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Dissolution of cellobiose in the aqueous solutions of chloride salts: Hofmeister series consideration

Zhijing Liu · Chao Zhang · Ruigang Liu · Wushou Zhang · Hongliang Kang · Pingping Li · Yong Huang

Abstract The effects of chloride salts on the dissolution of cellobiose in aqueous solution were investigated using calorimetry and ^{1}H NMR. The dissolution of cellobiose in salt solutions is a typical entropy-driven process. The activity of $ZnCl_2$ and LiCl hydrated ions is enhanced as the hydration number decreases with increasing temperature. Zn^{2+} and Li^+ hydrates can interact with the oxygen atoms at the O5 and O6 positions of cellobiose and associate with the Cl^- anions, leading to the breakage of cellobiose hydrogen bonds. We found that the solubility of cellobiose in aqueous solutions is on the order of $ZnCl_2 > LiCl > NaCl > H_2O > KCl > NH_4Cl$, which is consistent with the Hofmeister series. For the first time, we recognized the specific ionic effects of the Hofmeister series on the dissolution of cellobiose in salt aqueous solutions. This finding is helpful for understanding the dissolving mechanism of cellulose in aqueous solvents with salts and providing fundamental knowledge for finding and designing new cellulose solvents.

Keywords Cellulose · Salt · Aqueous solution · Interactions · Hofmeister series

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Introduction

Cellulose is the most abundant renewable and biodegradable material in nature (Nishiyama et al. 2002; Ragauskas et al. 2006; Solomon et al. 2007) and

has been widely utilized in various fields such as the paper, pulp, film, filter and textile industries (Isobe et al. [2013]). However, the application of cellulose is limited since it cannot be melted or dissolved in common solvents. The insolubility of cellulose is predominantly due to the highly developed intra- and intermolecular hydrogen bonding networks (Heinze [1998]; Heinze and Liebert [2001]; Klemm et al. [2005]). In addition, Lindman and coworkers refer to the amphiphilic nature of cellulose (Lindman et al. [2010]; Medronho and Lindman [2014]). Dissolution of cellulose is very important for both producing regenerated cellulose articles and the modification of cellulose. Cellulose solvents can be divided into derivating and non-derivating or into aqueous and non-aqueous solvents. The effects of salts on non-derivating salt aqueous solvents for dissolving cellulose are well known. Cellulose can only be swollen in $ZnCl_2$ aqueous solution with a $ZnCl_2$ content of 55 % (w/w), while it can be dissolved in $ZnCl_2$ aqueous solution with a $ZnCl_2$ content of 63 % (w/w) (Letters [1932]). $Ca(SCN)_2/H_2O$ (Hattori et al. [1998a], [c]), $LiSCN/H_2O$ (Fischer et al. [2003]; Hattori et al. [1998a]) and $LiBr/H_2O$ (Yang et al. [2014]) are also effective solvents for cellulose. Eutectic melts of NaSCN/KSCN with different additives such as $Ca(SCN)_2 \cdot 3H_2O$ or DMSO were also found to dissolve cellulose (Lukanoff et al. [1984]). In recent years, such inorganic molten salt hydrates or mixtures with these compounds have attracted increasing attention as new solvents or media for modifying polysaccharides. Dissolution of cellulose in $Ca(SCN)_2 \cdot 3H_2O$ occurs at temperatures of 120–140 °C within 40 min (Kuga [1980]). IR, ^{13}C- and ^{1}H-NMR measurements confirmed that the dissolution arises from Ca^{2+}, which can attack the oxygen atoms of cellulose at O5 and O6 to form a five-membered ring, leading to the breakage of cellulose hydrogen bonds. Meanwhile, two water molecules and two SCN^- groups associate with Ca^{2+} to achieve its 6-valence coordination (Hattori et al. [1998a], [b], [c]). Moreover, thiocyanate-containing media, molten salt hydrates such as $LiX \cdot nH_2O$ ($X^- = I^-$, NO_3^-, CH_3COO^- or ClO_4^-), have been revisited and found to be efficient non-derivatizing solvents for cellulose (Fischer et al. [1999]). Direct interactions between the Li^+ and cellulose hydroxyl groups are observed by means of 2D [7]Li–[1]H heteronuclear Overhauser effect spectroscopy (HOESY); cations and/or anions from the salt interact with hydroxyl groups of cellulose to break hydrogen bonds (Fischer et al. [2003]). Discussions on the dissolution mechanism of cellulose in molten salt systems have mainly focused on whether or not the cellulose hydroxyl groups participate in the coordination of the cations (Medronho and Lindman [2014]). Many pure molten salt hydrates as well as salt mixtures have been investigated with respect to their interactions with cellulose. As a result it has become reasonable to divide the salt hydrates into two groups according to dissolving or swelling cellulose (Table [1]).

