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CuCl₂ 和 CuSO₄ 的核磁共振系数、粘度系数及其与水分子结构的关系

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摘要：　测定了较低浓度范围内 CuCl₂、CuSO₄ 水溶液的粘度系数(B)、核磁共振(NMR)系数(B')及其对水 ¹⁷O NMR 化学位移的影响, 进一步计算了 Cu²⁺、Cl⁻、SO₄²⁻的粘度系数及核磁共振系数, 并与文献值进行了比较. 利用 ¹⁷O NMR 化学位移、粘度系数和核磁共振系数与水团簇结构和水分子缔合的关系, 分析了 CuCl₂、CuSO₄ 对水结构的影响. 结果表明, CuCl₂ 和 CuSO₄ 均具有促进水分子缔合, 使水团簇加大的作用, 且 CuSO₄ 对水的缔合作用大于 CuCl₂, Cl⁻对水缔合的破坏作用大于 SO₄²⁻. Cu²⁺作为顺磁离子, 在核磁共振弛豫过程中, 具有明显的缩短水中质子的自旋-晶格弛豫时间, 使谱线变宽的作用.

关键词：　水结构；　CuCl₂；　CuSO₄；　化学位移；　粘度系数；　核磁共振系数

中图分类号：　O645

NMR and Viscosity Coefficients of CuCl₂ and CuSO₄ and Their Relationship to Water Structure

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Abstract：　The viscosity coefficient (B) and nuclear magnetic resonance (NMR) coefficient (B') of CuCl₂ and CuSO₄ and their effects on the ¹⁷O NMR chemical shift (δ) of water were determined at low concentrations. From these B and B' values, individual ion's B and B' values were further calculated. These coefficients and the relationship between aqueous solution concentrations and $\delta(^{17}OH_2)$ represented the effect of ions on water structure and the median water cluster size in aqueous solutions. CuCl₂ and CuSO₄ were both "structure-makers". The effect of CuSO₄ on water structure and median water cluster size was more powerful than that of CuCl₂. Cl⁻ broke more water clusters than SO₄²⁻. Cu²⁺ had an obvious effect on shortening the proton spin-lattice relaxation time in water and broadening the line width of the NMR spectrum during the NMR relaxation process.

Key Words：　Water structure；　CuCl₂；　CuSO₄；　Chemical shift；　Viscosity coefficient；　NMR coefficient

Water is the most common substance in the world. It has many unique properties resulting from its structure. The hydrogen bond of water molecule can be influenced by chemical and physical factors such as ions, temperature, and pressure, etc[1,2].

It is generally assumed that ions affect the structure of water by enhancing or weakening its hydrogen bond. Many studies[3−5] have proved that strongly hydrated ions, such as Mg²⁺, Ca²⁺, Li⁺, SO₄²⁻, and HPO₄²⁻, have strong interactions with water molecules and increase water association, resulting in lower mobility (or higher viscosity) of the solution. Therefore, these ions are named "structure-makers" or "kosmotropes". On the other hand, some ions are weakly hydrated in aqueous solutions, such as SCN⁻, I⁻, NO₃⁻, BF₄⁻, and Cs⁺, which have weak interactions with water and destroy the tetrahedral hydrogen-bond structure, leading to a

relatively high mobility. These ions are often referred to as "structure-breakers" or "chaotropes". The ion kosmotropicity, which represents the capacity of an ion to strengthen the water structure, can be reflected by different thermodynamic parameters including viscosity coefficient (B), structural entropy, nuclear magnetic resonance (NMR) coefficient (B'), and ion mobility, etc[6]. Within all the parameters, B is the most widely used parameter in comparing ion kosmotropicity. It can be calculated by the Jones-Dole expression[7–10]:

$$\eta/\eta^0 = 1 + Ac^{1/2} + Bc + Dc^2 + \cdots \qquad (1)$$

where η is the viscosity of the solution, η^0 is the viscosity of pure water, c is the ion concentration. A, B, and D refer to different impact coefficients. The coefficient A represents solute-solute or electrostatic interaction between the ions. However, the constant A is so small that it can be omitted from the calculations. The coefficient B is the viscosity coefficient, which represents the influence on the hydrogen bond structure by the ion, or called solute-solvent interaction. Strong structure-makers (kosmotropes) have positive B, that is, the viscosity will increase with concentration, vice versa. The coefficient D reflects both the solute-solute interaction and the solute-solvent interaction. For low concentration salt solution (<0.5 mol·L⁻¹), D and further coefficients can be neglected.

