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The role of the molecular formula of $ZnCl_2{\cdot}nH_2O$ on its catalyst activity: A systematic study of zinc chloride hydrates in the catalytic valorisation of cellulosic biomass

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We demonstrate the efficient and direct transformation of a range of low value substrates, such as lignocellulose and algal biomass, into significantly higher value chemicals, including low molecular weight reducing saccharides, 5-(hydroxymethyl)furfural, furyl hydroxymethyl ketone and furfural. This is based on a systematic study of $ZnCl_2{\cdot}nH_2O$ (n = 2.5–4.5), in particular the role of the molecular formula (the amount of H_2O) on its activity in the catalytic transformation of cellulosic materials into value added small molecules. The study includes various model transformations based on refined saccharides and applies the new insights to the highly selective transformation of raw biomass.

Introduction

The acid-catalysed conversion of cellulosic biomass is a promising way to produce organic building block chemicals (platform molecules), as renewable replacements to many petrochemical products.[1–4] There is a current focus on the application of ionic liquids (ILs) in the catalytic valorisation of (poly)carbohydrates into platform chemicals.[4,5] In distinct contrast to common aqueous or organic solvents, ILs are able to dissolve cellulosic material enabling its conversion into desirable products under mild processing conditions.[4–7] While imidazolium salts are most commonly employed, inorganic molten salt hydrates remain less investigated ionic media for the processing of carbohydrates.[4,5] Many of these salts fully dissolve polysaccharides and in due course catalyse their transformation into platform molecules.[4,8] Zinc chloride hydrate, with the conventional formula $ZnCl_2{\cdot}nH_2O$ (this system is a true IL with the molecular formula $[Zn(OH_2)_6][ZnCl_4]$ in the case of n = 3),[9,10] is excellent for the synthesis of some useful molecules directly from cellulose (e.g., cotton fibres, microcrystalline cellulose, or cellobiose).[11–13] Some remarkable examples include the transformation of polysaccharides into glucose (solvent $ZnCl_2{\cdot}3.73H_2O$),[11] HMF (biphasic solvent system $ZnCl_2{\cdot}3H_2O$/methyl isobutyl ketone),[12] or into a mixture of furyl hydroxymethyl ketone and furfural (FHK and FF, biphasic solvent system $ZnCl_2{\cdot}3H_2O$/anisole),[13] all of which present a significant advantage relative to the existing processes based on aqueous solvents or commonly used imidazolium salts. Within these exemplary findings, including our recent work in which some changes in response to the molecular formula of $ZnCl_2{\cdot}nH_2O$ were noted,[13] the exact role of the molecular formula of the $ZnCl_2{\cdot}nH_2O$ system is unclear, on the outcomes and the catalyst activity. For example, a study on the low temperature (70 °C) pretreatment of corncob[14] for n = 3, 4, 5, 6, 7 in $ZnCl_2{\cdot}nH_2O$ revealed an ability of the lower hydrates (n = 3, 4) to dissolve and convert small amounts of the biomass but with no rationalisation of the differences in underpinning features of these systems. An improved fundamental understanding would therefore be an enabler for the selective transformation of varied cellulosic substrates in this IL. The successful conversion of cellulosic substrates such as hemicellulose, algal materials (an upcoming non-terrestrial source of energy), and lignocellulose (the most readily available terrestrial biomaterial), is a key step towards sustainable industrial development,[1,4,15] and the present study addresses this topical issue.

In the present work, we systematically probe the activity associated with given $ZnCl_2{\cdot}nH_2O$ systems‡ in model reactions of purified saccharides, building our understanding, which we ultimately apply to the high yielding selective conversion of lignocellulose and algal biomass. We detail the acid-catalysed transformation of polysaccharides into low molecular weight carbohydrates and furan type molecules in $ZnCl_2{\cdot}nH_2O$ (n = 2.5–4.5).