The composition of the molten salt hydrates that can dissolve cellulose can vary greatly. In order to find new cellulose solvents based on molten salt hydrates,

Table 1 Molten salt hydrates that cause a swelling or dissolution of cellulose

Group	Pure melt	Melt mixtures	Refs.
Dissolution	$ZnCl_2 + 3–4H_2O$	$LiClO_4 \cdot 3H_2O–\leq 25$ % $Mg(ClO_4)_2/H_2O$	Leipner et al. ([2000]), Letters ([1932])
	$LiClO_4 \cdot 3H_2O$	$LiClO_4 \cdot 3H_2O–\leq 10$ % $NaClO_4/H_2O$	Fischer et al. ([1999]), Leipner et al. ([2000])
	$LiSCN \cdot 2H_2O$	$LiClO_4 \cdot 3H_2O–MgCl_2 \cdot 6H_2O$	Leipner et al. ([2000]), Warwicke ([1967])
	$LiI \cdot 2H_2O$	NaSCN/KSCN (eutectic)–$LiSCN \cdot 2H_2O$	Fischer et al. ([1999], [2003])
	$LiBr + 3–4H_2O$	$LiCl/2ZnCl_2/H_2O$	Fischer et al. ([2003]), Yang et al. ([2014])
	$FeCl_3 \cdot 6H_2O$		Liebert ([2010])
	$Ca(SCN)_2 \cdot 3H_2O$		Kuga ([1980])
Swelling	$LiCl + 2–5H_2O$	$LiClO_4 \cdot 3H_2O \rightarrow 25$ % $Mg(ClO_4)_2/H_2O$	Fischer et al. ([2003]), Leipner et al. ([2000])
	$NaClO_4/H_2O$	$LiClO_4 \cdot 3H_2O \rightarrow 10$ % $NaClO_4/H_2O$	Fischer et al. ([2003], Leipner et al. ([2000])

Designation of salt-water systems: The symbols '+' and '·' represent the hydrate in liquid and solid form at room temperature, respectively. The symbol '/' represents the variable compositions of the systems

some important factors should be considered, such as the salt composition (Li^+ or Zn^{2+} ions are necessary), water content, hydration deficiency of the coordination sphere and acidity (Leipner et al. 2000). The dissolution ability of molten salt hydrates in relation to cellulose is determined by both cations and anions.

It is known that the inorganic salts exhibit reoccurring trend effects on proteins and macromolecules in aqueous solutions. This phenomenon was called the Hofmeister series and first reported in 1888 (Kunz et al. 2004; Zhang and Cremer 2006). The Hofmeister series for anions is typically: $CO_3^{2-} > SO_4^{2-} > H_2PO_4^- > F^- > Cl^- > NO_3^- > Br^- > I^- > SCN^- > ClO_4^-$ (Kalcher et al. 2009). The species before and after Cl^- are referred to as kosmotropes and chaotropes, respectively. The terms of kosmotropes and chaotropes originally referred to the ability of an ion to alter the hydrogen bonding network of water (Collins and Washabaugh 1985). The kosmotropes, which were believed to be 'water structure makers,' are strongly hydrated and have stabilizing and salting-out effects on proteins and macromolecules, while the chaotropes, which were believed to be 'water structure breakers,' are known to destabilize folded proteins and give rise to salting-in behavior. Compared with anions, the Hofmeister effect of cations is generally weaker (Zhang and Cremer 2010). The series for uncharged systems like peptide backbones is typically: $N(CH_3)_4^+ > NH_4^+ > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ > Ca^{2+} > Mg^{2+}$ (Traube 1910). Cations of the series before and after Na^+ are chaotropes and kosmotropes, respectively. Contrary to the anion series, the most effective cations for salting proteins into solution are those most strongly hydrated, while the weakly hydrated cations lead to salting-out behavior. Despite being less pronounced than the anion series, specific cationic effects are still important for macromolecule folding, polymer–polymer interactions, cell signaling, enzyme catalysis and even biotechnology (Okur et al. 2013; Zhang and Cremer 2010). Anions with high water affinity can stabilize polymers and benefit the polymer crystallization (Collins 2004; Florin et al. 1984; Thormann 2012; Zhang et al. 2005). Strongly hydrated cations tend to bind to the polymer surface (Arakawa and Timasheff 1984; Nishio et al. 2002).

Considering the molten salt hydrates listed in Table 1 and the Hofmeister series, molten salt hydrates that can dissolve cellulose generally contain chaotrope anions and kosmotrope cations. Moreover, the dissolution power of the molten salt hydrates for cellulose is consistent with the Hofmeister series, which is similar to the dissolution of proteins in salt solutions. However, the sequence of ions on the dissolution of cellulose using inorganic salt hydrates has not been fully investigated. Investigations on the effects of ions on the dissolution of cellulose in salt aqueous solutions can provide useful information toward understanding the dissolving mechanism of cellulose and fundamental knowledge for finding and designing new cellulose solvent systems.

Given the complexity of the structure of cellulose, its repeat unit, *D*-cellobiose, was used as the model compound to study the interactions among cellulose/ salt aqueous solutions via transmittance, calorimetry and ^1H NMR. The dissolution behaviours of cellobiose and interactions in the solvent systems of water, $ZnCl_2$, LiCl, NaCl, KCl and NH_4Cl aqueous solutions were investigated. For the first time, we found that the specific ionic effects on the dissolution of cellobiose in salt aqueous solutions follow the Hofmeister series. This work clarified the specific ionic effects on the water solubility of cellobiose and provided fundamental information for understanding the dissolution of cellulose in salt aqueous solutions.

