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Review of Cellulose Non-Derivatizing Solvent Interactions with Emphasis on Activity in Inorganic Molten Salt Hydrates

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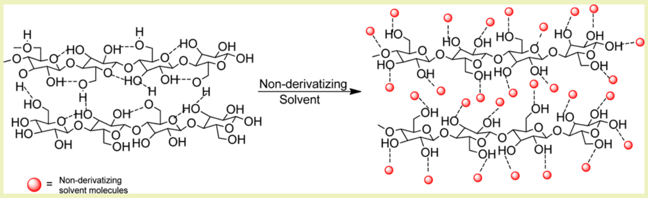

ABSTRACT: During cellulose dissolution in non-derivatizing solvents, the inter- and intramolecular hydrogen bonds of the polymer are deconstructed. This occurs either by hydrogen bond formation between one or more components of the solvent systems and the hydroxyl groups of the cellulose or by coordination bond formation between the metal ion present in the medium and the hydroxyl group of cellulose molecules. None of the polymer molecules are actually chemically modified during dissolution. In the first part of this review, we examine the literature pertaining to the different interaction mechanisms between cellulose and non-derivatizing solvent systems with emphasis on the inorganic molten salt hydrates. In the second part of this effort, we further review inorganic molten salt hydrates from the point of view of the changes they impart to the physical properties of the cellulose and the various chemical reactions that can be performed in it.

KEYWORDS: *Cellulose, Non-derivatizing solvents of cellulose, Inorganic molten salt hydrates, Crystallinity, Cellulose hydrolysis, Degradation of cellulose*

INTRODUCTION

Cellulose is a homopolysaccharide that is formed from linearly connecting D-glucose units condensed through the $\beta(1-4)$ glycosidic bonds.[1,2] This natural polymer has a 2-fold screw axis along the chain direction. The degree of polymerization (DP) of the macromolecule can vary from 100 to 20,000 depending on the sources.[3] Cellulose possesses a highly crystalline structure due to the presence of extensive intra- and intermolecular hydrogen bonding,[4−8] which has been examined in great detail.[9−12] Consequently this natural polymer is insoluble in water and typical organic solvents and can only be dissolved if the intra- and intermolecular hydrogen bonds are effectively disrupted. Cellulose dissolution processes can be broadly classified in two categories as will be discussed below:[13]

Cellulose Dissolution with Chemical Modification. A well-known method of cellulose dissolution is by prior chemical modification of the macromolecule. The main objective of this procedure is to functionalize the hydroxyl groups so as to disrupt the intra- and intermolecular hydrogen bondings but with minimal chain degradation. Functionalization reactions of cellulose include nitration,[14,15] xanthation,[7,16] esterification,[7,17,18] and etherification.[7,17] Though the solubility of the derivatized cellulose depends on the type and degree of derivatization, most of the derivatives are soluble in common polar organic solvents like DMF, DMSO, dioxane etc.[17,19] Detailed descriptions of such process are beyond the scope of this review.

Cellulose Dissolution without Chemical Modification. Solvents capable of dissolving cellulose without prior chemical modification are frequently described as non-derivatizing solvents. Such cellulose solvent systems are known to include ionic liquids,[5,7,20] organic solvents in the presence of an inorganic salt,[7,21−23] amine oxides,[7,24,25] aqueous alkali solutions,[7,26] aqueous complex solutions,[7,27] and inorganic molten salt hydrates.[7,28−30]

Ionic Liquids. Ionic liquids are one promising set of non-derivitaizing solvents of cellulose. Ionic liquids generally consist of large low charge density organic cations with low charge density inorganic or organic anions.[13,31,32] The low charge density and frequent size mismatch between the ions cause the salt to remain in the liquid phase at relatively low temperatures (<100 °C).[33] Some of them are non-flammable liquids even at room temperature,[5] which when coupled with their documented thermal and chemical stability and recyclability offer attractive characteristics for cellulose processing. Moreover, due to their low vapor pressures and reasonable ease of recovery, compared to other organic solvents, ionic liquids are promoted as an ideal green material.[5,20]

There have been reports regarding ionic liquid processing of cellulose as early as 1934.[34,35] However, in early 2000, Swatloski and co-workers reintroduced the concept of ionic liquids as potential solvents for cellulose.[36]

Remsing et al. studied the $^{35/37}$Cl NMR spectra relaxation times of cellobiose (the smallest possible repeat unit of cellulose that is also used as a model compound for this natural polymer) solvated in 1-*n*-butyl-3-methyl-imidazolium chloride ($[C_4mim]Cl$) at 90 °C to understand the interaction between cellulose and this solvent system.[37] This effort shows that

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$^{35/37}$Cl relaxation times (both T_1 and T_2) decrease dramatically with an increase in cellobiose concentration. A similar result is also observed when $^{35/37}$Cl NMR relaxation times of glucose in [C$_4$mim]Cl are studied.[37] However, $^{35/37}$Cl NMR relaxation times of glucose pentaacetate where all the −OHs are blocked by acetate groups show no decrease when studied under the same condition.[34] Thus, it is rational to conclude that Cl$^-$ forms hydrogen bonds with the hydroxyl groups of the cellulose disturbing the chloride ion's spherical symmetry and increasing its effective size. As such, its relaxation time decreases. Other than Cl$^-$, AcO$^-$ also shows a similar anionic effect when the ^{13}C NMR spectrum of cellobiose dissolved in 1-ethyl-3-methylimidazolium acetate (EmimAc) is studied.[38] Here, one can extrapolate and interpret that the anions of the ionic liquids provide a stoichiometric amount of hydrogen bonding to the hydroxyl groups of the cellulose molecules deconstructing the latter's inter- and intramolecular hydrogen bonds, which in turn solubilizes the macromolecule.

To further investigate the role of the anions of the ionic liquids in cellulose dissolution, Fukaya and co-workers studied the solubility of microcrystalline cellulose (MCC) in two different ionic liquids having the same cation ([C$_2$mim]$^+$) but different anions ([(MeO)MePO$_2$]$^-$/[(MeO)$_2$PO$_2$]$^-$).[39] They found that ([C$_2$mim][(MeO)MePO$_2$] is able to dissolve 10 wt % of MCC at 55 °C, while ([C$_2$mim][(MeO)$_2$PO$_2$] requires heating to 65 °C to dissolve the same amount of MCC keeping the other conditions constant. Latter Vitz et al. demonstrated a similar anion effect where [C$_4$(mim)Cl] is found to dissolve 25 wt % of cellulose, but [C$_4$(mim)Br] and [C$_4$(mim)SCN] dissolve only 2−3 and 5−7 wt % of cellulose, respectively, under the same conditions.[40] These efforts again explain that the anions of the ionic liquids play the key role in the cellulose dissolution, and the cellulose dissolution ability increases with the increase in the hydrogen bond-accepting ability of the anion. Recent reports further show that acetate and phosphate anions, which can readily form hydrogen bonds with the −OH groups, also display excellent cellulose solvating characteristics.[40,41]

Although the cations of the ionic liquids play a minor role in the cellulose dissolution process, it has been found that ionic liquids containing aromatic cations are more effective in dissolving cellulose than their aliphatic counterparts.[34,42] The charge delocalization of the aromatic cations results in weaker interactions between the cations and the anions allowing the latter to participate in the hydrogen bond formation with the −OH groups of cellulose more efficiently. Moreover, the cations also form weak hydrogen bonds with the hydroxyl groups of the macromolecule. However, their bulky size limits their hydrogen bond formation ability.[38] It has been also found that ionic liquids having an even number of carbon atoms in their cation side chains are better cellulose solvents than ionic liquids having an odd number of carbon atoms in their side chains.[43] This observed difference in cellulose dissolution ability is mainly attributed to the differences in the polarity in the medium and the packing effects. The polarity of the side chain of the cation is also found to affect the cellulose dissolution.[31,34]

Organic Solvents in Presence of Inorganic Salts (LiCl/Dmac System). In 1979, McCormick and co-workers first reported that polysaccharides can be dissolved in a binary mixture of dimethylacetamide (DMac) and lithium chloride.[21,22] The ^{13}C NMR spectrum of cellulose in DMac/LiCl shows five peaks that are comparable to the ^{13}C NMR spectra of the same material dissolved in other non-derivatizing solvents.[44,45] This data suggests that DMac/LiCl behaves as a non-derivatizing solvent for the cellulose.