On the other hand, B' is another useful parameter in comparing the ion kosmotropicity. It is an analogy to the Jones-Dole viscosity equation, from which B' can be deduced[11,12].

$$T_1^0/T_1 = 1 + B'c + D'c^2 + \cdots \qquad (2)$$

where T_1^0 and T_1 represent the proton spin-lattice relaxation time of water in the absence and presence of ions, respectively. Similarly, the coefficient D' can be neglected at low concentrations. In general, it seems to be in agreement with the same ion kosmotropicity order resulting from B' and B[6,9], the higher the B' value, the stronger the ion kosmotropicity.

The degree of ions effect on water structure is related to ionic radius, ionic charge, ionic outside electron structure, and ionic structure. The effects of salts of alkali metals and alkaline earth metals, including halide, sulphate, carbonate, and hydroxide, on water structure have been studied using ¹⁷O NMR chemical shift by many scholars[13–16]. From these researches, we can see that ¹⁷O NMR chemical shift is an effective mean to indirectly reflect the median water cluster size. The chemical shift (δ), which reflects the average number of hydrogen bonds of a water cluster[17], can be used to demonstrate the effect of ions on water structure. For structure-makers (kosmotropes), $\delta(^{17}OH_2)$ increases with the growing size of water cluster, while the structure-breakers (chaotropes) show the opposite property. Although the effects on water resulting from the ionic radius, the ionic charge, the ionic outside electron structure, and the ionic structure are reported differently according to literature[13–18], it is believed that for most cations and anions, $\delta(^{17}OH_2)$ increases with ionic radii (where the strength of the electrical field around the ion decreases) and ionic charge effect is much bigger than that of the ionic radius.

Cu²⁺, Cl⁻, and SO₄²⁻, which have important effects on human

health, are common ions in natural water and human body. Cu²⁺ is essential microelement for human health at low concentration, but harmful at high concentration. With the development of industry, the pollution of Cu²⁺ in water is becoming more serious. To ensure the safety of drinking water, several water quality indexes, such as hardness, the concentration of chloride, sulphate, and microelements, etc, have been introduced as standards to judge the water quality. However, all these indexes were paid attention only to the amount of ions in water but not their effects on water structure[19]. The research of ion effects on water structure at molecular level can bring meaningful support to explain the harm of ions to human health. There are many researches on the effects of salts of alkali metals and alkaline earth metals, including halide, sulphate, carbonate, and hydroxide, on the water structure and even on biological macromolecule stability[20]. However few have been done on the relations between Cu²⁺ and water structure, so in this study, the aim is to measure B and B' of CuCl₂, CuSO₄, and their individual ions, deducing the relationship between ¹⁷O NMR chemical shift and aqueous solution concentrations, consequently extrapolating the effects of these ions on median water cluster size and water structure.

1 Experimental

The salts and reagents used in this study were analytical grade chemicals without further purification. The water used was trinal distilled water with total organic carbon (TOC) and dissolved oxygen (DO) below 1.0×10⁻³ and 5.0×10⁻³ mg·L⁻¹, respectively.

Viscosities were measured using capillary Ubbelohde viscometer at 25 ℃ thermostatic water bath (CH1015, Shanghai Hengping Instrument Co., China), the diameter of the capillary was 0.5–0.6 mm, the circulating bath was stable to ±0.05 ℃. Each sample was measured three times with the measure time error between every measurement below ±0.5 s, the average viscosity was the viscosity of the measured sample.