Experimental section

Materials

D-cellobiose ($\geq$99.0 %, Fluka) and alkali halide (LiCl, NaCl, KCl and NH_4Cl AR, Sinopharm Chemical Regent Beijing) were dried in vacuum overnight at 60 °C before use. Zinc chloride ($ZnCl_2$, AR, Alfa Aesar) and deuteroxide (D_2O, 99.9 %, Cambridge Isotope Laboratories Inc.) were used as received. Milli-Q water was used in all experiments.

Sample preparation

Samples for the transmittance measurements were prepared by adding different concentrations of cellobiose to H_2O, LiCl/H_2O, NaCl/H_2O, KCl/H_2O and $ZnCl_2$/H_2O solutions. Samples for NMR experiments were prepared by dissolving cellobiose (5 wt%) in D_2O, $ZnCl_2$/D_2O, LiCl/D_2O, NaCl/D_2O, KCl/D_2O and NH_4Cl/D_2O solutions. The molar ratio of $[Cl^-]:[D_2O]$ was kept at the desired concentration.

Measurements and instruments

The solubility of cellobiose in water and different salt solutions was determined by transmittance of the mixed solution at a 500-nm wavelength on a Shimadzu UV-1601PC UV-Vis spectrophotometer.

The calorimetry experiments for dissolving cellobiose in different solvents were carried out on an LKB 8700 Precision Calorimetry System. The calorimeter is a 100-ml vessel made by super-pure silica glass fitted with a thermistor for sensing temperature, a heater for calibration, a glass ampoule and a stirrer. A glass ampoule can be placed in the stirrer. The bath temperature was controlled within 0.001 °C. The calorimeter was tested by the dissolution of KCl in Milli-Q water at 25 °C. The dissolution enthalpy ($\Delta_{sol}H_m$) was 17.82 ± 0.08 kJ/mol, consistent with the 17.55 ± 0.04 kJ/mol data in the literature (Cox and Riedel 1974). In each experiment, 0.200 g cellobiose was filled into a glass ampoule and 100.00 ml solvent, water or aqueous solution of LiCl, NaCl, KCl and $ZnCl_2$ was added to the sample vessel. The relative standard deviation of each enthalpy value was <2 %.

The ^1H NMR spectra were measured on a Bruker AVANCE 600 spectrometer with 32 scans for ^1H NMR at 298 K and on a Bruker AVANCE 500 spectrometer with 32 scans for ^1H NMR at a settled temperature range from 298 to 368 K. Sodium salt of 2,2-dimethyl-2-silapentane-5- sulfonic acid (DSS) was sealed in a coaxial capillary as external reference.

Results and discussion

Solubility of cellobiose in different salt solutions

The solubility of cellobiose in water and salt solutions was measured by a UV-Vis spectrophotometer at 25 °C. Figure S1 shows the transmittance of the cellobiose/H_2O mixtures as a function of cellobiose content at $\lambda = 500$ nm. It can be seen that there is a turning point on the curve of the transmittance as a function of the cellobiose content, located at the cellobiose concentration 0.394 mol/l, at which the solubility of cellobiose in water at 25 °C can be determined. The solubility of cellobiose in different salt solutions at different temperatures was also determined by a similar method.

Figure 1a shows the solubility of cellobiose in $ZnCl_2$, LiCl, NaCl and KCl solutions as a function of the molar ratios of Cl^- to water at 25 °C. The results indicated that the solubility of cellobiose increases with an increasing molar ratio of Cl^- to water ($n[Cl^-]:n[H_2O]$) in aqueous solutions of $ZnCl_2$, LiCl and NaCl, whereas the solubility of cellobiose decreases with an increase in the KCl content in the solutions. The solubility of cellobiose in salt solutions is on the order of $ZnCl_2 > LiCl > NaCl > H_2O >$ KCl at the same $n[Cl^-]:n[H_2O]$, suggesting that the cations influence the dissolution power of cellobiose in aqueous solution. The binding of chaotropes to water molecules is weaker than the binding of water molecules to each other, while KCl binding of kosmotropes to water is stronger than KCl binding of water molecules to each other. Chaotropicity correlates with a low charge density; thus, large singly charged ions tend to be chaotropic and have smaller effects on the local hydrogen bonding. Kosmotropicity correlates with a high charge density; thus, small or multiply charged ions tend to be kosmotropic and strongly influence the local water hydrogen bonding (Collins et al. 2007). The distance between cations and water oxygen decreases with the increasing charge density, say from K^+ to Na^+ to Li^+ to Zn^{2+} in this work. The Na^+–oxygen distance in the solutions is smaller than that of the oxygen–oxygen distance of pure water, which indicates the strong hydration of Na^+ ions, while the K^+–oxygen distance is larger than that of the oxygen–oxygen distance of pure water, which indicates the weak hydration of K^+ ions (Collins 2004). Therefore, Zn^{2+}, Li^+ and Na^+ cations are kosmotropes. The strongly hydrated cations tending to bind to the cellobiose surface lead to increased salting-in behavior, while K^+ is a chaotrope leading to salting-out behavior (Collins and Washabaugh 1985).