There are numerous suggestions about the mechanism by which cellulose dissolves in LiCl/DMac. However, the most accepted one is the formation of Li$^+$[DMac]$_x$ macrocation.[46−48] DMac is a stronger Lewis base than Cl$^-$, and lithium is a very oxophilic cation. Thus, it is reasonable to suggest that in the presence of DMac, a complex cation Li$^+$[Dmac]$_x$ will form. The formation of the Li$^+$[Dmac]$_x$ macrocation is also verified by the ^{13}C NMR spectra and crystallographic studies.[49−51] The "free" chloride ions form hydrogen bonds with the cellulose hydroxyl groups destroying the inter- and intramolecular hydrogen bonding patterns of the polymer. The macrocation is also thought to have a weak interaction with the cellulose molecules (contributing 10% to the dipolar−dipolar interaction between cellulose and DMac).[22,44,47,52] Besides DMac, the binary mixture of lithium chloride and N-methyl-2-pyrrolidinone (NMP) is also found to dissolve cellulose.[53]

Any DMac/lithium halide binary system other than LiCl does not dissolve cellulose. In an effort to explain this effect, Spange and co-workers did a comparative study of the interaction of DMac/LiCl and DMac/LiBr systems with cellulose[52] and determined the Kamlet−Taft solvatochromic parameters [hydrogen bond donation ability (α), hydrogen bond acceptor ability (β), and dipolarity−polarizability (π^*)][54] of the solvent systems using probe dye indicators.[52] This work shows that the hydrogen bond basicity (β) of a 5 wt % DMac/LiCl system (1.90) is much higher than that of a 5 wt % DMac/LiBr system (1.50), indicating that the lithium salts exist as solvent-separated ion pairs. The larger sized and more polarizable Br$^-$ is more solvated by the solvent molecules than the Cl$^-$, which makes the latter more available for hydrogen bond formation with the hydroxyl group of cellulose.

Striegel et al. studied the interaction of different alkali metal halides with DMac by eletrospray ionization mass spectrometry (EIS−MS).[44,55] Their work shows that the ion−dipole interaction between the cation and Dmac is inversely proportional to the radius of the cation.[44] The smallest alkali cation, Li$^+$ is of highest charge density, and it is most oxophilic. As such, its coordination to Dmac is preferred, thus forming a tight ion pair with the solvent. The more weakly bound anion is available for hydrogen bonding with the hydroxyl groups of the cellulose. It is these unique Li$^+$/Dmac and Cl$^-$·····HO-cellulose interactions that impart in LiCl (compared to all alkali halides) the ability to dissolve cellulose.

In an effort to rationalize the unique nature of the DMac/LiCl and NMP/LiCl systems to dissolve cellulose, Elkafrawy examined the ^{13}C NMR spectra of different *N,N* disubstituted amides in the presence of LiCl.[53] All the carbons of the solvents show downfield shifts in the presence of LiCl with the carbonyl carbon showing the maximum shift due to their direct interaction with the Li$^+$. However, these downfield shifts of the carbonyl carbons have seen to be the highest for DMac (−1.68 ppm) and NMP (−1.46 ppm) among all the *N,N* disubstituted amides (dimethylformamide = −1.14 ppm, N,N-dimethylpropionamide = −1.14 ppm, and tetramethylurea= −0.22 ppm), suggesting that LiCL/Dmac and LiCl/NMP are unique solvent systems where the cation forms adequately strong coordination with the solvent molecules so that the anions possess the appropriate basicity to form hydrogen bonds with the cellulosic hydroxyls.

Morgenstern and group proposed a mechanism of cellulose dissolution in DMac/LiCl that is different from macrocation formation.[56] They studied the ^{7}Li NMR in order to probe the LiCl/DMac/cellulose system and observed that the chemical shift of ^{7}Li does not change with an increase in the concentration of the LiCl. It is, however, seen to significantly decrease with an increase in the cellulose concentration. Considering the fact that the hydroxyl groups of cellulose shield the lithium nuclei more than the carbonyl groups from DMac, the authors concluded that an increase in the cellulose concentration causes the lithium cations to dissociate from DMac allowing them to directly coordinate with the cellulosic hydroxyl groups, thus explaining the decrease in the chemical shift of ^{7}Li.

Tetra Butyl Ammonium Fluoride/DMSO System. Another similar and efficient cellulose-dissolving medium of this type is the mixture of tetra butyl ammonium fluoride trihydrate ($TBAF \cdot 3H_2O$) (salt) in the presence of the organic solvent dimethyl sulfoxide (DMSO) (1:36.6 mol ratio of $TBAF \cdot 3H_2O$ to DMSO).[23,57] Ostlund et al. used ^{19}F NMR spectra to explain the dissolution of cellulose in this solvent system.[58,59] The influence of cellulose on the ^{19}F chemical shift suggests that the cellulose dissolution power of the TBAF/DMSO system is primarily due to the strong ion–dipole interaction between fluoride ions from TBAF and the hydroxyl groups of cellulose. The highly electronegative fluoride ions form hydrogen bonds with the cellulose hydroxyl groups deconstructing the hydrogen-bonded cellulose network. The authors also found that addition of small amounts of water to the TBAF/DMSO cellulose solution results in the formation of a gel. This provides a competitive system to probe the preferred species to hydrogen bond to the F^- anions because the ^{19}F NMR spectra of the TBAF/DMSO solution system is sensitive to the ratio of water added to the system both in the presence and in the absence of cellulose. In the absence of cellulose, the ^{19}F NMR spectrum shows an upfield displacement in the chemical shift of the F^- anion when water is added to the system from outside and continues shifting with an increase in the amount of water added. This is attributed to the change of electronic environment around the fluoride ions as it shifts from a DMSO-rich to a water-rich environment. However, in the presence of cellulose, the chemical shift of F^- also moves toward the upfield direction and to a greater extent compared to the pure solvent system (cellulose being more shielding than water), which suggests that the F^- not only interacts with the water molecules but also interacts with the hydroxyl groups of the cellulose molecules.

