Interactions of D-cellobiose with selected chloride salts: a ^{13}C NMR and FT-IR study

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Abstract: The interactions of cellulose model compound D-cellobiose with chloride salts of Zn^{2+} , Ca^{2+} , Li^+ , Sn^{2+} , La^{3+} , Mg^{2+} , K^+ and NH_4^+ were evaluated by measuring the ^{13}C NMR chemical shift changes ($\Delta\delta$) of the disaccharide due to the addition of salts in D_2O . The KCl and NH_4Cl showed similar $\Delta\delta$ changes due interactions only with the Cl^- anion. Whereas other chloride salts showed interactions with both cation and anion. Among these salts the total interactions are in the order: $\text{Zn}^{2+} > \text{Sn}^{2+} > \text{Li}^+ > \text{Ca}^{2+} \sim \text{La}^{3+} > \text{Mg}^{2+}$. The FT-IR spectra of D-cellobiose - chloride salt 1:2 mixtures also indicate that KCl and NH_4Cl interacts similarly with D-cellobiose in the solid state.

Keywords: cellobiose, metal chloride, chelation, NMR, FT-IR

1. Introduction

The depolymerization or hydrolysis of cellulose to glucose is a formidable challenge due to its complex molecular architecture with stiff polymeric chains and close packing *via* strong, inter and intra-molecular hydrogen bonds [1]. The currently used technology for this process is the high temperature-pressure dilute acid pretreatment followed by the use of a cellulase enzyme cocktail for the hydrolysis [1],[2]. However certain deficiencies in the current technologies like enzyme costs and energy consuming pretreatment requirements have encouraged the research into more efficient catalytic methods for harvesting the full potential of the most abundant renewable carbohydrate polymer.

There are a number of ways to affect non-enzymatic cellulose depolymerization in relatively low yield, and a few researchers have taken interest in the mechanisms of these

processes in an attempt to develop efficient catalytic systems for the important cellulose depolymerization step. The widely studied approaches include the use of dilute mineral acids [3], solid acids [4],[5],[6], mineral acid in neutral ionic liquids [7], acidic ionic liquids [8],[9], metal salts in mineral acid solutions and ionic liquid solutions [10].

Even though metal salts or complexes are the traditional catalytic systems in most industrial catalytic processes the use transition metal salts have not attracted attention in the cellulose hydrolysis until recently. The new developments in this direction have shown that incorporation of transition metal ions like Mn^{2+} , Fe^{3+} , Cu^{2+} , and Zn^{2+} as Lewis acid co-catalysts to the Brönsted acid system can be used to improve the cellulose pretreatment and acid hydrolysis efficiencies [11],[12],[13],[14]. In addition, we have recently found that addition of a catalytic amount of Mn^{2+} , Fe^{3+} or Co^{2+} chloride salt can be used to improve the sugar yields during the acid catalyzed saccharification of corn stover in water at 140-170 °C [15].

These co-catalytic effects of the metal ions in cellulose depolymerization and pretreatments are most likely due to interaction or chelation of salts with carbohydrate. There are several reports on isolation of monosaccharide - metal complexes and structure determination using X-ray crystallography, this includes Ca^{2+} complexes of D-fructose [16], D-galactose [17], lactose [18], D-mannose [19], trehalose [20], D-xylose [21], D-arabinose [22], D-ribose [23] and LaCl_3 -ribose [24]. However, the only structural study of a metal complex of the cellulose model compound D-cellobiose is the X-ray structure of α -cellobiose $\cdot$ 2NaI $\cdot$ 2H₂O complex [25]. The theoretical calculations could also be used to elucidate the interactions between carbohydrates and metal ions. Nevertheless only a few studies are reported in the literature, which include the molecular dynamics studies on Na^+ -glucose interactions [26], computational evidence for the complex formation between Cr^{3+} [27], and Cr^{2+} [28] with glucose. Furthermore, only a handful of studies have attempted to address the mechanisms of metal promoted depolymerization and dissolutions of cellulose [29]. In a recent example, Zhang et al. have studied the role of Li^+ and Cl^- ions in the dissolution of cellulose in dimethyl acetamide (DMAc) - LiCl system by NMR methods [30]. Where they found that the hydroxyl protons of cellulose form strong hydrogen bonds