Figure 1b shows the solubility of cellobiose as a function of the temperature in salt solutions with $n[Cl^-]:n[H_2O]$ of 0.04:1. The results indicate that the solubility of cellobiose increases with increasing temperature in all the salt solutions. The solubility follows the order of $ZnCl_2 > LiCl > NaCl > KCl$ in the salt solutions. However, the temperature dependence of the solubility varies in different salt solutions. The slope obtained by the linear fitting of the experimental data represents the temperature dependency of the solubility, which decreases from 6.75×10^{-3} mol/(l °C) in $ZnCl_2$ aqueous solution to
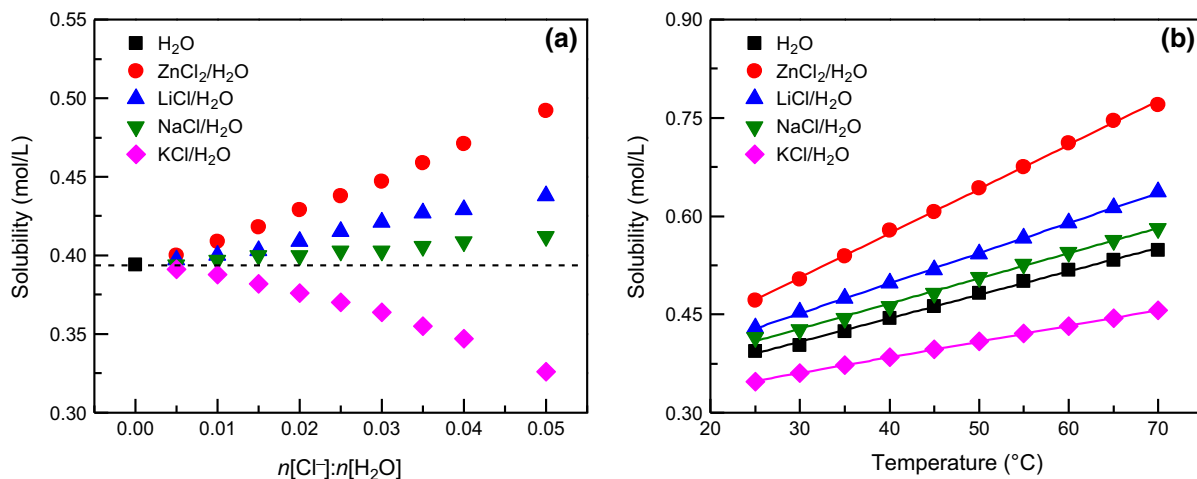
Fig. 1 The solubility of cellobiose in salt solutions **a** as a function of the chloride ion concentration at 25 °C and **b** as a function of temperature with a molar ratio of $n[Cl^-]:n[H_2O] = 0.04:1$ in the salt solutions

2.40×10^{-3} mol/(l °C) in KCl aqueous solution. The results suggest that the temperature and cations of salt influence the dissolution of cellobiose. It is known that more hydrogen bonds of water are broken with increasing temperature (Muller 1965). Moreover, hydrated salt ions become more active with a decrease in the hydration number (Allolio et al. 2013). The temperature dependence of the solubility of cellobiose in NaCl aqueous solution is similar to that in water because the hydration numbers of NaCl are independent of temperature (Malinows et al. 1966). At the same temperature, Zn^{2+} and Li^+ hydrates have higher activity so can interact with cellobiose more easily.

Dissolution enthalpies of cellobiose in salt aqueous solutions

The dissolution of cellobiose in water and salt aqueous solutions was also investigated by using calorimetry, an effective technique to understand the dissolving process (Cooper 2011; Liu et al. 2015; Piekarski and Nowicka 2010). The dissolving processes of cellobiose in water and salt aqueous solutions are endothermic, as typically shown in Fig. S2. The results suggest that the dissolving of cellobiose in water or salt aqueous solutions is a typical entropy-driven dissolving process. When cellobiose is mixed with aqueous solutions, hydrogen bonds between the hydroxyl groups of cellobiose and water molecules can form, leading to the breakage of the hydrogen
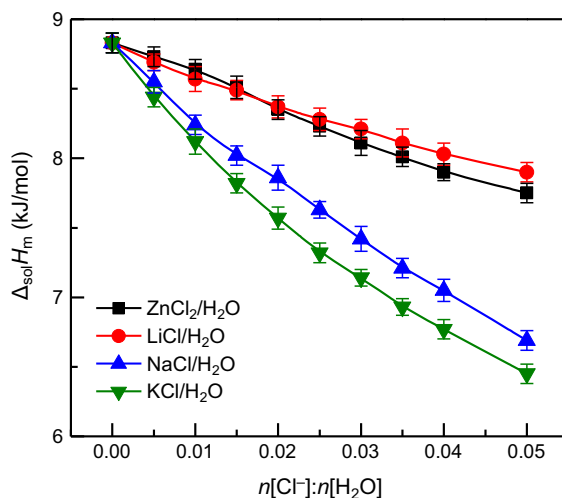

Fig. 2 The dissolution enthalpies of cellobiose in different salt aqueous solutions as a function of the chloride ion concentration at 25 °C

bonding network structure in water. Therefore, the degree of disorder in the system increases accordingly, leading to the endothermic dissolution process.