Moreover, in the case of the pure TBAF/DMSO solvent system, the peak width at half height of the fluorine spectrum [$\Delta_{1/2(F^-)}$] gradually increases with an increase in the moles of water added with respect to the moles of F^- present ($N_{H2O/F}{}^-$) in the system.[59] However, in the presence of cellulose, first $\Delta_{1/2(F^-)}$ decreases with the addition of water and reaches a minimum at $N_{H2O/F}{}^- = 2$, then increases as observed in the case of a pure solvent system. This trend of $\Delta_{1/2(F^-)}$ is independent of the field strength of the NMR instrument used and purely due to the difference in the spin–spin relaxation rate of the system. In the case of the pure solvent, the number of water molecules coordinated with the F^- ion increases with an increase in $N_{H2O/F}{}^-$, increasing the effective size of the coordinated species and decreasing its rotation rate. Therefore, an increase in the relaxation rate of F^- is observed, which is depicted as an increase in the $\Delta_{1/2(F^-)}$ of the ^{19}F NMR spectrum. However, in the presence of cellulose, initially F^- ions are bounded to the large inflexible polymer molecules, which decrease the initial rotational freedom of the anion more than the water coordinate species, and it has a higher relaxation rate. With an increase in $N_{H2O/F}{}^-$, F^- dissociates from the bulkier cellulose molecules and starts to interact with comparatively smaller water molecules decreasing its effective size and increasing the rotation rate. As such, the rate of relaxation decreases and reaches a minimum at $N_{H2O/F}{}^- = 2$. Beyond this point, however, hydrated F^- species get bulkier due to coordination with more and more water molecules, and its relaxation rate increases again similar to the case of the pure solvent system. As a result, $\Delta_{1/2(F^-)}$ of the ^{19}F NMR spectrum shows an initial reduction followed by an increment. TBA^+ does not form macrocations like a LiCl/Dmac system. However, the bulky counterion is easily solvated by DMSO, which helps to form the free anion F^-.

Amine Oxides. This is another important class of non-derivatizing solvents of cellulose due to the ease of preparation and broad application range. *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) (13% water) is considered as the superior cellulose solvent among the amine oxides. The cellulose-dissolving ability of the amine oxide depends on the electron-donating and electron-accepting ability of the amineoxides.[60] Pure NMMO melts at 184 °C under normal conditions; however, the presence of cellulose dramatically decreases its melting point, as it destroys NMMO's crystal structure.[7,61] Because the N–O bond of NMMO is highly polar, it forms hydrogen bonds with the –OH groups of the cellulose molecules destructing its intra- and intermolecular hydrogen bonds.

In the presence of water, the cellulose-dissolving ability of NMMO and N,N-dimethyl ethanolamine N-oxide (DMEAO) is restricted as soon as the water to amine oxide ratio reaches 2 and 1, respectively.[24] Because water is more acidic than the cellulose hydroxyl groups in an aqueous medium, NMMO coordinates with water instead of forming a hydrogen bond with the hydroxyl groups of cellulose. As the molar ratio of water to NMMO reaches 2, all the available lone pairs of the oxygen in of NMMO are engaged in coordination with the water molecules, precluding them from forming hydrogen bonds with the hydroxyl groups of the cellulose molecule causing the eventual precipitation of the latter. Similarly, in the case of DMEAO, as one of the lone pairs is always engaged in the formation of intramolecular hydrogen bonding, the free one is used to coordinate with the cellulose molecules. As soon as the water to DMEAO mol ratio reaches 1, all the available lone pairs are used to coordinate with the water molecules restricting its cellulose dissolution.

Latter, Michael and co-workers reported that the ^{13}C NMR relaxation time of the cellobiose molecules (specially the C-6 carbon) in dimethylsulfoxide-d^6 was seen to decrease with the addition of NMMO in the medium.[62] This is only possible if the intermolecular hydrogen bonds of cellobiose (C-6 carbon) are broken, providing the model compound with more rotational freedom. As such, NMMO deconstructs the intra- and intermolecular hydrogen bonds of the system and, therefore, effectively dissolves it.

Aqueous Base Solutions. Aqueous base solutions have been shown to be another set of effective non-derivatizing solvents of cellulose. It has been shown that a 7–10 wt % aqueous solution of sodium hydroxide is able to dissolve cellulose samples of low molecular weight and of low crystallinity by freezing the suspension followed by thawing it at room temperature.[26,63]

To rationalize the interaction between cellulose and aqueous sodium hydroxide solutions, Egal and group examined the DSC traces of the NaOH/water binary system at different NaOH concentrations (20%, 12%, 9%, and 7.6%) and observed two melting temperatures for each concentration, except for the 20% solution.[64] The lower melting temperature (between −33 and −34 °C) represents the melting of the eutectic mixture of $NaOH\cdot 5H_2O$ + $4H_2O$, and the higher one (between −5 and −11 °C) represents the melting of ice. Similarly, DSC traces of the cellulose/NaOH/water ternary system (7.6 wt % aqueous NaOH is used because at this concentration aqueous NaOH is able to dissolve cellulose) also shows two melting temperatures. The lower melting temperature coincides with that of the NaOH/water binary system (between −33 and −34 °C) indicating the presence of the eutectic mixture of $NaOH\cdot 5H_2O$ + $4H_2O$ in the ternary system, too. The amount of heat absorbed by this system is found to decrease with an increasing amount of dissolved cellulose, with a minimum of zero when 7.6 g of cellulose is dissolved.[64] On the basis of these results, it can be concluded that aqueous NaOH interacts with the cellulose molecules, and at least 4 mols of NaOH are required to dissolve 1 mol of an anhydro glucose unit. As the amount of cellulose is increased, more NaOH is thought to interact with it, decreasing the amount of $NaOH\cdot 5H_2O$ as demonstrated by an decrease in the amount of heat absorbed. During the dissolution of 7.6 g of cellulose, all the NaOH is engaged to interact with the polymer leaving no free NaOH to form $NaOH\cdot 5H_2O$. As such, the DSC trace shows zero heat absorption at this level of cellulose in the solution.[64]

However, during the dissolution in an aqueous basic medium, the hydroxyl groups of the cellulose are ionized forming the corresponding salts. In this respect, this particular solvent system can also be considered as a derivatizing cellulose solvent system.

Yan and Gao discovered that the presence of 1 wt % poly(ethylene glycol) (PEG) in 9 wt % aqueous solution of sodium hydroxide offers a homogeneous and stable cellulose solution.[65] The presence of a small amount of urea or thiourea also shows improvements in the solubility of cellulose in the aqueous sodium hydroxide media.[66,67] In both cases, PEG and urea are seen as acting as proton acceptors preventing the intermolecular hydrogen bonding of the polymer.

Aqueous Solutions of Metal Complex. Aqueous solutions of metal complexes have also been used as cellulose solvents since the mid-19th century. Currently transition metal amine complexes are used to dissolve cellulose. According to earlier reports, the interaction between cellulose and the metal complexes forms in a two-step process. First, an acid base reaction proceeds between the −OH of the complexes and the hydroxyl groups of the cellulose, and finally, the coordination bond forms between the deprotonated hydroxyl group of the cellulose with the metal cations.[68] The coordination with the metal ions is actually the key step for the cellulose dissolution.[27] Burchard and co-workers have shown that the aqueous solution of metal complexes can dissolve cellulose by forming a complex with the cation through the C2 and C3 hydroxyl groups (as vicinal −OH groups are required to form coordination with the cation) of the cellulose molecules and thereby replaces ligands from the coordination sphere of the cation.[69,70] Burchard and co-workers have also studied the solubility of different types of cellulose (with different DPs) in three different aqueous solutions of metal complexes, namely, cuoxam, Ni-tren, and Cd-tren. They found that Cd-tren is able to dissolve the cellulose molecules with highest DP (= 9700), while Ni-tren has the medium cellulose-dissolving ability (DP < 5500), and cuoxam has the lowest cellulose-dissolving ability.[27] The authors described that the cellulose-dissolving ability of the aqueous solution of metal complexes is strictly dependent on the polymer chain stiffness in that particular solvent. However, the detail discussion of this procedure is beyond the scope of this review.[27,70]

