# Effects of ions in natural water on the $^{17}$O NMR chemical shift of water and their relationship to water cluster

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## Abstract

Effects of temperature and some aqueous solutions of electrolytes consisting of ions in natural water on the chemical shifts of NMR of water ($^{17}$O NMR) have been measured. Combining the cluster model of liquid water structure and the dependence of $\delta(^{17}OH_2)$ on temperature a relationship deduced of $\delta(^{17}OH_2)$ to median water cluster size effects of ions on median water cluster and the size are analyzed. The relationships between $^{17}$O NMR and concentration of ions are linear. Cations increase the median water cluster size and anions decrease it. The bigger the radius of ions with equal ionic charge, the stronger the effect of the ion. The extent of the ionic charge effect is much bigger than that of the ionic radius. The order of the effect of cations and anions is $Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Al^{3+} < Fe^{3+}$, and $OH^- < HCO_3^- < Cl^-$, and $CO_3^{2-} < SO_4^{2-}$, respectively.
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## 1. Introduction

Many ions exist in natural water. $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Al^{3+}$, $Fe^{3+}$ and $OH^-$, $HCO_3^-$, $Cl^-$, $CO_3^{2-}$, $SO_4^{2-}$ are usual in natural water and have important influence on human health. To ensure safety of drinking water, several water quality indexes such as hardness, pH, turbidity, chloride, sulphate, total dissolved solid, etc, have been introduced as water quality standards. However, all these indexes pay only attention to the amount of ions in water neglecting their effects on water structure [1].

There are two main models of liquid water structure: the continuum model and the cluster model. The continuum model is based on a random continuous hydrogen-bonded network of macroscopic extent breaking and reforming on a timescale of $10^{-12}$ s and with a continuous spectrum of hydrogen-bond strengths. The cluster model assumes that water consists of a continuous distribution of cluster sizes,

the median cluster size of this distribution decreasing with increasing temperature [2–4].

In liquid water, three time-averaged water structures, I-structure (instantaneous structure), V-structure (vibrationally averaged structure) and D-structure (diffusionally averaged structure), have been defined according to different time intervals [3]. Structures of liquid water have been investigated in different fields such as physics, chemistry and physical chemistry over 100 years [4,5]. There are many approaches such as statistical thermodynamics [2,6], molecular dynamics simulation [7], using infrared spectrum [8], Raman spectrum [9], X-ray diffraction [1,2], neutron diffraction [10] and nuclear magnetic resonance [11], etc. to study the structure of water. Different approaches probe different time-averaged water structures. Nuclear magnetic resonance (NMR) is thought to be one of the most effective approaches for investigating the D-structure of water on a timescale of $10^{-8}$ s in liquid water and aqueous solutions.

It was pointed out [12] that the proton chemical shift increases when hydrogen nuclei are involved in hydrogen bonds. Subsequently there are many researches on the relationships between chemical shift of NMR and hydrogen

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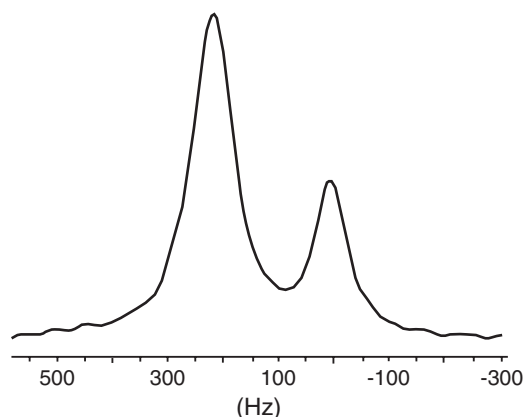*E-mail address:* jchen1@tsinghua.edu.cn (R. Li).

Fig. 1. Typical $^{17}$O NMR spectra of water.

bond with both $^1$H-NMR and $^{17}$O-NMR. They try to signify the intensity of the hydrogen bond by the chemical shift of NMR in hydrogen bonded liquids [13–16].