Figure 2 shows the dissolution enthalpies of cellobiose in salt aqueous solutions. The results indicate that the dissolution enthalpies of cellobiose in salt solutions investigated in the present work are all smaller than that in water. Moreover, the dissolution enthalpy of cellobiose decreases with increasing salt concentration in all the systems investigated. The heat

absorbed during the dissolution in the salt aqueous solutions is on the order of $ZnCl_2 \approx LiCl > NaCl > KCl$.

Considering the influence of inorganic salts on water is essential for understanding the structure of hydrogen-bond networks in aqueous solutions. Depending on the gain or loss of hydrogen bonding per water molecule due to the presence of ions, the effects of ions on the structure of water can be described by the concept of structure-making ions (i.e., kosmotropes) or structure-breaking ions (i.e., chaotropes). This description views aqueous salt solutions as homogeneous liquids with modified intermolecular interactions (Garbacz and Price 2014). The anion Cl^- and cation K^+ are chaotropes that break down the hydrogen bond structure of water. Zn^{2+}, Li^+ and Na^+ are kosmotropes that make a strong hydrogen bond structure of water. The dissolving processes of $ZnCl_2$ and LiCl in water are exothermic with dissolution enthalpies of -44.5 ± 0.07 and -36.7 ± 0.09 kJ/mol, respectively. The results indicate that the addition of $ZnCl_2$ and LiCl to water could lead to a more highly ordered structure in the system. The dissolving processes of NaCl or KCl in water were endothermic with dissolution enthalpies of 4.0 ± 0.06 and 17.82 ± 0.08 kJ/mol, respectively, which indicates the decrease in the order degree of the system. Without considering other factors, the dissolving process of cellobiose in $ZnCl_2$ or LiCl aqueous solutions should absorb more heat than that in water. However, the actual dissolution enthalpy of cellobiose in $ZnCl_2$ or LiCl aqueous solutions is smaller than that in water. This could be because there are interactions between the Zn^{2+} (or Li^+) cationic hydrates and the cellobiose molecules (Zhang et al. 2005).

The dissolution enthalpies of cellobiose in salt solutions at different temperatures were also measured. The results of cellobiose dissolved in water, LiCl and $ZnCl_2$ solution are listed in Table 2. The dissolution enthalpies of cellobiose in water, LiCl and $ZnCl_2$ solution decrease with rising temperature. The results can be attributed to more hydrogen bonds among water molecules being destroyed with rising temperature and more freedom of water molecules in the solutions, which can interact with the –OH groups of cellobiose. Therefore, the heat absorbed during the dissolving process of cellobiose decreased with the increase in the dissolution temperature. The dissolution enthalpy of cellobiose

Table 2 Dissolution enthalpies of cellobiose in water, LiCl and $ZnCl_2$ solutions at different temperatures

Temp. (°C)	$\Delta_{sol}H_m$ (kJ/mol)[a]		
	Water	LiCl solution	$ZnCl_2$ solution
20	10.11 ± 0.08	9.02 ± 0.08	9.32 ± 0.10
25	8.83 ± 0.07	7.84 ± 0.08	7.97 ± 0.06
30	7.31 ± 0.06	6.90 ± 0.07	6.92 ± 0.07
35	6.63 ± 0.06	5.89 ± 0.09	5.80 ± 0.08

[a] The molar ratio of $n[Cl^-]:n[H_2O]$ is 0.04:1

in $ZnCl_2$ or LiCl aqueous solutions is lower than that in water at all temperatures measured, which suggests that there are interactions between $ZnCl_2$ or LiCl hydrates and cellobiose (Thormann 2012; Zhang et al. 2005).