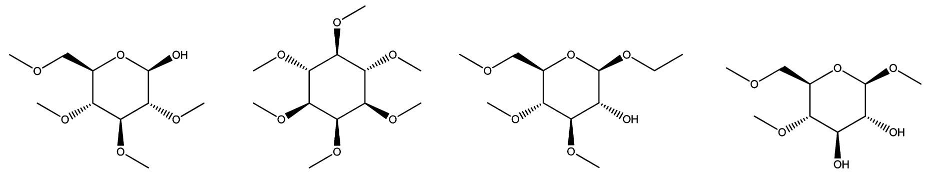
Inorganic Molten Salt Hydrates. Inorganic molten salt hydrates are another important class of cellulose solvents whose exploration dates as far back as the early 20th century.[7,29,30] These are the materials that have a water to salt molar ratio close to the coordination number of the strongest hydrated cation,[71] with the water molecules being tightly bound to the inner coordination sphere of the cation. Some of the reported cellulose-dissolving inorganic molten salt hydrates are $LiClO_4\cdot 3H_2O$, $LiI_2\cdot 2H_2O$, $LiSCN\cdot 2H_2O$, $ZnCl_2\cdot 3H_2O$, $Ca(NCS)_2\cdot 3H_2O$, and an eutectic mixture of NaSCN/KCN/$LiSCN\cdot 3H_2O$.[28,72] However, there are some inorganic salt hydrates ($LiNO_3\cdot 2H_2O$, LiCl·2−5 H_2O, $ZnCl_2\cdot 2H_2O$, and $ZnCl_2\cdot 4H_2O$) that swell the cellulose to a fine distribution of the polymer but are unable to form a clear solution.[28,72]

Inorganic molten salt hydrates are inexpensive and easier to prepare compared to the other non-derivatizing cellulose solvents. Furthermore, they are environmentally friendly as no toxic and volatile organic compounds are required to prepare such solvent systems. During the regeneration of cellulose from inorganic molten salt hydrate solutions, one simply needs to add water and no organic solvents. Moreover, the main component of this solvent system, the inorganic salts, can be recovered by evaporating the water after cellulose regeneration and can be recycled for further use. As such, this solvent system is recently seen augmented attention with respect to its applicability in cellulose processing.[7,25,26]

The ^{13}C NMR spectra of the cellulose in different molten salt hydrates ($LiClO_4\cdot 3H_2O$, $LiSCN\cdot 2.5H_2O$, and $ZnCl_2\cdot 4H_2O$) resemble the ^{13}C NMR spectra of cellulose dissolved in other non-dervatizing solvents like the aqueous solution of sodium hydroxide.[28] The FTIR spectrum of bacterial cellulose regenerated from $ZnCl_2\cdot 3H_2O$ is similar to that of the starting material without any additional peak.[30] These interesting observations offer the conclusion that the above inorganic molten salt hydrates act as non-derivatizing solvents for cellulose.

In the early 1970s, Richards and Williams conducted numerous model experiments to understand the interaction between cellulose and $ZnCl_2$.[73] In their study, they used methyl *β*-D-glucopyranoside solubilized in aqueous $ZnCl_2$ as a model system and found that there is a deviation in the optical rotation of this sample when compared to the aqueous solution of methyl *β*-D-glucopyranoside in the absence of $ZnCl_2$. This change in optical rotation is most likely a result of change of the electronic environment of the model compound in presence of $ZnCl_2$. To support this data, the ^{1}H NMR spectrum of methyl *β*-D-glucopyranoside was also examined both in the presence and in the absence of $ZnCl_2$. Deviation in the chemical shift of both the anomeric and ring protons in the presence of $ZnCl_2$ imply a direct interaction of the model compound with the inorganic salt.

During the same work, and in an effort to precisely locate the positions of interaction on the D-glucopyranoside ring with



2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside Hexa-*O*-methyl-myo-inositol Ethyl-3,4,6-tri-*O*-methyl-β-D-glucopyranoside Methyl-4,6-di-*O*-methyl-β-D-glucopyranoside

Figure 1. Different D-glucopyranosides with varying degreed of O-methylation to study the interaction between zinc chloride hydrate and D-glucopyranosides.

$ZnCl_2$, the authors examined the ^1H NMR spectra of different D-glucopyranosides with varying degrees of O-methylation (2,3,4,6-tetra-*O*-methyl-*β*-D-glucopyranoside, hexa-*O*-methyl-myo-inositol, ethyl 3,4,6-tri-*O*-methyl-*β*-D-glucopyranoside, and methyl-4,6-di-*O*-methyl-*β*-D-glucopyranoside) as shown in the Figure 1 both in the presence and in the absence of $ZnCl_2$.[73] The deviation in the chemical shifts of the proton peaks (in the presence of $ZnCl_2$) for each of the samples were determined and compared with that of methyl *β*-D-glucopyranoside. Among these samples, only methyl-4,6-di-*O*-methyl-*β*-D-glucopyranoside was found to show deviation in the chemical shift in the ^1H NMR spectrum in the presence of $ZnCl_2$ similar to that of the standard methyl *β*-D-glucopyranoside.

This result indicates that the presence of free vicinal hydroxyl groups is essential for the D-glucopyranoside to form a complex with $ZnCl_2$.

The UV spectra of cellulose and cellobiose dissolved in 67 wt % $ZnCl_2$ (mol ratio of $ZnCl_2:H_2O = 1:3.73$) shows distinct peaks at 290 nm, which is not observed in the UV spectra of either glucose or *α*- or *β*-glucopyranoside dissolved in $ZnCl_2$.[74] The structural differences between these compounds are that cellulose and cellobiose have *β*-1,4 linkage and a pair of hydroxyl groups across this *β*-1,4 linkage. At this point, it is rational to conclude that in the case of cellulose and cellobiose Zn^+ forms a complex involving the *β*-1,4 linkage and hydroxyl groups across the *β*-1,4 linkage that absorbs at 290 nm.

Hattori et al. investigated the interaction of cellulose with the molten salt hydrate, $[Ca(NCS)_2{\cdot}nH_2O]$.[75] They found that an aqueous solution of the salt at a concentration higher than 48.5 wt % is capable of dissolving cellulose at an elevated temperature (depending on the concentration of cellulose). This concentration corresponds to the cation with a hydration number less than 4. The authors also studied the DSC traces of cellulose/aq $Ca(NCS)_2$ (5 mg of cellulose in 20 mg of aqueous solution of $Ca(NCS)_2$) solution as a function of the salt concentration in a closed system. In this effort, they found that an exothermic peak appeared at higher salt concentrations, and the amount of the heat dissipated was increased with an increase in the salt concentration, showing a minimum of 0 at 48.5 wt % (limiting the concentration of $Ca(NCS)_2$ to dissolve cellulose). It can be rationalized that these peaks correspond to the energy required to form the cellulose Ca^{2+} adduct.[76] On the basis of the fact that the calcium's coordination number is six (octahedral geometry) and two of the coordination positions are always occupied by NCS^-, it can be explained that above 48.5 wt % salt concentration (hydration number less than 4) there are not enough water molecules to satisfy all the available coordination positions of the $Ca^{2+.}$ In this situation, the hydroxyl groups of the cellulose enter the coordination sphere of Ca^{2+} and form a coordination bond between the cation and the oxygen from the hydroxyl group.[75] Below 48.5 wt % salt concentration, all the available coordination positions of Ca^{2+} are occupied by the water molecules. With an increase in salt concentration, more cellulose hydroxyl groups are engaged in the coordination with Ca^{2+} breaking the intra- and intermolecular hydrogen bonds, which is reflected in the generation of greater exotherms at higher salt concentrations.