with the Cl^- during which the intermolecular hydrogen bonding networks of cellulose is broken with simultaneous splitting of the Li^+ and Cl^- ion pairs. The Li^+ cations are further solvated by free DMAc molecules, which accompany the hydrogen-bonding of Cl^- to meet the charge balance. Thereafter the cellulose chains are dispersed in the solvent system to form homogeneous solution. This work clarifies the interactions in the cellulose/DMAc/LiCl solutions at molecular level and the dissolution mechanism of cellulose in DMAc/LiCl system [30]. In another example, solvation state of cellulose in aqueous onium hydroxide solutions are discussed with the aid of ^{13}C NMR chemical shift of D-cellobiose signals in these solutions. Where Abe and coworkers related cellulose dissolution ability to chemical shifts of D-cellobiose carbons in aqueous onium hydroxide solutions [31].

Since a number of recent studies as well as our own experiments on using metal ions like Mn^{2+} , Fe^{3+} and Co^{2+} have shown to improve the acid hydrolysis of cellulose, most likely *via* interaction of the metal salts with carbohydrate, we instigate a study on interactions of metal salts with cellulose and cellulose model compound D-cellobiose in water [32]. As a part of this study we have examined the ^{13}C NMR chemical shift changes in D-cellobiose due to the addition of some common diamagnetic chloride salts in an attempt to evaluate the interactions of salts with the cellulose model compound.

2. Experimental

2.1. Instrumentation and materials

D-cellobiose (99.9%), analytical grade chloride salts; LiCl, CaCl_2 , LaCl_3 , ZnCl_2 , SnCl_2 , MgCl_2 , NH_4Cl and KCl were purchased from Aldrich Chemical Co and were used without further purification. ^{13}C NMR spectra in D_2O were recorded on a Varian Mercury plus spectrometer operating at 100 MHz, $\text{rd} = 1$ s, spectral width of 17,094 Hz, and typically 4000 scans were collected for ^{13}C spectra. All NMR spectra were collected at room temperature, 25 °C. FT-IR spectra were recorded on a Thermo Nicolet IR 200 using KBr pellets at 1.0 cm^{-1} resolution.

2.2. Interaction of D-cellobiose with chloride salts - ^{13}C NMR study, general procedure

A solution of D-cellobiose (50.0 mg, 0.146 mmol) in 0.50 mL of D_2O was prepared in a 5-mm NMR tube. The sample was allowed to stabilize at room temperature for 4 h, then ^{13}C NMR (rd = 1 s, sw = 17094 Hz, NS = 4000) spectrum was recorded as the initial baseline data. Afterward, chloride salt (2.20 mmol) was added and thoroughly mixed using EW-04726-01 Cole-Parmer Vortex Mixer for 2.0 min., allowed to stabilize at room temperature for 4 h. Then ^{13}C NMR spectrum was recorded as with pure cellobiose solution. The ^{13}C NMR chemical shift change ($\Delta\delta$) was calculated for each signal in the spectrum using the formula:

$\Delta\delta = \text{chemical shift of pure D-cellobiose} - \text{chemical shift of D-cellobiose in chloride salt}$

The $\Delta\delta$ values for 18 signals from the α and β D-cellobiose epimers were used to draw the plot shown in figure 2.

2.3. Interaction of D-cellobiose with chloride salts - FT-IR study, general procedure

A mixture of D-cellobiose (45.0 mg, 0.5 mmol) and metal chloride (1.0 mmol) were prepared and ground together for 2.0 min. in a pestle and mortar. Then a 5 mg portion of the mixture was thoroughly mixed with 100 mg of dry KBr and was used in making the KBr pellet for recording the spectrum. All spectra were collected with 32 scans and 1.0 cm^{-1} resolution. A FT-IR spectrum of pure cellobiose recorded under identical conditions was used as the reference spectrum.