The ^{1}H NMR of cellobiose in salt aqueous solutions

The effects of salt on the dissolution of cellobiose in aqueous solutions were further investigated by ^{1}H NMR, a powerful tool for studying structures and interactions in solutions because chemical shifts are sensitive to the establishment and breakage of hydrogen bonds (Altaner et al. 2014; Jiang et al. 2014; Liu et al. 2015; Zhang et al. 2014). When strong electrolytes are added to water, the proton shift is found to be strongly dependent upon the concentration (Shoolery and Alder 1955). The addition of salts leads to either upfield or downfield shifts of the nuclear magnetic resonance signals. The chemical shift of the single resonance line observed is an average of the various proton environments. At least four factors contribute to these shifts: (1) bond breaking, (2) polarization, (3) structural and (4) non-electrostatic effects. The ^{1}H NMR spectra of cellobiose in $ZnCl_2$/D_2O solutions are shown in Fig. 3. In D_2O (Fig. 3a), the resonances of the active hydrogens such as –OH of cellobiose and HOD merged into one peak at the chemical shift of 4.75 ppm because of the fast proton exchange. The signals crowded in a narrow range of 3.0–5.3 ppm belong to the protons of the glucose rings of cellobiose (Roshind et al. 2008). The chemical shift of 4.78 ppm belongs to the proton of the H_2O in a coaxial capillary as external reference. With the increase in the content of $ZnCl_2$ in solution, the signal of an active hydrogen shifts to upfield because more
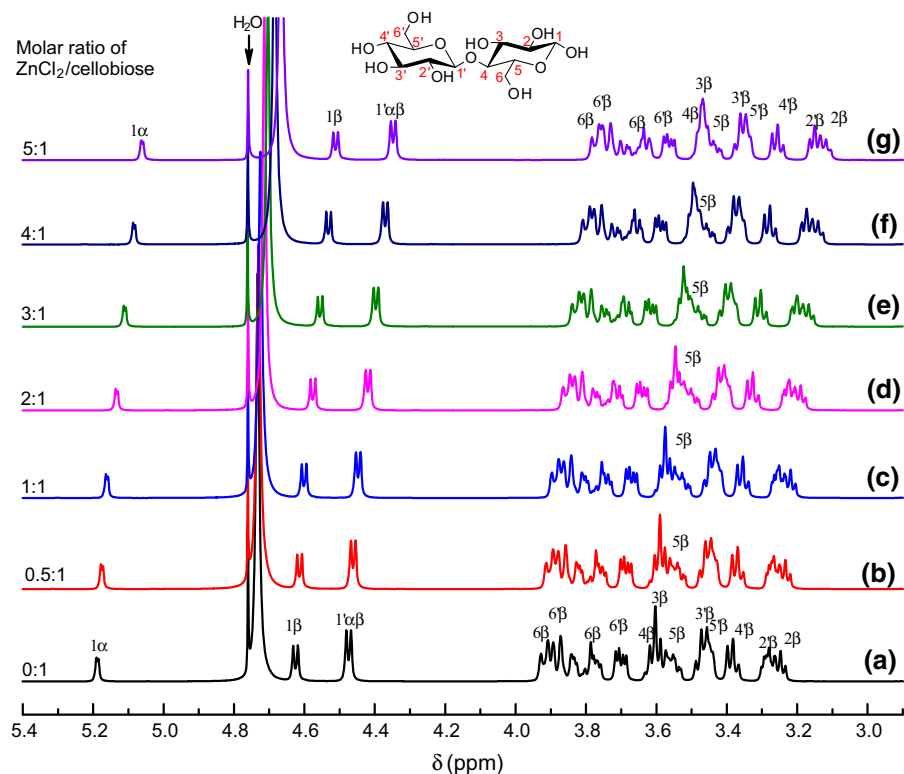
Fig. 3 ^{1}H NMR spectra of cellobiose in ZnCl$_2$/D$_2$O with different molar ratios of ZnCl$_2$ and cellobiose
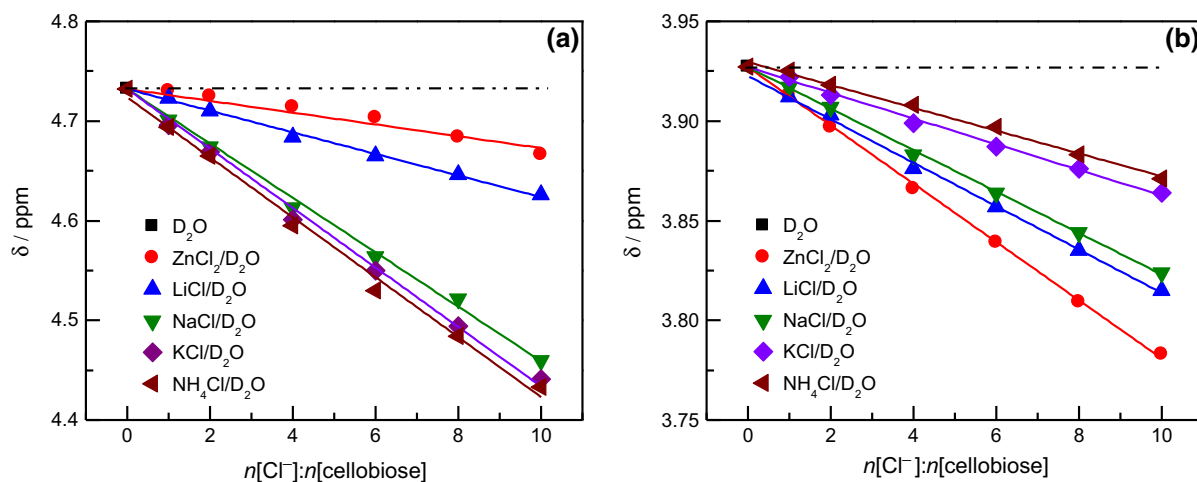

Fig. 4 Chemical shifts of **a** the protons including hydroxyl and HOD and **b** the H6 of cellobiose as a function of Cl$^-$ concentration

hydrogen bonds of water are broken, the resonances of H6 and H6' are closer, and the signal of H5 becomes weaker, indicating that there are interactions between Zn^{2+} hydrates and the oxygen atoms at the O5 and O6 positions of cellobiose.