Like calcium−thiocyanate hydrates, sodium−thiocyanate hydrates are also capable of dissolving cellulose.[77] However, the type of interaction between cellulose and sodium−thiocyanate hydrates is different from that of between cellulose and calcium−thiocyanate hydrates. The DSC traces of cellulose/aq NaNCS ternary system show endothermic peaks in contrary to the exothermic peaks in the case of cellulose/aq $Ca(NCS)_2$ ternary system. During cellulose dissolution process, two events seem to occur simultaneously. First, the intermolecular and intramolecular hydrogen bonds of cellulose are broken due to the addition of the inorganic salt that is an endothermic process, and finally, coordination bonds are formed between the metal ion and the oxygen of the hydroxyl groups of cellulose, which is an exothermic process. In the case of $Ca(NCS)_2$ hydrates due to the presence of highly oxophilic Ca^{2+}, the coordination bond formation dominates over the hydrogen bond destruction. As such, a resultant exothermic peak is observed. However, for NaSCN hydrate, the hydrogen bond destruction dominates, and an endothermic peak can be seen.

Among different lithium-containing salt hydrates, $LiClO_4{\cdot}3H_2O$ and $LiSCN{\cdot}2H_2O$ are able to dissolve cellulose effectively, but $LiNO_3{\cdot}3H_2O$ does not. In an effort to rationalize this fact and to understand the interaction between cellulose and lithium-containing inorganic molten salt hydrates, the crystal structures of the above-mentioned three salts were carefully examined.[28,78] In all three cases, Li^+ has an octahedral geometry. In the case of $LiClO_4{\cdot}3H_2O$, each water molecule is shared by two Li^+ to satisfy the six coordination positions. The ClO_4^- is not involved in the coordination with the Li^+. In the case of $LiSCN{\cdot}2H_2O$, two water molecules and one SCN^- are shared between two Li^+ ions. It is likely that a hydroxyl group of cellulose can coordinate to the Li^+ ion by breaking one of the water bridges in the case of above-mentioned two salts. In $LiNO_3{\cdot}3H_2O$, two water molecules and one NO_3^- are shared between two Li^+. The remaining water is non-coordinated lattice water. Both the coordination of the NO_3^- ion and the extra lattice water are thought to make the cellulose hydroxyl groups a non-competitive ligand to coordinate to Li^+. Therefore, $LiNO_3{\cdot}3H_2O$ is not able to dissolve cellulose.[28]

To confirm the direct interaction between Li^+ with cellulose molecules, Brendler and co-workers examined the ^7Li NMR spectrum of $LiCLO_4{\cdot}3H_2O$ in the presence of cellulose.[78] The Li^+ chemical shift moves upfield with increasing carbohydrate concentration. It can only be possible if the water molecules of the inner coordination sphere of Li^+ are replaced by more shielding cellulose hydroxyl groups. On the other hand, the $^7Li-^1H$ HOESY spectrum of cellobiose dissolved in $LiCl\cdot5D_2O$ (D_2O: 99.98%) shows correlation signals for the lithium and the water protons as well as for the lithium and the methylene protons (from cellulose).[28,78] In general, the intensity of the correlation signals is found to increase with the decrease in inter-nuclear distances. In the $^7Li-^1H$ HOESY spectrum, strong correlation signals between lithium and the methylene protons of cellulose can be found that are comparable to the intensity of the correlation signals between lithium and the water protons (water is already present in the first coordination sphere of Li^+). This result leads to the conclusion that cellobiose has actually entered in the first coordination sphere of the Li^+. Extrapolating this result it is rational to conclude that the hydroxyl groups of cellulose can also form direct coordination bonds with Li^+ cation.[28,78]

In summary, it has been established that inorganic molten salt hydrates dissolve cellulose generally as non-derivatizing solvents. The reports infer that the dissolution of cellulose depends on the direct interaction of the cellulose hydroxyl groups with the metal ions. However, our own work shows that the cellulose-dissolving ability of zinc chloride hydrates is completely dependent on the structure of the inner coordination sphere of the cation. Moreover, much of the reported work also states that cellulose has been solubilized in aqueous zinc chloride when the $ZnCl_2$ to water molar ratio is maintained close to 1:3.[76,92,100,101] More specifically, Lu and Shen reported that bacterial cellulose is soluble in $ZnCl_2\cdot3H_2O$, while it is insoluble in either of $ZnCl_2\cdot2H_2O$ or $ZnCl_2\cdot4H_2O$ (though cellulose swells in these two solutions). These results definitely show that the cellulose-dissolving ability of molten inorganic salt hydrates, especially $ZnCl_2$, is dependent on the amount of water present in the inner coordination sphere of the cation. Otherwise, a more concentrated solution of $ZnCl_2$ would have dissolved cellulose better. As such, despite the fact that many authors have concluded that dissolution of cellulose depends on the direct interaction of the cellulose hydroxyl groups with the metal ions, much of the same data could be rationalized by invoking hydrogen bonding of cellulose hydroxyl groups with the water molecules directly bonded to the metal cations. Hence, significant additional effort is necessary to delineate the actual mechanism of interaction of cellulose in the molten salt hydrates.

■ REGENERATION OF CELLULOSE FROM INORGANIC MOLTEN SALT HYDRATE MEDIUM

The dissolved cellulose is regenerated by addition of a precipitating solvent. Most commonly, water is used as the precipitating solvent; however, there are some efforts reported where alcohols (methanol, ethanol, and isopropanol) and acetone are used for cellulose regeneration.[79−81] Jianlong Ni in his Ph.D. dissertation studied the wide-angle X-ray diffraction patterns of the cellulose regenerated from zinc chloride hydrate by addition of different alcohols (methanol, ethanol, and isopropanol).[80] He found peaks for the zinc hydroxide along with that of the cellulose in the X-ray diffraction patterns in each case. However, he did not observe any peak for free zinc chloride. The observation of Ni suggests that 100% of the zinc chloride was not removed from the cellulose during regeneration and washing, but zinc chloride was converted to zinc hydroxide in the process.[80] However, in all cases the removal of the residual zinc salt was possible by washing the sample with 0.1N HCl solution.[80] This is also verified by our own work where the cellulose is regenerated from zinc chloride hydrate by the addition of water. In this effort, about 40% of the inorganic salt is found to remain even after several thorough washes with water. Washing, however, with a dilute solution of sodium hydroxide (1 weight%) effectively removed the zinc chloride. A detailed account of this study will be discussed in ensuing publications.

■ CHANGE IN THE PROPERTIES OF CELLULOSE AFTER REGENERATION FROM INORGANIC MOLTEN SALT HYDRATES

In general, it has been found that the properties, especially the molecular weight and the crystallinity of the regenerated cellulose, differ from the starting materials. The following section of this review will discuss the changes in the polymer properties of cellulose after regeneration from a molten salt hydrate.

Molecular Weight and Degree of Polymerization. Commonly, the inorganic molten salt hydrates are found to decrease the molecular weight of cellulose. Fischer and co-workers have reported that the average molecular weight (M_w) of cellulose with a degree of polymerization (DP) of 1511 reduces from 751,400 to 284,000 g/mol when heated in $LiClO_4\cdot3H_2O$ at 100 °C for 2.5 h and to 568,300 g/mol when heated in $LiI_2\cdot2H_2O$ at the same temperature for 3.0 h.[72] Kuga examined the reduction in the DP of three different types of cellulose samples (Whatman CF-1 cellulose powder with initial DP 180, dissolving sulfite pulp with initial DP 770 and purified cotton linter cellulose with initial DP 1620) after regeneration from hydrated $Ca(SCN)_2$.[82] He noticed that the cellulose sample with the smallest chain length (Whatman CF-1 cellulose powder with final DP 170) shows minimum reduction in DP, while the longer polymer chains show higher reduction in DP (dissolving sulfite pulp with final DP 490 and purified cotton linter cellulose with final DP 500). It is likely that the requirement of higher dissolution temperatures and longer dissolution times for the longer polymer chains (120 °C for 40 min for dissolving sulfite pulp and 140 °C for 40 min for cotton linter cellulose) compared to those applied for CF-1 cellulose Powder (120 °C for 20 min) are responsible for the greater reduction in the DP.[82] The DP of bacterial cellulose (initial DP 4135) also decreases after regeneration from $ZnCl_2\cdot3H_2O$. Moreover, the elevated temperature facilitates the reduction in DP of cellulose. The DP of the bacterial cellulose decreases to 3196 and 855 when heated at 30 °C for 10 h and at 95 °C for 0.5 h, respectively.[30] At this point, it is rational to conclude that the inherent Lewis acidic nature of the inorganic salts hydrates is responsible for the polymer chain scission and thereby reduction of the molecular weight. It appears that the degree of decrease in molecular weight is dependent on the acid strength of the inorganic salt.

