0.60 contain water in the liquidlike region (see Fig. 1).

Since the capillary is parallel to the external magnetic field H_0 the magnetic field exerted on a proton is given by $H_0[1 + (4\pi/3)\chi(T)]$, where $\chi(T)$ is the (volumetric) magnetic susceptibility at the temperature T. The resonance condition is then expressed as

$$\omega(T) = \gamma H_0\left[1 - \sigma(T) + \frac{4\pi}{3}\chi(T)\right], \qquad (1)$$

where γ is the proton magnetogyric ratio, $\omega(T)$ and $\sigma(T)$ are, respectively, the resonance frequency and the shielding constant of water at the temperature T, and higher-order terms with respect to $\sigma(T)$ and $\chi(T)$ are neglected. Since the magnetic susceptibility per unit number of water molecules, χ_0, can be assumed to be independent of the temperature and pressure [17], $\chi(T)$ is simply given by $\chi_0\rho(T)$, where $\rho(T)$ is the density of water at the temperature T. The quantity of physical significance is the shielding constant $\sigma(T)$, and the negative of its deviation from a reference value is called the chemical shift $\delta(T)$. In this work, the reference for the chemical shift is taken to be an isolated water molecule in dilute gas, so that $\delta(T)$ represents the effect of the interaction of water with the surroundings. In the two-phase region, each of $\delta(T)$, $\omega(T)$, $\sigma(T)$, and $\rho(T)$ is two-valued and the values corresponding to the liquid and gas phases are specified by the subscripts l and g, respectively. It is then easy to see from Eq. (1) that

$$\begin{aligned}\delta(T) - \delta_g(200\,^\circ\mathrm{C}) = {} & \frac{\omega(T) - \omega_g(200\,^\circ\mathrm{C})}{\omega_g(200\,^\circ\mathrm{C})} \\ & - \frac{4\pi}{3}\chi_0[\rho(T) - \rho_g(200\,^\circ\mathrm{C})],\end{aligned} \qquad (2)$$

where higher-order terms with respect to $\sigma(T)$ and $\chi(T)$ are neglected. Since the water molecules in the gas phase at 200 °C can be considered isolated from one another [18,19], we set $\delta_g(200\,^\circ\mathrm{C}) = 0$. We can thus determine $\delta(T)$ from $\omega(T)$ and $\rho(T)$ without employing any reference material. The values of $\rho_l(T)$ and $\rho_g(T)$ in the two-phase region are obtained from the saturation curve provided by IAPWS [20].

When a reference material is used, it is called either internal or external, depending on whether it is contained in the sample vessel or in a separate vessel. When an internal reference is used, the chemical shift involves the difference between the sample shielding constant and the reference shielding constant. In the extreme conditions treated in this work, however, the reference shielding constant may not be invariable with a change in the state of the system. In addition, a reference material possibly decomposes at high temperatures. Therefore, an external reference needs to be employed which is kept at constant temperature and pressure. Our procedure to determine $\delta(T)$ with Eq. (2) is an external reference method in which an isolated water molecule in dilute gas is taken to be the reference.

The NMR spectra for the water content $x = 0.41$ are shown in Fig. 2 as a function of the temperature T. While the peak shifts upfield as the temperature is raised, $\delta(T)$ does not drop to 0 ppm even at 400 °C. In Fig. 3(a), we show the chemical shift $\delta(T)$ as a function of the temperature T for each capillary with the water content x. In this figure, there are two values of $\delta(T)$ at each temperature in the two-phase region. The curve in Fig. 3(a) with the lower-field values of $\delta(T)$ represents the chemical shift of water in the liquid phase and the curve with the higher-field values represents the chemical shift of water in the gas phase. For each capillary, the chemical shifts corresponding to the liquid and gas phases are, respectively, on the lower-field and higher-field branches in Fig. 3(a) up to the transition temperature T_t. This behavior corresponds to the fact that water is on the saturation curve up to T_t. When the temperature