3. Results and Discussion

3.1. ^{13}C NMR study

The interactions of eight chloride salts with D-cellobiose in D_2O were studied by ^{13}C NMR spectroscopy in the first part of this work. In the set of chloride salts studied, SnCl_2 has the lowest molar solubility in water at $25\text{ }^\circ\text{C}$ [33]. In the preliminary experiments we have found that a maximum amount of 2.20 mmol of anhydrous SnCl_2 can be dissolved in the

NMR sample containing 50 mg of D-cellobiose in 0.5 mL of D₂O at 25 °C. Therefore, in all NMR experiments 2.20 mmol of anhydrous chloride salts were used to achieve uniform salt concentrations. A representative ¹³C-NMR spectrum of α/β D-cellobiose - SnCl₂ mixture in D₂O at 25 °C is shown in figure 1. The ¹³C NMR spectra of D-cellobiose in different salt mediums were recorded under identical conditions and changes in chemical shifts ($\Delta\delta$) for 18 peaks from the two anomeric forms of D-cellobiose were calculated with respect to pure D-cellobiose in D₂O.

The $\Delta\delta$ curves of 18 D-cellobiose ¹³C peaks in eight different chloride salt mediums are shown in the same plot for comparison in figure 2. Two chloride salts KCl and NH₄Cl showed negative $\Delta\delta$ values for all 18 carbons producing a curve in the - $\Delta\delta$ region of the plot, whereas other six chlorides showed positive and negative $\Delta\delta$ values. The similar curves from KCl and NH₄Cl can be interpreted as a result of similar interactions with cellobiose in these mediums. This behavior in the $\Delta\delta$ curves may be due to the fact that in the cases of KCl and NH₄Cl the dominant effect is the interaction of cellobiose with Cl⁻ anion. Whereas in other six salts both cation and Cl⁻ anions interact with the carbohydrate. As in an earlier NMR study by Zhou et al. to explain the well known solubility behavior of cellulose in LiOH and KOH they concluded that Li⁺ can interact with cellulose whereas K⁺ cannot interact with cellulose due to the size of the hydration shell [29]. Furthermore, it is interesting to note that, during another ¹³C NMR study on interactions of alkyl halides with D-ribose, Ortiz et al. have concluded that interaction of carbohydrate -OH groups with anions are weak compared to cations [34].

In the six salts where both cation and Cl⁻ anion may interact with cellobiose, the highest $\Delta\delta$ value changes are observed with ZnCl₂, suggesting that strongest interactions are observed with Zn²⁺ ions. We have attempted to quantify the total interaction by calculating the sum of the magnitudes of the chemical shift changes. These calculated total magnitude values of $\Delta\delta$ for eight chloride salts ($\sum |\Delta\delta|$) are shown in table 1. Among the salts with both cation and anion interact with cellobiose the total interaction is in the following order: Zn²⁺>Sn²⁺>Li⁺> Ca²⁺~La³⁺>Mg²⁺. In all the strongly interacting metal ions $\Delta\delta$ plots showed approximately similar profile, suggesting that these metal ions interact with the disaccharide in a similar mode. The most noticeable $\Delta\delta$ value changes are observed at

carbons C5, C6, C1' α and C5', C6', C1' β regions of the molecule. This effect may be due to binding or interaction of metal ions in the C5, C6, C1' α and C5', C6', C1' β regions of the cellobiose molecule.

3.2. *FT-IR study*

In addition, the interaction of D-cellobiose with these eight metal chlorides in the solid state was examined by recording FT-IR spectra of D-cellobiose : chloride salt 1:2 mole ratio mixtures and comparison with the FT-IR of pure cellobiose recorded under identical conditions. The major peaks of pure cellobiose and D-cellobiose salt mixtures in the 400-1700 cm^{-1} region are shown in table 2. The band around 1637 cm^{-1} in pure cellobiose can be assigned to bending mode (δ HOH) of coordinated water [35]. The same band can be found in most chloride salt - cellobiose mixtures as well; for instance this band was observed at 1622 and 1636 cm^{-1} in ZnCl_2 and CaCl_2 mixed samples. In comparison with the pure cellobiose spectrum some of the IR bands are found shifted or split in cellobiose : chloride salt mixtures.

