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Effects of nano-materials on ^{17}O NMR line-width of water clusters

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HIGHLIGHTS

- The effect of nano-materials on ^{17}O NMR line-width of water was studied.
- The value of ^{17}O NMR line-width was decreased by adding nano-materials.
- The change of ^{17}O NMR line-width was stable with time and temperature.
- We studied the relationship between adding nano-materials and changing water cluster size.

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ABSTRACT

Effects of nano-materials on ^{17}O NMR line-width of water clusters have been measured. Different water samples were prepared by adding nano-materials into distilled water and tap water. The average particle size and distribution of nano-materials were characterized, meanwhile, the ions, pH values, total dissolved solids (TDS) and ^{17}O NMR line-width of different water samples were also tested. The effects of time and temperature on ^{17}O NMR line-width of water sample prepared by adding nano-materials into tap water (pH = 8.3) were analyzed as well. The experimental results showed that the particle size distribution of the nano-materials is from 1 to 300 nm, the average particle size is 95.5 nm and the median particle size is 44.7 nm. The nano-materials were mainly composed of calcium. After adding moderate nano-materials into different water samples, the ^{17}O NMR line-width of distilled water decreased from 59 Hz to 44 Hz and the tap water decreased from 113 Hz to 53 Hz. The ^{17}O NMR line-width of water sample prepared by adding a certain amount of nano-materials into tap water (pH = 8.3) is almost the same after 42 days, and the value keeps nearly unchanged as the temperature increases from 30°C to 85 °C.

1. Introduction

Water is one of the most important substances for human life in the world with some special properties, such as a high melting point, a high boiling point and strong surface tension. These phenomena can be well explained by the cluster model of liquid water structure [1,2]. The cluster model supposed that water consists of a continuous distribution of cluster sizes, the median size of this distribution decreases as temperature rises [3]. Some theories and experiments have been studied for the structure of water clusters. In 1977, Dyke has observed the structural information of water dimer which has been fitted to a rigid rotor model using electric resonance spectroscopy [4]. A number of high-level ab initio calculations have predicted the structure of water clusters. For the small water clusters, a quasi-planar cyclic structure with each monomer acting as both proton donors and acceptors fits the structure of water trimer through pentamer and a cage rather than a ring structure fits the water hexamer better. For the water heptamer and larger clusters, a tendency towards three-dimensional structure is predicted [5–10]. In 1992, Saykally and his co-workers had probed the structure of water trimer through the vibration–rotation tunneling (VRT) band of the perdeuterated cluster by tunable far infrared laser absorption spectroscopy, aroused the interest of confirming the structure of larger water clusters predicted by theoty [11–13].

Liquid water can be divided into three time-averaged structures on the basis of different time intervals. Different methods study different time-average water structures [3]. There are many methods to investigate the structure of water including theoretical quantum chemical approach [14], inelastic neutron scattering [15], infrared [16], Raman [17] and nuclear magnetic resonance [18] spectroscopy. Nuclear magnetic resonance (NMR) is an excellent method with studying the diffusionally averaged structure of water on a timescale of 10^{-8} s, some parameters of the ^{17}O NMR can be regarded as effective means for probing structure, dynamics, intermolecular and intramolecular hydrogen bonding effects of liquid water, such as ^{17}O NMR line-width [19–21]. The relation-

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ship between ^{17}O NMR line-width and water clusters has been investigated and the results show that the line-width decreases as the temperature rises.

Water structure related to hydrogen bonding can be influenced by chemical and physical factors such as ions, temperature and pressure [22]. It is well known that water cluster size and distribution will be decreased with increasing temperature and falling pressure. Ions in water also can change the water cluster size and distribution by affecting hydrogen bonding [23]. Walrafen observed the Raman intensity of liquid water decreases as the temperature rises [24], Ruihua obtained the relationship between the chemical shifts of NMR of water and the concentration of ions are linear [3]. Many methods can be realized to change the structure of water clusters such as external electric field, external magnetic field, microwave irradiation and laser radiation. Dhurba studied the structure of water clusters induced by a uniform static external electric field using the density functional theory; it has been proved the number of hydrogen bonds decreases with the field strength increase. Evgenii observed the microwave irradiation changes the state of water, the result is tempting to consider the irradiated and unirradiated water samples are different in size and concentration of water clusters [25–28].

In this study, the aim is to observe the effect of nano-materials on ^{17}O NMR line-width of different kinds of water, investigating the influence of temperature and time on the ^{17}O NMR line-width of the water sample prepared by adding nano-materials, extrapolating the effects of nano-materials on median water cluster size.