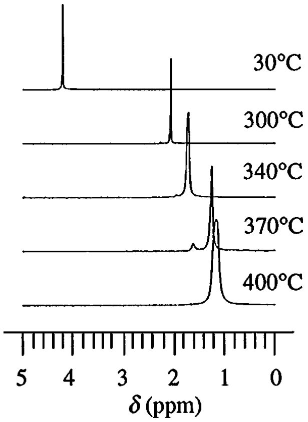

FIG. 2. Proton spectra of water from the capillary with the water content $x = 0.41$. The magnetic susceptibility correction is already made for the main peaks. At temperatures of 340 and 370 °C, the main peaks are from water in the liquid phase and the small peaks on the downfield side are from water in the gas phase.

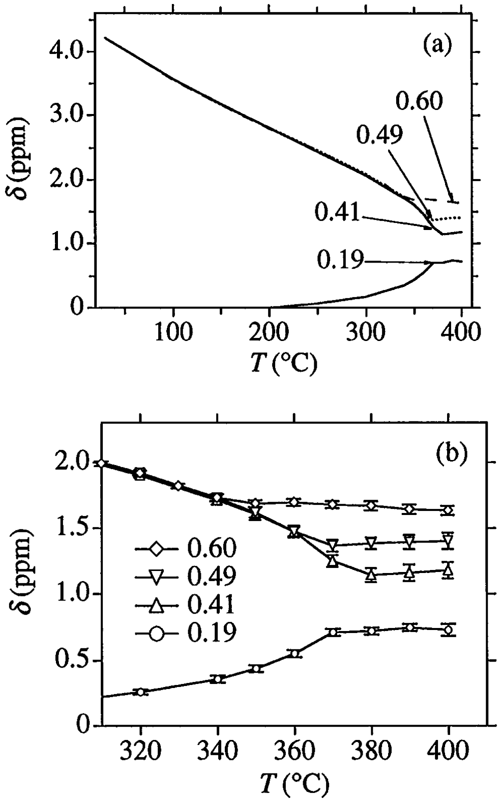

FIG. 3. (a) The chemical shifts δ as functions of the temperature T. At subcritical temperatures, the peaks from both the liquid and gas phases are seen in the NMR spectra for each capillary. The δ values for the stronger peaks are plotted, which correspond to the gas phase for $x = 0.19$ and to the liquid phase for $x = 0.41$, 0.49, and 0.60. The dashed line represents $x = 0.60$, the dotted line represents $x = 0.49$, the upper solid line represents $x = 0.41$, and the lower solid line represents $x = 0.19$. For both the liquid and gas peaks, the δ curves from the different capillaries overlap in the two-phase region. (b) A magnification of (a) in the super- and subcritical regions.

is above T_t, where water is in the one-phase region, the chemical shift is a function of both the temperature T and the density x. The chemical shift $\delta(T)$ in the super- and subcritical regions is shown in Fig. 3(b). As expected, the chemical shift increases with the density at each temperature above the critical temperature. It is striking, on the other hand, that at each density, the chemical shift is constant within the error bars against variation in the temperature above T_t. In other words, $\delta(T)$ reaches a plateau value beyond the transition temperature.

The plateau values of the chemical shift shown in Fig. 3 are measures of the strength of the hydrogen bonding in supercritical water. Since the chemical shifts of water in nonpolar and weakly polar organic solvents were found to be less than 1.1 ppm relative to an isolated water molecule in dilute gas [21], Fig. 3 shows that the hydrogen bonding of water persists in the supercritical region at the densities $x = 0.41$, 0.49, and 0.60 g/cm^3. This is consistent with an infrared spectroscopic evidence [22], in which the frequency of the O-D stretching mode of HDO in supercritical water is lower than that of an isolated HDO molecule. In addition, the plateau behavior of the chemical shift shown in Fig. 3 implies that the strength of the hydrogen bonding does not change with the temperature once the density is fixed. The probability of formation of the hydrogen bonding in a neighboring pair of water molecules will be estimated in a semiquantitative manner after Fig. 4 is shown.