All ¹⁷O NMR experiments were conducted on a Bruker AV 400 spectrometer (Bruker Inc., Germany) at Peking University. ¹⁷O resonance frequency was 54.243 MHz, each free induction decay (FID) had 1536 scans with a recycle delay of 0.3 s. The experimental temperature was maintained at (25.0±0.1) ℃. To measure the ¹⁷O chemical shift quantification, a sealed capillary tube of D₂O, a locking substance, was inserted at the center of a 5 mm sample tube. The chemical shift spectra of the sample were referenced to the ¹⁷O resonance peak of D₂O. The typical ¹⁷O NMR spectrum of heavy water (peak 1) and water (peak 2) are showed in Fig.1. Resolution of NMR spectroscope was 1.06 Hz.

The proton spin-lattice relaxation times of water in the absence (T_1^0) and presence (T_1) of ions were measured for each sample using a 180°-τ-90° pulse sequence, under the condition with a 90° pulse width of 13.95 μs, the pulse delay time (τ) values were 0.01, 0.05, 0.1, 0.3, 0.6, 1, 2, 4, 6, 8, 11, 15, 20, and 100 ms, and the longest delay time exceed $5T_1$[21]. The acquisition time was 0.16 s and repetition delay was 0.3 s. All T_1 values were deduced by
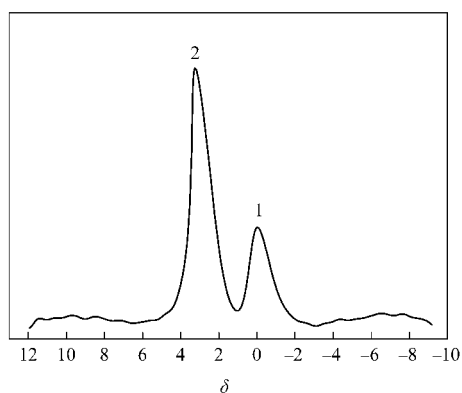
Fig.1 Typical ^{17}O NMR spectrum of heavy water (peak 1) and water (peak 2)

an exponential regression of the signal intensity (M) equation: $M_\tau = M_0(1-e^{-\tau/T_1})$[22]. The fitting errors were within 1%−3%.

2 Results

2.1 Viscosity coefficients (B) of CuCl$_2$ and CuSO$_4$ aqueous solutions

The measured η/η^0 values of aqueous solutions of CuCl$_2$ and CuSO$_4$ to trinal distilled water are shown in Fig.2. It can be seen that the relations between η/η^0 and concentrations of CuCl$_2$ and CuSO$_4$ are linear and can be expressed by regression curve Eqs. (3) and (4), respectively. The linear relations are quite precise.

$$\eta/\eta^0=1.057+0.279c(\text{CuCl}_2) \qquad (R^2=0.9912) \qquad (3)$$
$$\eta/\eta^0=1.053+0.567c(\text{CuSO}_4) \qquad (R^2=0.9984) \qquad (4)$$

From the Jones-Dole expression[7], viscosity coefficients of CuCl$_2$ and CuSO$_4$ are 0.279±0.014 and 0.567±0.006, respectively. The values of $B(\text{CuCl}_2)$ and $B(\text{CuSO}_4)$ are both positive, and $B(\text{CuCl}_2)<B(\text{CuSO}_4)$. Thus it can be concluded that CuCl$_2$ and CuSO$_4$ are both "structure-makers" or "kosmotropes" which increase the water association structure and raise median water cluster size, and the effects of CuSO$_4$ on water structure and median water cluster size are more powerful than that of CuCl$_2$.

