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NMR Study of Water Structure in Supercritical States

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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/cm³. The magnetic susceptibility correction is made in order to express the chemical shift relative to an isolated water molecule in the gas phase. Comparison of the observed chemical shift to that of a solitary water molecule in an organic solvent shows that the hydrogen bonding persists in the supercritical water. At each density, the strength of the hydrogen bonding is found to reach a plateau value at high temperatures.

Keywords: Supercritical/ Water/ Hydrogen bonding/ NMR/ Proton chemical shift

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. In these extreme conditions, water loses its characteristics in ambient conditions and the solvation properties change drastically. 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. Since the hydrogen bonding is the origin of the unique properties of liquid water at ambient conditions, it is desirable to study supercritical water with an experimental method which sensitively probes the hydrogen bonding of water. In this work, we study water in super- and subcritical conditions using high-resolution NMR spectroscopy combined with the capillary method. 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.

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, and the density of water remains constant when the temperature is raised beyond T_t . 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. The water contents examined in this work are $x = 0.19, 0.41, 0.49, \text{ and } 0.60$, where x is the ratio of the water volume in the capillary to the total volume of the capillary at room temperature.

When the chemical shift is to be determined, a reference

INTERFACE SCIENCE —Solution and Interfaces—

Scope of research
Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biological interests are systematically studied by NMR under extreme conditions. High pressures and high temperatures are employed to shed light on microscopic controlling factors for the structure and dynamics of solutions. Vibrational spectroscopic studies are carried out to elucidate structure and orientations of organic and water molecules in ultra-thin films. Crystallization of protein monolayers, advanced dispersion systems at liquid-liquid interfaces, and biomembranes are also investigated.



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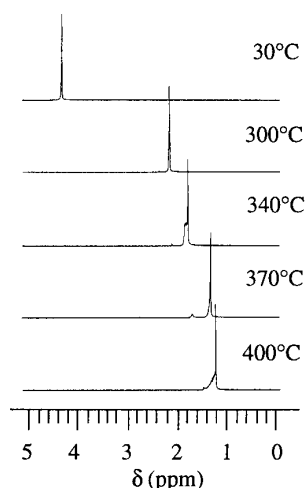


Figure 1. Proton spectra of water from the capillary with the water content $x = 0.41$.

material needs to be chosen. In this work, we do not employ any reference material by directly correcting the effect of the bulk magnetic susceptibility on the magnetic field exerted on a water proton. The magnetic field exerted on a proton differs from the applied magnetic field by a factor determined by the bulk magnetic susceptibility of the fluid. It is thus possible to correct the effect of the bulk magnetic susceptibility from the knowledge of the susceptibility as a function of the temperature and density. The chemical shift of water in the fluid relative to an isolated water molecule in the gas phase can then be obtained from the resonance frequency.

The proton spectra for the water content $x = 0.41$ are shown in Fig. 1 as a function of the temperature T . While the peak shifts upfield as the temperature is raised, the chemical shift δ does not drop to 0 ppm even at 400°C. In Fig. 2(a), we show the chemical shift δ as a function of the temperature T for each capillary with the water content x . Below the critical temperature (374°C), the curve with the lower-field values of δ 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. When the temperature is above T_c , 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 δ in the super- and subcritical region is shown in Fig. 2(b). As expected, it is shown in Fig. 2(b) that the chemical shift increases with the density at each temperature above the critical temperature. It is striking in Fig. 2(b), on the other hand, that the chemical shift at a temperature above T_c is constant within the error bars at each density. In other words, δ reaches a plateau value beyond the transition

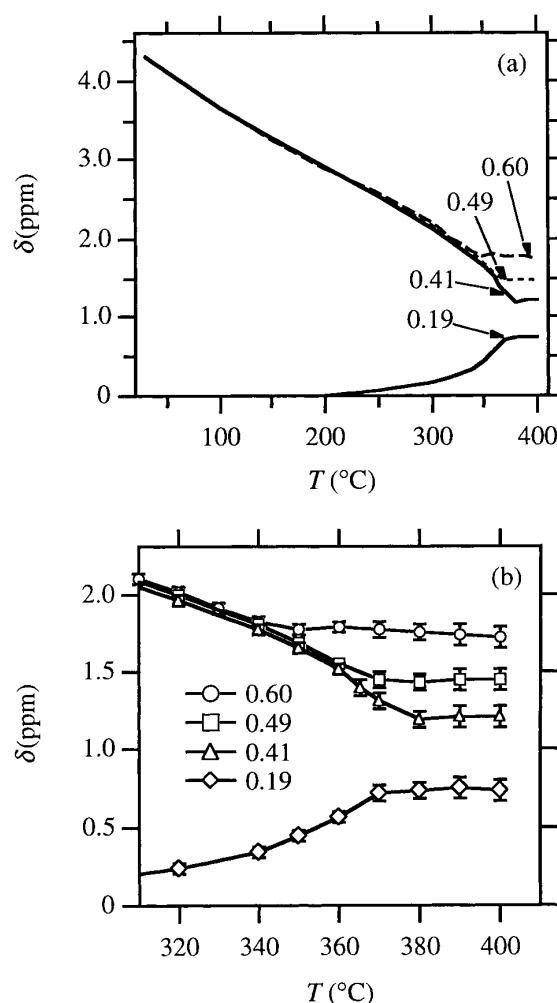


Figure 2. (a) The chemical shifts δ as functions of the temperature T . (b) A magnification of (a) in the super- and subcritical region.

temperature.

Since the chemical shift of a solitary water molecule in weakly hydrogen bonding chloroform solvent was found to be 1.2 ppm relative to an isolated water molecule in the gas phase, Fig. 2 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 . A simple two-state model provides a semi-quantitative estimate of the lower bound of the probability of formation of the hydrogen bonding in a pair of water molecules. The probability at 400°C is larger than 0.7 at a density of 0.60 g/cm^3 , it is larger than 0.4 at 0.49 g/cm^3 , and it is larger than 0.1 at 0.40 g/cm^3 . These estimates agree well with those from computer simulations.