Crystallinity. The crystallinity of the cellulose regenerated from inorganic molten salt hydrates was studied using X-ray scattering and compared with that of the starting materials. It is thus concluded that cellulose loses part of its crystallinity when regenerated from inorganic molten salt hydrate solvents (zinc chloride and lithium perchlorate). Upon regeneration, the highly crystalline cellulose I is seen to be converted to less crystalline cellulose II.[28,30,72]

Because the earlier work by Atalla et al. showed that the molecular orientation of the cellulose chains can be studied using Raman spectroscopy,[83,84] regenerated cellulose samples were further examined using such techniques.[85−87]

Cellulose I and cellulose II are known to possess different conformations within their anhydroglucopyranose (AGU) skeletons that can be distinctly seen in the Raman spectra.[11] Cellulose I contains two stereo chemically different $-CH_2OH$ groups producing two different signals in the Raman spectra at 1476 and 1455 cm^{-1}, respectively, while cellulose II shows only one type of $-CH_2OH$, which provides a single peak at 1461 cm^{-1}.[85,87,88] A weak intensity peak at 1261 cm^{-1} can also be seen exceptionally in the case of cellulose II.[85,87,88]

Schenzel and Fischer used FT Raman spectroscopy with near-infrared or red excitation lasers to circumvent the interfering fluorescence of cellulose for the crystallization study in different inorganic molten salt hydrates ($ZnCl_2$ + $4H_2O$, $LiSCN·2.5H_2O$, $LiClO_4·3H_2O$, and $2ZnCl_2·6H_2O$ + LiCl with 5 wt % bacterial cellulose concentration). They found that the Raman spectra of cellulose I samples regenerated from molten salt hydrates show distinct signals at 1461 and 1262 cm^{-1}, which are characteristics of cellulose II.[85−87] In addition, the regenerated cellulose samples also show peaks at 418, 352, and 311 cm^{-1}, which are characteristically seen in the FT Raman spectrum of cellulose II.[85] This result indicates that there is polymorphic transformation of cellulose I to cellulose II as a result of dissolution in the molten salt hydrates.

In general, the C−4 carbon of cellulose shows different chemical shifts in the solid state of ^{13}C NMR spectra depending on the crystallinity of the polymer.[89] For highly crystalline cellulose, it shows a downfield peak between 87.5 and 88.5 ppm, whereas for lesser crystalline cellulose shows an upfield peak at 84 ppm.[89] To investigate the crystallinity of cellulose, Leipner and co-workers examined the solid state ^{13}C CP/MAS spectra of the polymer regenerated from $LiClO_4·3H_2O$ and $ZnCl_2·4H_2O$.[71] Comparing the peaks of the pure and the regenerated cellulose, the authors concluded that cellulose regenerated from $ZnCl_2·4H_2O$ shows higher crystallinity than the cellulose regenerated from $LiClO_4·3H_2O$. Considering $LiClO_4·3H_2O$ as a true cellulose solvent and $ZnCl_2·4H_2O$ only able to swell cellulose to form fine distribution, it is expected that $LiClO_4·3H_2O$ will destroy the crystallinity of cellulose to greater extent than $ZnCl_2·4H_2O$.

Thermal Properties. Lu and Shen examined the thermal stability of bacterial cellulose before and after regeneration from $ZnCl_2·3H_2O$ and found that the onset of the polymer degradation temperature was decreased from 330 to 305 °C (25 °C) after regeneration.[30] The amount of residual mass remaining after heating increases after regeneration. This may be due to the presence of some remaining zinc chloride salt in the cellulose sample.[30]

In summary, morphological changes of cellulose occur as a result of regeneration from inorganic molten salt hydrate solutions with cellulose I generally being converted to cellulose II. The chain degradation or the decrease in its molecular weight depends on the inherent Lewis acidity of the salt, the duration of dissolution, and the temperature of dissolution. Overall, the observed decrease in the molecular weight and the degree of crystallinity also affected the thermal properties of cellulose.

■ REACTIONS PERFORMED IN INORGANIC MOLTEN SALT HYDRATE SOLUTIONS

As discussed earlier, dissolution or swelling in inorganic molten salt hydrates decrease the degree of crystallinity in the cellulose molecules making it more susceptible toward chemical reactions. In this section of the review, we will now discuss the chemical reactions of cellulose performed in the inorganic molten salt hydrate solution media.

Acid Hydrolysis. More than 70% of the weight of lignocellulosic materials consists of cellulose and hemicellulose. Both of these carbohydrates can be hydrolyzed to their monomaric forms (glucose, xylose, arabinose, etc.) in the presence of an acid. Biofuels and other important biochemicals are obtained from such hydrolysis products.[90,91] Cellulose can be hydrolyzed to glucose in acidic media in the presence of a catalyst or an enzyme. In the presence of mineral acids alone, the rate of hydrolysis is slow, and the product yields are low due to side reactions especially at elevated temperatures and prolonged times.[92] These reactions, however, can be favorably mediated by the inorganic salt hydrates.

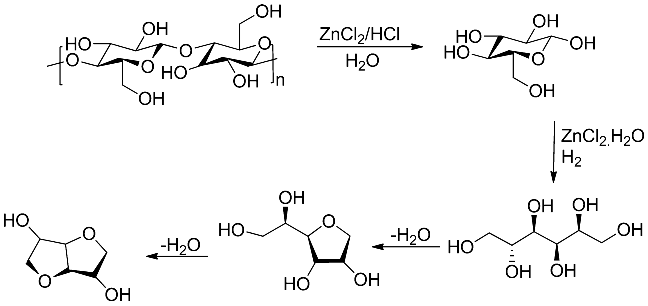
Cao and co-workers reported that the acid hydrolysis of cellulose becomes much faster when it is regenerated from 70% aqueous solution of $ZnCl_2$ (mol ratio of $ZnCl_2:H_2O$ = 1:3.25) by addition of ethanol prior to the acid hydrolysis.[81] The authors dissolved MCC in $ZnCl_2$ solution by heating at 65 °C for 30 min. The pretreatment was followed by acid hydrolysis in the presence of hydrochloric acid. The progress of the reaction was monitored by measuring the concentration of glucose produced during the hydrolysis. This effort shows that the cellulose regenerated from aqueous $ZnCl_2$ completely hydrolyses within 20 h, while earlier reports shows that it takes about 80 h to hydrolyze 10% of the untreated cellulose. The product yield for cellulose regenerated from $ZnCl_2$ solution increases significantly (mainly due to lower reaction time). Dissolution of cellulose in aqueous $ZnCl_2$ at elevated temperature reduces its molecular weight as discussed earlier. Moreover, it reduces the crystallinity of the cellulose making it more accessible to the acidic hydrolysis reagents decreasing the reaction time and increasing the product yield significantly.