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Experimental

Materials

Microcrystalline cellulose (MCC), corn starch, low molecular weight sugars, metal chlorides (anhydrous), hydrochloric acid (HCl, 32 wt% aqueous solution), phosphoric acid (H_3PO_4, 85 wt% aqueous solution), sulfuric acid (H_2SO_4, 98 wt% aqueous solution) and *p*-toluenesulfonic acid monohydrate (TsOH) were used as supplied from commercial sources. Lignocellulose (softwood chips and corncob) was sourced from local growers (Australia). The macroalga *Ulva lactuca* was provided as a generous gift by Dr Wayne O'Connor, Department of Primary Industries Fisheries, Port Stephens Fisheries Institute (Australia). The microalga *Porphyridium cruentum* was grown and supplied by Climate Change Cluster (C3), University of Technology Sydney (Australia). Hemicellulose was extracted from corncob by treatment with aqueous NaOH using an optimised method.[16] Polysaccharides from *Ulva lactuca* were obtained following the method described by Mihranyan et al.[17] Dried algal powder (10.00 g) was defatted with repeated extraction with toluene/ethanol (5 × 30 mL, 7:3 v/v) for 24 h with stirring, treated with 4% aqueous NaOH for 2 h at 80 °C, followed by bleaching with 50.0 mL acetate buffer (pH 4.8) containing $NaClO_2$ (0.9 g) at 70 °C for 2 h. The residue was washed repeatedly with water (5 × 30 mL), filtered and dried at room temperature. The dried product was heated to boiling in 1.5% aqueous hydrochloric acid (50 mL) and the resultant slurry was kept overnight at ambient temperature (30 °C), followed by washing with water (5 × 30 mL). The precipitate was filtered and lyophilised to obtain the polysaccharide fraction. Vacuum oven-dried (60 °C, 1 mbar, 12 h) cellulosic materials were used for acid-catalysed reactions. The carbohydrate content of the cellulosic substrates was established by standard analytical procedures: NREL/TP-510-42618[18] for lignocellulose, NREL/TP-5100-60957[19] for algal biomass. The total amount of carbohydrates in the given biomass is specified in ESI Table S1. Zinc chloride hydrate solvents ($ZnCl_2{\cdot}nH_2O$) were prepared by mixing the anhydrous salt[‡] with the appropriate amount of deionised water, resulting in transparent colourless IL.[10]

Chromatography-analysis

Carbohydrates was analysed employing liquid chromatography-mass spectrometry on a Shimadzu LCMS-8060 instrument with electrospray ionisation source in negative ion mode. The separation was performed on a Supelco apHera NH2-Polymer analytical column (150 mm × 4.6 mm, 5 µm) using a mixture of acetonitrile and water (65:35 v/v) as the mobile phase at a flow rate 0.6 mL·min^{-1} and a run time of 18 min. Five transitions *m/z* 149.10 → 89.05 (fragmentor voltage 12 V, collision energy 7 eV; detection of xylose), *m/z* 178.85 → 89.15 (fragmentor voltage 19 V, collision energy 8 eV; detection of glucose and fructose), *m/z* 341.30 → 161.20 (fragmentor voltage 16 V, collision energy 8 eV; detection of cellobiose and cellobiulose), *m/z* 503.35 → 161.20 (fragmentor voltage 24 V, collision energy 13 eV; detection of cellotriose) and *m/z* 665.25 → 503.10 (fragmentor voltage 26 V, collision energy 12 eV; detection of cellotetraose) were monitored. Liquid chromatography analysis of furan type molecules was conducted using an Agilent 1290 LC instrument equipped with an Agilent Zorbax Eclipse XDB–C18 analytical column (150 mm × 4.6 mm, 3 µm) and Agilent 1260 DAD VL+ detector (detection wavelength 278 nm). The mobile phase was a mixture of methanol and water (15:85 v/v) at a flow rate of 1.1 mL·min^{-1} with a run time of 20 min. Quantitative analysis was performed with the use of a standard curve plotted with analytical standards.

pH Measurements

pH Measurements were performed at room temperature (22–23 °C) using a Mettler Toledo pH meter adapted with a standard glass electrode with prior calibration with two buffer solutions (pH = 4.00, pH = 7.00). Measurements were performed in triplicate and the average values are presented.

Acidity readings by the ^{13}C NMR probe method[20]

The binding ability of the various zinc chloride hydrate solvents to mesityl oxide was performed using a ^{13}C NMR method described in the literature.[20] $ZnCl_2{\cdot}nH_2O$ (5.000 g) and mesityl oxide (250 mg to form a 5 wt% solution based on the solvent) were introduced to the round-bottom flask equipped with a magnetic follower and the mixture was agitated at room temperature for 1 h, resulting in a yellowish transparent solution. The solution (0.5 g) was transferred in a 5 mm NMR tube equipped with a coaxial insert containing deuterodimethyl sulfoxide-d_6 (external lock, ^{13}C: δ = 39.7 ppm) and the sample was immediately analysed by NMR spectroscopy (Agilent 500 MHz NMR) at 25 °C.