In Fig. 4, we show the chemical shift divided by the density $\delta(T)/x$ as a function of the density x at a temperature of 400 °C. Since the chemical shift is almost constant at a temperature above the critical temperature, the corresponding figures at temperatures of 380 and 390 °C are similar to Fig. 4. According to Fig. 4, $\delta(T)/x$ is constant within the error bars except when $x = 0.19$. In other words, when the density is larger than the critical density (0.32 g/cm^3), the chemical shift is proportional to the density. This indicates that the cooperative nature of the hydrogen bond network is absent in the supercritical region, in agreement with the neutron scattering studies [12–14] and the x-ray diffractometry [15].

When the hydrogen bond network is destroyed, only dimers are to be considered to account for the hydrogen bonding in the supercritical region. In this case, a simple two-state model provides a semiquantitative estimate of the probability of formation of the hydrogen bonding in a neighboring pair of water molecules. Let ΔE_{HB} be the energy of the hydrogen bonding of a dimer, which is typically taken to be 4 to 6 kcal/mol. The probability of the hydrogen bonding, $P(T)$, at a temperature T is then

$$P(T) = \frac{V_{\mathrm{HB}} \exp(\Delta E_{\mathrm{HB}}/k_{\mathrm{B}}T)}{V_{\mathrm{HB}} \exp(\Delta E_{\mathrm{HB}}/k_{\mathrm{B}}T) + V_{\mathrm{non-HB}}}, \quad (3)$$

where k_{B} is the Boltzmann constant and V_{HB} and $V_{\mathrm{non-HB}}$ are, respectively, the volumes of the configuration spaces of hydrogen-bonded and non-hydrogen-bonded dimers. When the temperature is raised from T_1

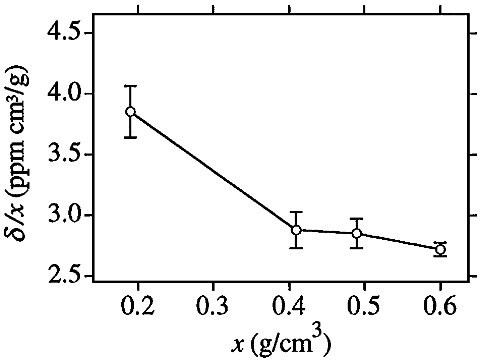

FIG. 4. The chemical shift divided by the density δ/x as a function of the density x.

to T_2,

$$\frac{P(T_2)}{P(T_1)} - 1 = [1 - P(T_2)] \times [\exp(\Delta E_{\mathrm{HB}}/k_{\mathrm{B}}T_2 - \Delta E_{\mathrm{HB}}/k_{\mathrm{B}}T_1) - 1]. \tag{4}$$

When the chemical shift $\delta(T)$ is considered proportional to the number of hydrogen bonds per water molecule, Fig. 3 gives $|P(400\,^\circ\mathrm{C})/P(T) - 1| \lesssim 0.1$ for a temperature T in the one-phase region, provided that the coordination number of a water molecule is a weak function of T [15]. It is then easy to see from Eq. (4) that

$$P(400\,^\circ\mathrm{C}) \gtrsim 1 - \frac{0.1}{1 - \exp(\Delta E_{\mathrm{HB}}/1.34 - \Delta E_{\mathrm{HB}}/k_{\mathrm{B}}T)}, \tag{5}$$

where ΔE_{HB} is expressed in the unit of kcal/mol. When Eq. (5) is used to obtain a lower bound of $P(400\,^\circ\mathrm{C})$, T is to be taken as the lowest temperature in the plateau region of $\delta(T)$. For the capillary with $x = 0.60$, $T = 340\,^\circ\mathrm{C}$ and $P(400\,^\circ\mathrm{C}) \gtrsim 0.7$ when the hydrogen bond energy ΔE_{HB} is taken to be 5 kcal/mol. Similarly, $T = 370\,^\circ\mathrm{C}$, and $P(400\,^\circ\mathrm{C}) \gtrsim 0.4$. Note that these values of the lower bound of $P(400\,^\circ\mathrm{C})$ are of semiquantitative nature. The contribution to $\delta(T)$ of interactions other than the hydrogen bonding may decrease the estimates of $P(400\,^\circ\mathrm{C})$, while in view of Fig. 3, the above lower bounds are conservative since $\delta(T)$ is expected to be almost constant somewhat beyond 400 °C.