The main component of hemicelluloses, xylan, produces xylose on hydrolysis. In general, rapid hydrolysis of xylan can be done between 100 and 160 °C in the presence of 3% hydrochloric acid with higher temperature facilitating the reaction.[90] However, the product xylose is not stable at elevated temperatures. In addition, some of the amorphous cellulose also undergoes hydrolysis along with xylose at higher temperatures generating glucose. Therefore, a mixture of xylose and glucose are obtained as the products, and the separation of these two monosaccharides is by no means simple.

However, Cao and co-workers showed that xylan can be hydrolyzed in aqueous $ZnCl_2$ (mole ration of $ZnCl_2:H_2O$ = 1:4.2 to 1:2.1) below 75 °C, without any additional mineral acids.[90] At this temperature, not only a higher yield of xylose is obtained, but in addition, hydrolysis of cellulose is restricted. Hence, no glucose is generated. Therefore, the presence of zinc chloride removes the aforementioned difficulty of product separation because using two different streams at different temperatures xylose and glucose could be obtained separately from the same starting material.

A variety of commercially valuable low molecular weight products can be obtained from cellulose. Almeida et al. reported the conversion of cellulose to isosorbide, a valuable compound used in the pharmaceutical industry,[93−95] in aqueous $ZnCl_2$ (molar ration of $ZnCl_2:H_2O$ = 1:3.2) medium in a single-pot reaction (Scheme 1).[96] This is accomplished by the reduction of the monosaccharides hydrolysis products of cellulose to the less polar derivatives in the same zinc chloride

Scheme 1. Hydrolysis of Cellulose Followed by Dehydration To Synthesize Isosorbide



solution.[91] After the hydrolysis of cellulose to glucose, the product can be hydrogenated to glucitol in the same $ZnCl_2$ medium.

The presence of $ZnCl_2$ retards the hydrogenation reaction by 2-fold. However, it prevents the isomerization of glucose to fructose (probably due to the formation of hydrogen bonds between the hydroxyl groups of glucose and $ZnCl_2$ hydrate and thereby limiting the glucose molecules to rearrange to the mandatory conformation for isomerization) and thereby formation of manitol after hydrogenation as is generally formed when glucose is hydrogenated in the absence of zinc chloride. Next, glucitol is dehydrated to isosorbide (Scheme 1) in two sequential steps in the presence of a co-catalyst ($CuCl_2$ or $NiCl_2$).[96] First, glucitol is dehydrated to sorbitan and finally to isosorbide. The yield of isosorbid is better in the $ZnCl_2$ medium than the normal acidic dehydration of glucitol as $ZnCl_2$ most likely prevents the formation of a 2,5-sorbitan isomer (which is unable to dehydrate to isosorbide) by hydrogen bond formation with the intermediates and thereby restricting it to a certain conformation and increase the yield of isosorbide.

The elevated temperatures required for the thermal degradation of cellulose produces large quantities of ash. However, it has been found that the presence of some inorganic salts ($MgCl_2$, NaCl, Na_2CO_3, NaOH, $NiCl_2$, and $FeSO_4$) mediates the thermal degradation of cellulose and lignocellulosic biomass.[95,97−99]

Later, Amarasekara and Ebede examined the effect of Zn^{2+} on the thermal degradation of cellulose using thermogravimetric analysis.[100] Whatman filter paper No. 1 was used as the cellulose source that was impregnated with $ZnCl_2$ by first swelling it with an aqueous solution of the salt (mol ratio of $ZnCl_2$:H_2O = 1:55.5) and then by evaporating the water from the cellulose $ZnCl_2$ mixture. The thermal degradation of this system was examined by heating the cellulose zinc chloride mixtures between the temperature ranges of 20−620 °C. It was found that the cellulose degradation temperature decreases with the increase in $ZnCl_2$ to anhydroglucose unit ratio. (The initial degradation range of pure cellulose decreases from 338−354 °C to 192−238 °C when 0.50 mols of zinc chloride are impregnated per mole of AGU units in cellulose). The degradation products were found to be furan derivatives, furfural, hydroxymethylfurfural (HMF), and levulinic acid. Among these, HMF and levulinic acid are particularly important because these are used in the plastic and pharmaceutical industries and as biobased fuel additives.[101−103]

5-Hydroxymethylfurfural (5-HMF) can be selectively obtained when cellulose solution in aqueous $ZnCl_2$ (mol ratio of $ZnCl_2$:H_2O = 1:3.9) is heated at 50 °C under UV irradiation (power 21 W) in the presence of a titanium oxide photocatalyst and under an oxygen atmosphere.[104] UV irradiation in the presence of TiO_2 generates OH radicals. These OH radicals also participate in the breaking of the glycosidic linkages of cellulose and likewise $ZnCl_2$ generates monosaccharides. As such, a 10-fold increase in the yield of 5-HMF is noticed compared to when cellulose is degraded in zinc chloride hydrate itself.

1-(Furan-2-yl)-2-hydroxyethanone (FHE), an isomer of HMF, can be obtained when cellulose (cotton fiber) is degraded in an aqueous $ZnCl_2$ medium under microwave heating.[105] The $ZnCl_2$ to water molar ratio in the solvent influences the yield of FHE significantly. The yield increases from 6.3% to 12.0% when the $ZnCl_2$ to water molar ratio is changed from 1:3.78 to 1:3.36, keeping the other reaction conditions constant. This is mainly due to the better dissolution of cellulose in the solvent with an increase in concentration of zinc chloride. However, a further increase in the $ZnCl_2$ concentration (mol ratio of $ZnCl_2$:H_2O = 1:3.03) reduces the yield to 9.0%, which is due to the degradation of 1-(furan-2-yl)-2-hydroxyethanone in a $ZnCl_2$-rich environment. The yield of 1-(furan-2-yl)-2-hydroxyethanone also decreases from 8 to 6 mol % with an increase in the reaction temperature (135 to 150 °C) or the reaction time (5 to 10 min), keeping the $ZnCl_2$ to water ratio (1:3.36) constant. This decrease in yield was mainly due to degradation of 1-(furan-2-yl)-2-hydroxyethanone under the aforementioned reaction conditions.

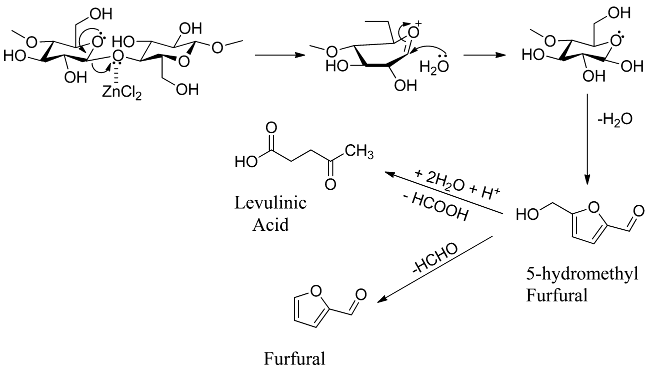
Lv and co-workers also reported the degradation of cotton cellulose to FHE, FF, and HMF in a biphasic medium (aqueous $ZnCl_2$ as the reaction medium and organic solvent as the extraction medium).[106] They used an aqueous $ZnCl_2$ solution (mol ratio of $ZnCl_2$:H_2O = 1:3.55) as the aqueous phase and different organic solvents (TBP, EDC, *n*-BuOH, MIBK, and *n*-OcOH) as the organic phase. The authors found that using the organic medium for product extraction significantly increases the product yield. Extraction of the products from the medium helps the reaction to proceed in the forward direction according to Le Chatelier's principle. As a result, the organic solvents, which can easily dissolve the products, provide better yield.