The ^{1}H NMR spectra of cellobiose in different chlorine salts as a function of Cl$^-$ concentration were measured (Fig. 3 and Figs. S2–S5). The chemical shifts of the active hydrogen, including hydroxyl groups of cellobiose and HOD, and the H6 of

cellobiose are shown in Fig. 4. The results indicate that the signals of the active hydrogen shift to upfield with an increase in the salt content in the solutions (Fig. 4a). It is known that NH_4^+, K^+ and Cl^- are chaotropes (Traube 1910), while the charge density of the kosmotropes in the present work decreases from Zn^{2+} to Li^+ to Na^+. Therefore, the strength of hydrogen bonds can be estimated by NMR chemical shifts, which are on the order of $ZnCl_2 >$ LiCl > NaCl > KCl > NH_4Cl. The signals of cellobiose H6 also move to upfield with an increase in the salt content in the solutions (Fig. 4b). NH_4^+ and K^+ are chaotropes, while Zn^{2+}, Li^+ and Na^+ are kosmotropes; the most effective cations for salting polymers into solution are those most strongly hydrated, while the weakly hydrated cations lead to salting-out behavior. Therefore, the strength of the interactions between the cationic hydrates and cellobiose is on the order of $Zn^{2+} > Li^+ > Na^+ > K^+ > NH_4^+$ hydrate. The ^1H NMR spectra of

cellobiose in different aqueous solutions with the molar ratio $n[Cl^-]:n[D_2O] = 0.04:1$ are shown in Fig. 5. Chemical shifts of the protons of the glucose rings of cellobiose also move upfield. The resonances of H6 and H6′ become closer and the signal intensity of H5 becomes weaker, suggesting that there are interactions between cationic hydrates and the oxygen atoms at the O5 and O6 positions of cellobiose. The strength of the interactions between the salt and cellobiose is on the order of $ZnCl_2 >$ LiCl > NaCl > KCl > NH_4Cl, consistent with the calorimetry results.

The ^1H NMR spectra of cellobiose in different salt solutions at a temperature range from 298 to 368 K were also measured (Figs. S6–S11). Figure 6 shows the chemical shift of the active hydrogen in different salt solutions as a function of temperature. The results show that the chemical shift of the active hydrogen in all aqueous solutions moves upfield linearly with the increase in temperature with a different slope. The
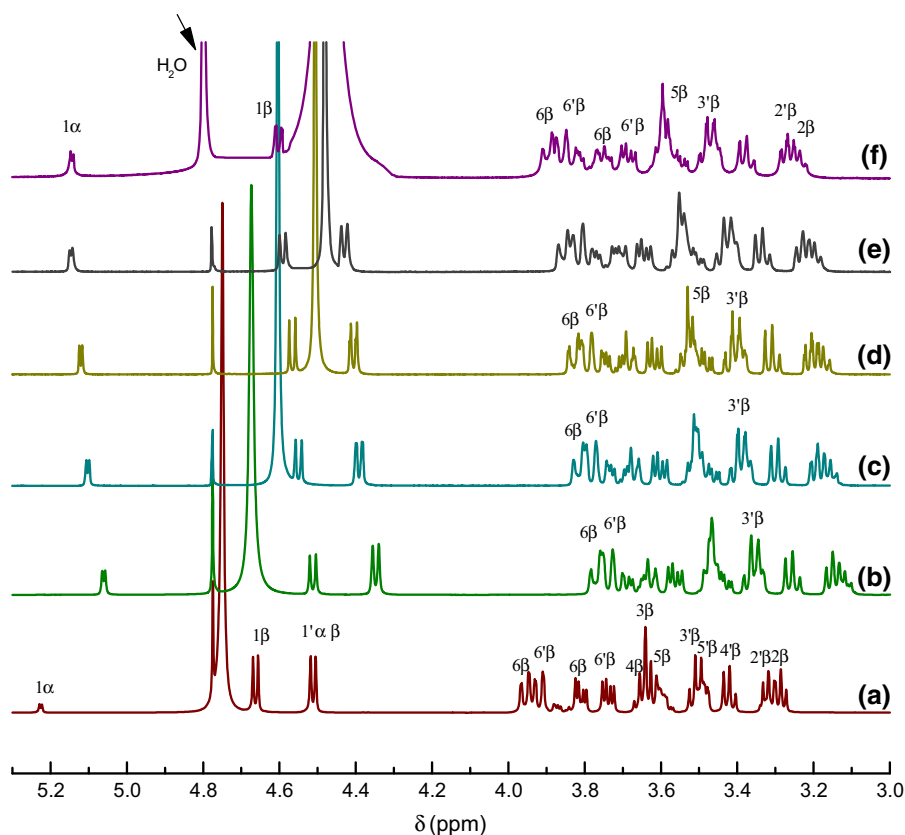