2. Experimental

2.1. Preparation

The nano-materials used in this study were provided by Guangzhou Lucky star Science and Technology Ltd. Water samples were prepared by adding nano-materials into different kinds of water, including distilled water (watsons distilled water) and tap water(collecting in the lab).

2.2. Characterization

The average particle size and distributions of nano-materials were determined by small angle X-ray scattering method with a X-ray diffractometer (Philips X' Pert Pro MPD) according to GB/T13221-2004. The cations concentration (Na^+, K^+, Ca^{2+}, Mg^{2+}) were determined by atomic absorption spectrum using a Varian AAFS240 instrument. The contents of anion (Cl^-, SO_4^{2-}, NO_3^-) were determined by ionic chromatography using a Dionex INC ICS-1000 instrument. All ^{17}O NMR experiments were conducted on a Bruker AVANCE Digital 400 MHz NMR, and the resonance frequency is 81.34 MHz.

3. Results

3.1. Particle size and distribution of the nano-materials

The XRD patterns of the nano-materials are shown in Fig. 1. The XRD patterns in Fig. 1 clearly present the size distribution of the nano-materials is 1–300 nm, the average size is 95.5 nm and the medium size is 44.7 nm.

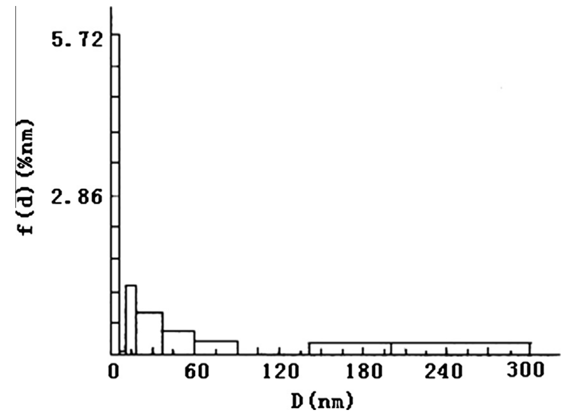

Fig. 1. Average particle size and distribution of nano-materials.

3.2. Physical and chemical properties of water samples

Water quality can be influenced by the physical and chemical properties such as ionic composition, acidity and total quantity of dissolved solid. Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} are common ions in natural water. Water sample 1 was prepared by adding 0.0050 g nano-materials into distilled water, and water sample 2 was prepared by adding 0.0050 g nano-materials into tap water. The ions, pH values and total dissolved solids of different water samples were tested and the results are shown in Table 1.

The figures in Table 1 clearly presented that the adding of the nano-materials resulted in the increment of alkalinity and total solid solute, it meant the ions in the water have raised, especially for Na^+, Ca^{2+}. The change of ionic concentration shows the ingredients of the nano-materials, including large amount of Ca^{2+}, little amount of Na^+ and a quantity of Cl^-, NO_3^-.

3.3. Measurement of ^{17}O NMR spectra

3.3.1. ^{17}O NMR line-width of different water samples

NMR is a useful method to study water structure. The ^{17}O NMR line-width has been measured in different water samples, the results are shown in Table 2 and Fig. 2. The figures and spectrograms present the ^{17}O NMR line-width of distilled water decreased from 59 Hz to 44 Hz and the ^{17}O NMR line-width of tap water decreased from 113 Hz to 53 Hz by adding nano-materials.

The relationship between ^{17}O NMR line-width and median water cluster size has been investigated by some studies, it can be deduced that the wider ^{17}O NMR line-width, the larger median water cluster size. Ions dissolved in water can affected the water clusters by the interaction of water molecules and ions or the formation of cluster of ion-water and water–water. Cations enlarge the median water cluster size and anions decrease it. In the range of low concentration, the larger concentration of ions dissolved in water, the stronger of the effect on the ^{17}O NMR line-width. The

Table 1
Composition and content of ions in different water samples.

Water sample	pH value	TDS value/mg L^{-1}	Cations/mg L^{-1}				Anions/mg L^{-1}		
			Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}
Distilled water	6.05	0	0	0	0	0	0	0	0
Tap water	7.42	82	14.91	4.05	4.86	1.67	15.55	11.08	11.49
Sample 1	10.02	21	0.28	0	14.96	0	2.44	2.10	0
Sample 2	9.13	94	15.15	4.11	22.2	1.67	15.72	11.13	11.72