In his computer simulations using the TIP4P model, Mountain showed that the number of hydrogen bonds per water molecule, N_{HB}, reaches a plateau value in the high temperature region at each density and that the plateau value of N_{HB} is proportional to the density except in the low density region [3]. Thus, the behavior of the calculated N_{HB} is in coincidence with that of the observed chemical shift shown in Figs. 3 and 4, while the van der Waals interactions also contribute to the chemical shift of water [23]. In the subsequent paper, we present combined analyses of the chemical shift using NMR spectroscopy and computer simulations, in order to obtain quantitative information on the hydrogen bonding of water in super- and subcritical conditions.

[1] L. W. Flanagin, P. B. Balbuena, K. P. Johnston, and P. J. Rossky, J. Phys. Chem. **99**, 5196 (1995), and papers cited therein.

[2] D. M. Pfund, J. G. Darab, J. L. Fulton, and Y. Ma, J. Phys. Chem. **98**, 13 102 (1994).

[3] R. D. Mountain, J. Chem. Phys. **90**, 1866 (1989).

[4] P. T. Cummings, H. D. Cochran, J. M. Simonson, R. E. Mesmer, and S. Karaborni, J. Chem. Phys. **94**, 5606 (1991).

[5] Y. Guissani and B. Guillot, J. Chem. Phys. **98**, 8221 (1993).

[6] T. I. Mizan, P. E. Savage, and R. M. Ziff, J. Phys. Chem. **98**, 13 067 (1994).

[7] G. Löffler, H. Schreiber, and O. Steinhauser, Ber. Bunsenges. Phys. Chem. **98**, 1575 (1994).

[8] A. A. Chialvo and P. T. Cummings, J. Chem. Phys. **101**, 4466 (1994).

[9] A. G. Kalinichev and J. D. Bass, Chem. Phys. Lett. **231**, 301 (1994).

[10] R. D. Mountain, J. Chem. Phys. **103**, 3084 (1995).

[11] E. S. Fois, M. Sprik, and M. Parrinello, Chem. Phys. Lett. **223**, 411 (1994).

[12] P. Postorino, R. H. Tromp, M. A. Ricci, A. K. Soper, and G. W. Neilson, Nature (London) **366**, 668 (1993).

[13] R. H. Tromp, P. Postorino, G. W. Neilson, M. A. Ricci, and A. K. Soper, J. Chem. Phys. **101**, 6210 (1994).

[14] A. K. Soper, F. Bruni, and M. A. Ricci, J. Chem. Phys. **106**, 247 (1997).

[15] K. Yamanaka, T. Yamaguchi, and H. Wakita, J. Chem. Phys. **101**, 9830 (1994).

[16] Since air is actually contained in the capillary, water is not exactly on its saturation curve. But when the temperature is higher than 200 °C, the effect of the air on the water saturation curve is negligible.

[17] According to the *CRC Handbook* [(CRC Press, Boca Raton, Florida, 1989), 70th ed.] the magnetic susceptibility of steam at a temperature above 100 °C is -13.1×10^{-6} emu/mol, and that of (liquid) water at 0 °C is -12.9×10^{-6} emu/mol.

[18] W. G. Schneider, H. J. Bernstein, and J. A. Pople, J. Chem. Phys. **28**, 601 (1958).

[19] J. C. Hindman, J. Chem. Phys. **44**, 4582 (1966).

[20] The International Association for the Properties of Water and Steam, IAPWS Formulation 1995, Fredericia, Denmark (1996).

[21] M. Nakahara and C. Wakai, Chem. Lett. **809** (1992).

[22] E. U. Franck and K. Roth, Discuss. Faraday Soc. **43**, 108 (1967).

[23] I. M. Svishchev and P. G. Kusalik, J. Am. Chem. Soc. **115**, 8270 (1993).