2.2 NMR coefficients (B') of CuCl$_2$ and CuSO$_4$ aqueous solutions

The measured T_1^0/T_1 values of trinal distilled water to aqueous solutions of CuCl$_2$ and CuSO$_4$ are shown in Fig.3. The
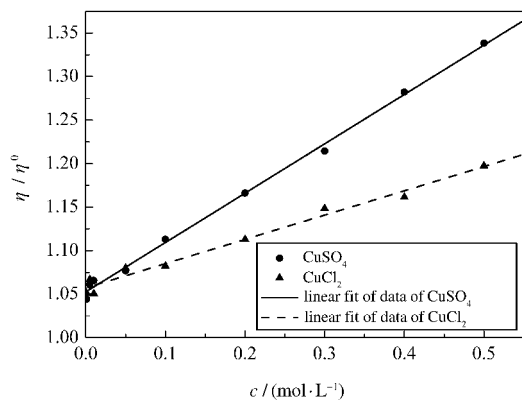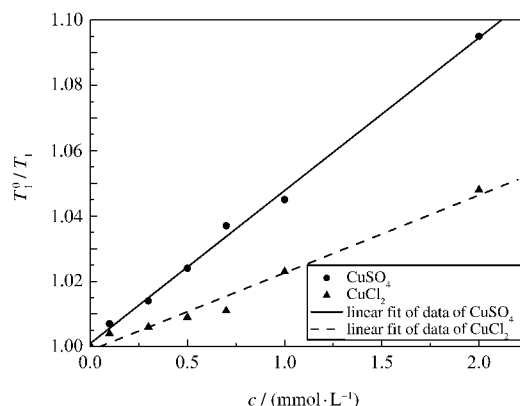

Fig.3 Concentration dependence of T_1^0/T_1 of CuCl$_2$ and CuSO$_4$

relationships between T_1^0/T_1 and concentrations of CuCl$_2$ and CuSO$_4$ are linear and can be expressed by regression curve Eqs. (5) and (6).

$$T_1^0/T_1=0.999+0.0238c(\text{CuCl}_2) \qquad (R^2=0.9892) \qquad (5)$$
$$T_1^0/T_1=1.001+0.0468c(\text{CuSO}_4) \qquad (R^2=0.9981) \qquad (6)$$

According to Eq.(2), $B'(\text{CuCl}_2)$ and $B'(\text{CuSO}_4)$ can be extrapolated easily. It is also obvious that CuCl$_2$ and CuSO$_4$ are both "structure-makers" or "kosmotropes" and the effects of CuSO$_4$ on water structure and median water cluster size are more powerful than that of CuCl$_2$, which is consistent to the conclusion of viscosity coefficients.

2.3 Effect of CuCl$_2$ and CuSO$_4$ on $\delta(^{17}\text{OH}_2)$

The measured values of $\delta(^{17}\text{OH}_2)$ in aqueous solutions of CuCl$_2$ and CuSO$_4$ are shown in Fig.4. As seen in Fig.4, the relationship between $\delta(^{17}\text{OH}_2)$ and concentrations of CuCl$_2$ and CuSO$_4$ are linear, and can be given by the following equations:

$$\delta(^{17}\text{OH}_2)=3.18+0.860c(\text{CuCl}_2) \qquad (R^2=0.9977) \qquad (7)$$
$$\delta(^{17}\text{OH}_2)=3.21+0.871c(\text{CuSO}_4) \qquad (R^2=0.9983) \qquad (8)$$

$\delta(^{17}\text{OH}_2)$ increases with growing concentrations of CuCl$_2$ and CuSO$_4$, showing their ability to enlarge the median water cluster size. From the slope of criteria curve, it can be concluded that the increasing effect of CuSO$_4$ on median water cluster size is a little more powerful than that of CuCl$_2$. It has been considered that anions break the water structure and decrease the median water cluster size[13], so Cl$^-$ decreases median water cluster size
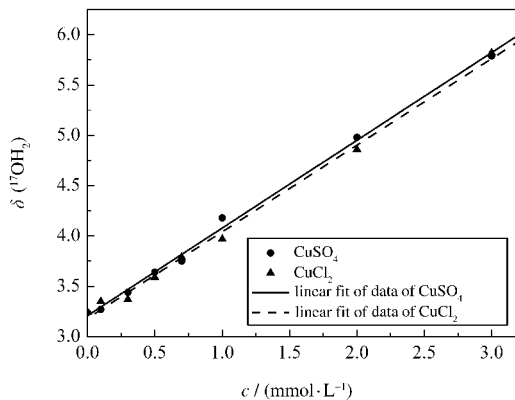

Fig.2 Concentration dependence of η/η^0 of CuCl$_2$ and CuSO$_4$

Fig.4 Effects of CuCl$_2$ and CuSO$_4$ concentrations on ^{17}O NMR chemical shifts (δ) of water

more than SO$_4^{2-}$ does.