From this discussion, it is evident that $ZnCl_2$ plays a key role in the degradation of cellulose at elevated temperatures. To clarify the zinc chloride-mediated degradation of cellulose, it is rational to consider that first Zn^{2+} ions forms a coordination bond with the glycosidic oxygen atom of the cellulose molecule.[100] This facilitates the polymer to cleave along the 1,4-glycosidic bond, yielding glucose monomeric units (Scheme 2). Then, the formed glucose unit undergoes the required rearrangement and dehydration to form the isolated furan derivatives.[107,108]

The presence of inorganic salts has also been reported to facilitate the pyrolysis of biomass like lignocellulosic materials. However, in these cases, the salts act as a catalyst rather than a solvent medium. As such, the discussion of pyrolysis of lignocellulosic materials is beyond the scope of this review.[109,110]

Etherification, Esterification, and Deprotection of Cellulose. Cellulose ethers and esters have vast applications in the fields of coating, membrane, and textile industries[17,111] making the esterification of native cellulose an important commercial reaction. In 2001, Heinze and his group reported that the carboxymethylation of cellulose can be done in the $LiClO_4·3H_2O$ solvent medium. They dissolved cellulose in $LiClO_4·3H_2O$ at 100 °C,[112] and carboxymethylation was performed at the same temperature using sodium monochlor-

Scheme 2. Zinc Chloride-Mediated Hydrolysis of Cellulose Followed by Dehydration and Rearrangement



oacetate in the presence of aqueous sodium hydroxide as the base. They reported an overall degree of substitution of 0.69.

Acetylation of cellulose can be done in the eutectic mixture of NaSCN/KSCN/LiSCN·2H_2O at 130 °C by heating with acetic anhydride for 3 h.[113] The product can be recovered by precipitation from ethanol and DMSO. The degree of substitution (DS) can be determined by ^{1}H NMR, and a maximum DS of 2.41 can be attained within 3 h, when a 1:100 ratio of AGU unit to acetic anhydride is used. However, the efficiency of acetylation (with respect to acetic anhydride required to get high DS) in a NaSCN/KSCN/LiSCN·2H_2O medium is much lower than the efficiency of acetylation in a DMac/LiCl medium. (A maximum DS of 2.8 can be obtained when cellulose is acetylated in a DMac/LiCl medium at 60 °C for 18 h using molar ratio of AGU unit to acetic anhydride = 1:4.5).[114] Acetylation of cellulose in a $LiClO_4$·3H_2O medium is found to work poorly as the higher acidity of $LiClO_4$·3H_2O causes deacylation of the acetylated products.[113]

Protection of the C-6 hydroxyl group of cellulose is important for regeoselective substitution of this natural polymer. Triphenylmethyl (trityl) is considered to be one of the most effective protecting groups for cellulose. Because of the high steric requirements, this protecting group preferentially reacts with the primary hydroxyl group of the polymer that allows the selective reaction of the secondary hydroxyl groups of the polymer. Fischer and co-workers reported that trityl-substituted cellulose (a cellulose ether) can be deprotected in $LiClO_4$·3H_2O and $ZnCl_2$·4H_2O media.[115] The authors treated trityl cellulose separately with $LiClO_4$·3H_2O and $ZnCl_2$·4H_2O at 110 and 65 °C, respectively, for 3 h, during which high acidity of the molten salts was seen to catalyze the hydrolysis reaction. The reactions were monitored by FTIR and ^{13}C NMR spectroscopies, and the disappearance of the aromatic bands in the spectra confirmed the completion of the deprotection reaction.

Other Applications. Cellulose films are widely used in the packaging industry. The most common methods to cast a film of cellulose are either the viscose process or the cuprammonium process. Neither method is environmentally friendly because of the challenges with respect to recovery and recycling. Xu and Chen used cellulose solutions in molten $ZnCl_2$ to cast clear films from it. $ZnCl_2$ can be easily recovered and recycled after film formation, which makes this process more environment friendly. Another advantage of this method is that the films could be casted from comparatively low molecular weight polymer. The authors dissolved microcrystalline cellulose (DP = 200−250) in a 67% solution of $ZnCl_2$ (mol ratio of $ZnCl_2$:H_2O = 1:3.73) at 65 °C for 30 min and cast films on TLC plates. The films were recovered from ethanol (most likely due to removal of the $ZnCl_2$ solution during addition of ethanol) and purified by washing several times with water and ethanol. Xu and Chen reported a lower degree of crystallinity for the cellulose films cast from aqueous $ZnCl_2$ solution than the starting material identified by wide-angle X-ray diffraction. The reduction in crystallinity in cellulose is most likely due to the presence of residual $ZnCl_2$ in cellulose. The authors also measured the tensile strength of the films and found that tensile strength of the cellulose film cast from aqueous $ZnCl_2$ is comparable to that of the commercial cellophane films prepared by other methods.[116]

In summary, inorganic molten salt hydrates can be considered as a potential solvent for the chemical modification of cellulose. Because of their inherent acidic nature, some of the solvents are very effective toward acid hydrolysis and degradation of cellulose. However, these solvent systems also have limitations because the effectiveness of molten salt hydrate systems is highly sensitive to water content. The acidity of the solvents almost unavoidably degrades the polymers yielding undesirably low molecular weights.

■ CONCLUSION AND FUTURE PROSPECTS

This effort offers a comprehensive overview of the cellulose-dissolving mechanisms that apply in various non-derivatizing solvent systems with emphasis on the molten salt hydrates. Non-derivatizing cellulose solvents dissolve the polymer via physical interactions with no evidence for chemical derivatization. More specifically, the inter- and intramolecular hydrogen bonds of cellulose are deconstructed either by hydrogen bond formation between the anion present in the solvent system and the hydrogen present in the hydroxyl group of cellulose or by the coordination interaction between the metal ion present in the solvent and the oxygen atoms of the cellulosic hydroxyl groups. The second and major part of this review focuses on the inorganic molten salt hydrates as the cellulose solvents because they are among several novel, substantial, and economically accessible potential solvents. The dissolution of cellulose in molten inorganic salt hydrates dramatically alters its crystal structure because upon regeneration the material is significantly less crystalline. Such polymorphic changes make the cellulose hydroxyl groups much more accessible toward chemical reactions, and for this reason, cellulose pretreated with molten inorganic salt hydrates requires considerably less drastic reaction conditions for chemical modifications. Among the drawbacks of molten inorganic salt hydrates are their sensitivity to moisture and on occasion the difficulty of removing traces of the metal from the regenerated material with cellulose.

In closing, one needs to point out that the reviewed material (related to molten inorganic salt hydrates) basically concludes that cellulose dissolution depends on the direct interaction of the hydroxyl groups of the macromolecule with the metal ions. However, in our view, much of the reported data could also be rationalized by invoking hydrogen bonding between the cellulosic hydroxyl groups and the water molecules that are directly bonded to the metal cations. Consequently, there is ample scope for future investigations toward unraveling the detailed interaction of cellulose with molten inorganic salt hydrates.

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Notes

The authors declare no competing financial interest.

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Dr. James D. Martin obtained his Ph.D. in 1990 from Indiana University (Bloomington, IN). After postdoctoral positions at the University of Paris (Orsay, France) and Iowa State University (Ames, IA), he joined the faculty at North Carolina State University (Raleigh, NC) where he is a Professor of Chemistry. He was recognized with a CAREER award from the National Science Foundation in 1995 and was named a Cottrell Scholar by the Research Corporation for Science Advancement in 1997. He maintains a research program in condensed matter inorganic chemistry that is currently focused on the study of structure in liquids and solutions, as well as on an understanding of the mechanisms of crystal formation. In addition to his research and teaching, he is significantly engaged in science and education public policy, serving as an elected representative to the Wake County (NC) Board of Education.

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