Fig. 5 ^1H NMR spectra of cellobiose in a D_2O, b $ZnCl_2/D_2O$, c $LiCl/D_2O$, d $NaCl/D_2O$, e KCl/D_2O and f NH_4Cl/D_2O. The molar ratio of $n[Cl^-]:n[D_2O]$ is 0.04:1
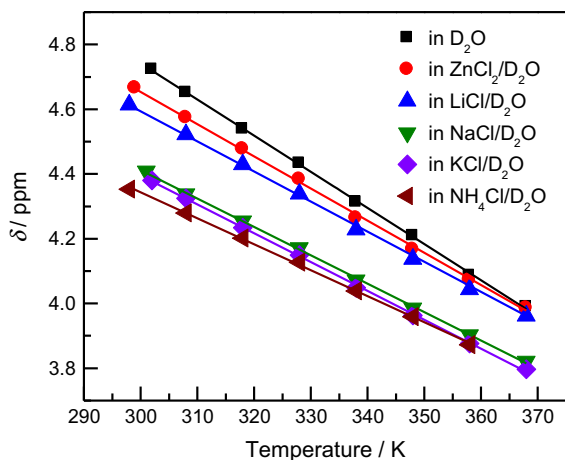
Fig. 6 Chemical shift of the active hydrogen including the hydroxyl of cellobiose and HOD as a function of temperature

proton shift of water is strongly dependent upon temperature (Schneider et al. 1958). It is widely believed that this shift is an average of the hydrogen-bonded and non-hydrogen-bonded environments of the proton. Water vapor, which has relatively few hydrogen bonds, has a high-field shift. Thus, one would expect the proton signal of liquid water to move upfield as the temperature is raised since more hydrogen bonds are broken. The single-resonance signal of a proton in an aqueous electrolyte solution is a weighted average of its varying environments, i.e., hydrogen-bonded, non-hydrogen-bonded and hydrated forms. The effects of temperature on proton shifts of aqueous salt solutions can give some idea of the primary hydration (Malinows et al. 1966). The temperature dependence of proton chemical shifts correlates with the hydration numbers of salt ions (Hindman 1962). The hydration number of NaCl is essentially independent of concentration and temperature (Malinows et al. 1966; Walrafen 1966). Compared with the chemical shift of the active hydrogen in salt aqueous solution, the chemical shift is on the order of $ZnCl_2 > LiCl > NaCl > KCl > NH_4Cl$ at the same temperature (Fig. 6), which is due to the cation of salt with decreasing charge density from Zn^{2+} to Li^+ to Na^+ to K^+ to NH_4^+. Therefore, the strength of the H bonds of aqueous solutions is on the order of $ZnCl_2 > LiCl > NaCl > KCl > NH_4Cl$. The absolute value of the slope in $ZnCl_2$ and LiCl solutions is bigger than that in NaCl, probably because of the increased competition between the anion and cation for water molecules and the possible formation of

aquo-ion pairs (Malinows et al. 1966). Moreover, the hydration number of $ZnCl_2$ and LiCl decreases, which enhances the activity ion hydrates to interact with cellobiose, and Cl^- groups associate with Zn^{2+} or Li^+ (Schaschel and Day 1968). The ability of salt ion hydrates to interact with cellobiose is on the order of $ZnCl_2 > LiCl$. Therefore, a certain content of $ZnCl_2$ aqueous solution can dissolve cellulose (Letters 1932). LiCl aqueous solution can swell cellulose (Fischer et al. 2003), and NaCl aqueous solution can disperse regenerated cellulose in the form of nanofibrils (Missoum et al. 2012). The effect of salt on cellulose in aqueous solution is consistent with the Hofmeister series.

In the present work, only the aqueous solutions of chlorine salts were investigated. Other strong electrolytes may behave in the same manner. The following of the Hofmeister series in this work could be extended to aqueous solutions of other salts and provide new information on the understanding of the dissolutions of cellulose in the salts with the consideration of the Hofmeister series. The new finding of the effect of salts on the dissolution of cellobiose in aqueous solutions of salts could extend the understanding of the dissolution mechanism of cellulose and help design new cellulose solvent systems.

Conclusions

Cellobiose was used as a model compound to study the effect of chlorine salt on the dissolution of cellulose in aqueous solution. The solubility of cellobiose in aqueous solutions is on the order of $ZnCl_2 > LiCl > NaCl > H_2O > KCl > NH_4Cl$. The dissolution of cellobiose in salt solutions was a typical endothermic entropy-driven process, confirming that higher temperature benefits the dissolution of cellobiose in a salt aqueous solvent system. With temperature increases, the activity of $ZnCl_2$ or LiCl hydrated ions is enhanced as the hydration number decreases. The Zn^{2+} or Li^+ hydrates can interact with the oxygen atoms at the O5 and O6 position of cellobiose, and Cl^- anions associate with the cations to break the hydrogen bonds among the cellobiose molecules. The effect of salt on cellobiose in aqueous solution is consistent with the Hofmeister series, which is recognized for the first time. The new finding

of this work could extend the knowledge about the dissolution of cellulose.

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