3　Discussion

Based on the above results, B and B' of CuCl$_2$ and CuSO$_4$ were obtained. Furthermore, the individual ion's contribution to B and B' follows the following equations[11,23],

$$B=\nu^+B^++\nu^-B^- \tag{9a}$$
$$B'=\nu^+B'^++\nu^-B'^- \tag{9b}$$

where ν^+ and ν^- are molar fractions of cations and anions in salt, respectively; $B^+(B'^+)$ and $B^-(B'^-)$ are $B(B')$ of cations and anions, respectively. We adopted the conventions $B^+(K^+)=B^-(Cl^-)$[24], $B'^+(K^+)=B'^-(Cl^-)$[11]. By measured B (KCl) and B'(KCl) at above experiment condition, B and B' of Cu^{2+}, Cl$^-$, and SO$_4^{2-}$ were calculated using Eq.(9) and shown in Table 1. Some literature data[4,9,11,25,26] are also listed in Table 1 for comparison. There are few differences for B and B' of Cu^{2+}, Cl$^-$, and SO$_4^{2-}$ between measured data and literature values.

From Table 1, it is obvious that CuCl$_2$ and CuSO$_4$ are both "structure-makers" or "kosmotropes" and the effects of CuSO$_4$ on water structure and median water cluster size are more powerful than that of CuCl$_2$. SO$_4^{2-}$ has more effect in promoting water structure than Cl$^-$. On the other hand, Cl$^-$ can break more water clusters than SO$_4^{2-}$, although SO$_4^{2-}$ has more ionic charge and bigger radius. Furthermore, for radius and charge of cations, the effect of ionic charge is much stronger than that of ionic radius, the more ionic charge, the stronger the effect of the cations on making water clusters. For the same charge anions, the bigger the radius of anions is, the stronger the effect of the anion on breaking water cluster[13]. So for Cl$^-$ and SO$_4^{2-}$, anions with different charges, cannot be compared of the breaking effect on water cluster just by ion radius and ion charge. B' is a more effective value in comparing the effect of Cl$^-$ and SO$_4^{2-}$ on water structure and median water cluster size.

It is inconsistent that B(SO$_4^{2-}$) is positive but B'(SO$_4^{2-}$) is negative, and it is considered that SO$_4^{2-}$ can form strong hydrogen bonds with water molecules as "structure-maker" of water[27]. Actually, ^{17}O NMR measures the chemical environment out of oxygen atoms over timescales of 10^{-8} s[11], in which all of the chemical environments out of oxygen atoms of water molecules, such as in hydration of Cu^{2+}, Cl$^-$, and SO$_4^{2-}$, and with various hydrogen bonds, are averaged out, so all of the studied ions are simplified

as isolated in water, NMR can be considered as the effects of isolated ions on water structure. This effect represents the interactions of short-range dispersion forces between solute and solvent which calculate the whole ions hydrated with water molecules[9], so B' displays changes of water structure more in detail than viscosity B. This is why SO$_4^{2-}$ can form strong hydrogen bonds with water molecules as "structure-maker" of water, but in NMR study, it is thought that cations increase the size of water cluster and anions destroy that of water cluster[13]. This study well explained the inconsistence described above.

Marcus and co-workers[9] measured B of 93 kinds of aqueous inorganic ions and 35 kinds of organic ions at 25 ℃, then correlated B' with B using the data of Engel and Hertz[11]:

$$B'=-0.14+0.845B \tag{10}$$

and yielding a correlation coefficient of 0.919. But the Eq.(10) is not applicable in some literature[4,28–30], the correlation of B and B' in this paper is poorer and not in accordance with Eq. (10) neither, so the relationship between B and B' is not the simple linear correlation. In general, it seems to agree with the same ion kosmotropicity order resulting from B and B'[6], and it is necessary to study the quantitative relationship between B and B' by other approaches in the future.