In supercritical water, the relationships between chemical shift and extent of hydrogen bonding are linear by $^1$H NMR [17]. The chemical shift is related to the average number of hydrogen bonds in which a water molecule is involved [15]. The $^{17}$O and $^1$H NMR chemical shifts of water in aqueous solutions show that they are largely specific quantities and are not well correlated with other solution properties. Assuming that the ammonium ion has no effect on the $^{17}$O and $^1$H NMR chemical shift of water, the $^{17}$O and $^1$H ionic molar chemical shifts for the individual ions are evaluated [18–20]. Studies by $^{17}$O NMR indicate that the effect of KCl on the water structure depends on temperature [21]. The relationship between water quality and dynamic structure in ultrapure water production system also has been studied by $^{17}$O NMR [22,23]. All of the above studies show that the chemical shifts of $^{17}$O and $^1$H-NMR are connected to the extent of hydrogen bonding in water and aqueous solutions, and water quality in related to water structure.

In this study, the aim is to measure the effect of temperature and of some salts on the $^{17}$O NMR chemical shift, deducing a relationship of $^{17}$O NMR chemical shift to median water cluster size, and extrapolating the effects of ions on median water cluster size by a relationship and exploring possible relationships between water structure and water quality.

## 2. Experiment

The salts and reagents used in this study are analytical grade chemicals without further purification. The used water is ultrapure water with resistivity of about 18.0 MΩ cm. TOC and DO of the water are below 1 ppb and 5 ppb, respectively.

All $^{17}$O NMR experiments were conducted on a Bruker AM 500 superconductor spectrometer at Tsinghua University. A sealed capillary tube of D$_2$O, a locking substance, was

inserted at the center of a 5-mm sample tube. The chemical shifts of the spectra were referenced to the $^{17}$O resonance peak of the external D$_2$O. $^{17}$O spectra were obtained at 67.8 MHz using a 90° pulse (24 µs). Each free induction decay (FID) had 1500 scans with a recycle delay of 0.15 s. The experimental temperature was maintained at 293 K except for the temperature-dependent experiments. The reproducibility of the chemical shifts was better than 5 Hz.

Fig. 1 shows the typical $^{17}$O NMR spectrum. The left peak is the spectrum of water and the right peak is the spectrum of heavy water. In this experiment, $^{17}$O chemical shifts are expressed in Hz (not in the usual ppm), because the low concentrations of solutions result in low chemical shifts.

All original data of chemical shifts except the temperature-dependent experiments are relative to pure water. The chemical shift of pure water, 211±2.5 Hz, was treated as 0 Hz.

## 3. Results

### 3.1. Temperature dependence of $^{17}$O NMR chemical shift of water

Temperature influences hydrogen bonding in water and many investigations have been done on this problem. However, the rule of temperature and $^{17}$O NMR chemical shift is not unambiguous [2].

The measured $^{17}$O NMR chemical shifts of pure water in the temperature range of 293 to 333 K in Fig. 2 show that the $^{17}$O NMR chemical shifts of water decrease with increasing temperature. The linear relationship between $\delta(^{17}OH_2)$ and temperature ($t$) can be expressed by the following Eq. (1)

$$\delta(^{17}OH_2) = -3.349t + 1189.9 \qquad R^2 = 0.9913 \qquad (1)$$

The result is in agreement with that of the literature [4] in which the slope is 3.206 (Hz/K) in the temperature range of 273–488 K.

Hydrogen bonding generally becomes weaker at increasing thermal motion of the atoms involved [24]. Therefore, as the temperature increases, the water structure breaks down. This has been confirmed by Raman spectrum [10], IR spectrum [9], X-ray diffraction and Neutron diffraction. The
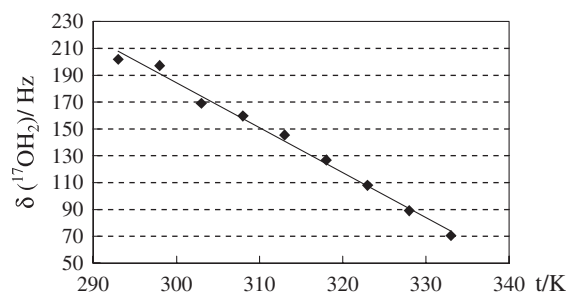


Fig. 2. Dependence of $\delta(^{17}OH_2)$ on temperature.