As reported in the literature, the absorption band at 1166 cm^{-1} in D-cellobiose spectrum is due to endocyclic C-C valence vibrations of pyranose rings, which is predominantly ring vibrational modes with some CCH, HCO and COH bending components [35],[36]. Interestingly, this 1166 cm^{-1} band displays only minor changes due to addition of chloride salts, in comparison to other bands related to oxygen atoms and -OH groups. This can be interpreted as there are minor or no changes in the pyranose ring conformations due to the addition of chloride salts in the solid state, whereas there are significant interactions of salts with oxygen atoms and -OH groups, even in the solid state. In addition, the cellulose samples mixed with KCl and NH_4Cl showed similar changes in IR spectra, especially in the 400-800 cm^{-1} region, distinguishable from the remaining six chloride salts. This may be due to similar mode of interaction in KCl and NH_4Cl with cellobiose, as we found in ^{13}C NMR experiments in the liquid state.

4. Conclusion

Among the eight chloride salts studied KCl and NH_4Cl showed similar $\Delta\delta$ curves due to interactions of only with the Cl^- anion. Whereas other chloride salts showed interactions with D-cellobiose in both cation and anion. Their total interactions were calculated by using the sum of $\Delta\delta$ values ($\sum |\Delta\delta|$) as a new parameter for quantification of the interaction of salts with carbohydrates. In these salts the total interactions are in the order: $\text{Zn}^{2+} > \text{Sn}^{2+} > \text{Li}^+ > \text{Ca}^{2+} \sim \text{La}^{3+} > \text{Mg}^{2+}$. This novel technique could be applied to many classes of compounds like amino acids, peptides and lipids to measure total interactions with metal ions and anions; however is suitable only for salts with diamagnetic metal ions.

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Fig. 1. ^{13}C -NMR spectrum of α/β D-cellobiose - SnCl_2 mixture in D_2O at 25 °C as a representative example (0.146 mmol of D-cellobiose and 2.20 mmol of SnCl_2 in 0.5 mL of D_2O)

Fig. 2. ^{13}C NMR chemical shift changes ($\Delta\delta$) of D-cellobiose due to interaction with different chloride salts at 25 °C. Chemical shifts changes are measured relative to D-cellobiose in D_2O

Table 1. The calculated total magnitude values of chemical shift change ($\sum |\Delta\delta|$) for D-cellobiose in eight chloride salts in D₂O medium

Chloride salt	$\sum \Delta\delta $ ppm
ZnCl ₂	6.708
CaCl ₂	4.212
LiCl	4.5
SnCl ₂	5.027
LaCl ₃	4.212
NH ₄ Cl	3.767
MgCl ₂	2.346
KCl	5.862

Table 2. The major FT-IR peaks of pure D-cellobiose and D-cellobiose : chloride salt 1:2 mixtures in the 400-1700 cm^{-1} region.

δ = bending mode, ν = stretching mode, τ = twisting mode, rg = ring

Cellobiose	ZnCl ₂ + cellobiose	CaCl ₂ + cellobiose	LiCl + cellobiose	SnCl ₂ + cellobiose	LaCl ₃ + cellobiose	NH ₄ Cl + cellobiose	MgCl ₂ + cellobiose	KCl + cellobiose	Possible Assignment [35]
485						485		489	δ CCO, COC
573					574	574		574	δ CCO, τ CO
664						664		667	δ CCO, τ CO
742	742			742		743		742	δ COC, CCO
892	893	894	893	893		893	893	892	δ CCH, HCO; ν CO
992	993		993	993		992	993	991	ν, τ CC _{rg} , ν CO
1042	1046	1042	1045	1046	1042	1047	1044		ν, τ CC _{rg} , ν CO
1126			1127			1127			ν, τ CC _{rg} , δ CCH
1166	1165	1163	1166	1165	1163	1166	1165	1166	ν, τ CC _{rg} , δ CCH
1211	1209		1206	1209		1210		1209	δ HC ₆ O, CC ₆ H
1286	1286		1287	1286		1286	1286		δ CCH, COH
1313									δ CCH, COH
1360	1361	1362	1364	1361		1361	1362	1356	δ HCH, HCO, CCH
1429	1429	1427	1428	1429	1429	1427	1428	1429	δ HCH, HCO, CCH
1489	1488		1489	1488		1488	1490	1488	δ HCH, HCO, CCH
1637	1622	1636	1642	1622	1632		1640		δ HOH (H ₂ O)

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Graphical Abstract

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