Cu^{2+} is a familiar paramagnetic ion. During the NMR relaxation process, there is a spin exchange interaction between the paramagnetic ions and the protons in the neighboring water molecules[31], which brings obvious effect on shortening proton spin-lattice relaxation time in water and broadening the line width of NMR spectrum. In this study, the influences of CuCl$_2$ and CuSO$_4$ on ^{17}O NMR chemical shifts and spin-lattice relaxation time (T_1) of water were tested only at mmol·L^{-1} order of magnitude. The signal cannot be acquired because of the high signal noise ratio when the concentrations of CuCl$_2$ and CuSO$_4$ aqueous solutions are above 5 mmol·L^{-1}. Compared B and B' of Cu^{2+} with alkali metal ions and alkaline earth metal ions (Table 2), the values of B and B' of alkali metal ions and alkaline earth metal ions have the same order, but for Cu^{2+}, B' is low abnormally because of the paramagnetic effect.

4　Conclusions

The viscosity coefficients (B) and NMR coefficients (B') of CuCl$_2$ and CuSO$_4$ and their effects on ^{17}O NMR chemical shift of

Table 2　B, B', and r values of Cu^{2+}, alkali metal ions, and alkaline earth metal ions at 25 ℃

Substance	r/nm	B	B'
Cu^{2+}	0.072	0.298	0.0517
Li$^+$	0.078	0.146[9]	0.14[11]
Na$^+$	0.098	0.085[4]	0.05[4]
K$^+$	0.133	−0.009[4]	−0.017[4]
Rb$^+$	0.149	−0.033[9]	−0.04[11]
Cs$^+$	0.165	−0.047[9]	−0.05[11]
Mg^{2+}	0.078	0.385[4]	0.60[4]
Ca^{2+}	0.106	0.284[9]	0.27[11]
Sr^{2+}	0.127	0.261[9]	0.23[11]
Ba^{2+}	0.143	0.216[9]	0.18[11]

Table 1　Effective ionic radii (r), B, and B' values at 25 ℃

Substance	r/nm	B		B'	
		this work	literature	this work	literature
CuCl$_2$		0.279±0.014		0.0238±0.0016	
CuSO$_4$		0.567±0.006		0.0468±0.0013	
KCl		−0.0193±0.0005	−0.014[9]	−0.0279±0.0008	−0.034[4]
Cl$^-$	0.168	−0.0096±0.0005	−0.005[9]	−0.0140±0.0008	−0.017[4]
			−0.007[25]		−0.01[11]
SO$_4^{2-}$	0.218	0.269±0.015	0.206[9]	−0.0049±0.0026	
			0.210[25]		
Cu^{2+}	0.072	0.298±0.014	0.376[9]	0.0517±0.0023	
			0.368[25]		
			0.385[26]		

water were determined. From the B and B' values, the individual ion's B and B' values were further calculated, which showed little difference according to literature. The relationships between concentration of ions and $\delta(^{17}OH_2)$ were linear. B, B' and the relationships between concentration of ions and $\delta(^{17}OH_2)$ showed that $CuCl_2$ and $CuSO_4$ were both "structure-makers" and the effects of $CuSO_4$ on water structure and median water cluster size were more powerful than that of $CuCl_2$. SO_4^{2-} had more effect in promoting the water association structure than Cl^-. On the other hand, Cl^- could break more water clusters than SO_4^{2-}.

The effects of SO_4^{2-} on water structure resulting from B and B' seemed to be contradictive. However, they were compatible with each other, ^{17}O NMR reflected water structure over 10^{-8} s and gave details of the water structure.

To compare the effect of Cl^- and SO_4^{2-} on water structure and median water cluster size, B' was a more effective parameter comparing anions with different charges.

As a paramagnetic ion, Cu^{2+} had obvious effect on shortening proton spin-lattice relaxation time in water and broadening the line width of NMR spectrum. In this study, NMR samples were tested only at low salt concentrations.

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