Dissolution and recovery of cellulose in/from zinc chloride hydrate

MCC (50 mg) and $ZnCl_2{\cdot}nH_2O$ (5.000 g) were introduced to a round-bottom flask equipped with a thermometer and magnetic follower and the mixture was heated and agitated at 80 °C for 2.5 h, resulting in a transparent solution, or a turbid suspension in the case of $ZnCl_2{\cdot}4.5H_2O$. The mixture was diluted with aqueous hydrochloric acid (40.0 mL, 0.01 M aqueous HCl was used to avoid co-precipitation of water-insoluble zinc salts, which commonly form upon dilution with neat water)[8] to regenerate cellulose, which was recovered, washed with deionised water (3 × 25.0 mL), vacuum oven-dried (60 °C, 1 mbar, 12 h) and weighed to determine the conversion of polysaccharide (ESI Table S2). A small amount of the diluted IL (0.25 mL) was neutralised with aqueous sodium bicarbonate (0.75 mL, 1 M), centrifuged (20,000 × g for 10 minutes) to remove water insoluble zinc salts, and decanted. The recovered solution was analysed employing the chromatographic methods given above.

Catalytic conversion of carbohydrates in zinc chloride hydrate

Polysaccharides (MCC, starch, hemicellulose, algal saccharides, 50 mg) and $ZnCl_2{\cdot}nH_2O$ (5.000 g) were introduced to a round-bottom flask equipped with a condenser, thermometer, and magnetic follower and the mixture was heated and agitated at 80 °C for 2.5 h, resulting in a transparent solution, or turbid suspension when $ZnCl_2{\cdot}4.5H_2O$ was used as a solvent. The mixture was heated and stirred at the predetermined temperature for a fixed period of time to promote the catalytic conversion (Table 1). In one instance (Table 1), water (0.71 mL) was added to $ZnCl_2{\cdot}3.0H_2O$ after dissolution of MCC when assessing the role of cellulose solubility in $ZnCl_2{\cdot}4.5H_2O$; this approach permitted the processing of cellulose in $ZnCl_2{\cdot}4.5H_2O$ under homogeneous conditions.[§] In some instances (Tables 3 and 4 only), Brønsted acids (HCl, H_3PO_4, H_2SO_4, or TsOH, 0.03 mmol) or Lewis acids ($AlCl_3$, $InCl_3$, $LaCl_3$, $GdCl_3$, $YbCl_3$ or $HfCl_4$, 0.03 mmol) were

added to the reaction media when investigating the role of added catalyst in the transformations of cellulose in zinc chloride hydrate solvent. After completion, the reaction mixture was cooled and diluted with deionised water (5.00 mL). A small amount of aqueous phase (0.25 mL) was retained for HPLC analysis. Work-up of the aqueous phase before chromatography-analysis included addition of aqueous sodium hydrogen carbonate (0.75 mL, 1 M), followed by centrifugation (20,000 × g for 10 minutes) and decantation. The recovered solutions were diluted with a known volume of deionised water, for analysis. The remaining reaction mixture was diluted with aqueous hydrochloric acid (40.0 mL, 0.01 M) to precipitate the unreacted substrate. The recovered solids were washed with deionised water (3 × 25.0 mL), vacuum oven-dried (60 °C, 1 mbar, 12 h) and weighed to calculate the conversion of substrate specified in the main text. The isolation of furanoid products from the diluted with water zinc chloride hydrate solvent was performed according to reference.[13] The furanoids all gave satisfactory analytical data.[13,21–23]
With low molecular weight sugars, the substrate (cellobiose, glucose, or fructose, 50 mg) and $ZnCl_2 \cdot nH_2O$ (5.000 g) were introduced to a round bottom flask equipped with a condenser, thermometer, and magnetic follower and the mixture was heated and stirred at the predetermined temperature for a fixed period of time. The products were recovered and analysed as detailed above. The conversion of substrates was established by chromatography-analysis.
For the conversion studies, the biomass (75, 75, 122, or 217 mg) corresponding to 50 mg of polysaccharides of corncob, wood chips, *Ulva lactuca*, or *P. cruentum*, respectively, and $ZnCl_2 \cdot 4.25H_2O$ (5.000 g) were introduced to a round bottom flask equipped with a condenser, thermometer, and magnetic follower and the mixture was heated and agitated at 80 °C for 5 h, resulting in a transparent solution, or a turbid suspension in case of wood chips or algal biomass. Hydrochloric acid (0.03 mmol of HCl) was added and the reaction mixture was heated and stirred at 120 °C for a fixed period of time. In some instances, hydrochloric acid (0.03 mmol of HCl) was added from the start of the processing, maintaining the ratio of Zn/H_2O within ±1%. The products were recovered and analysed as specified above to provide the results detailed in the main text.

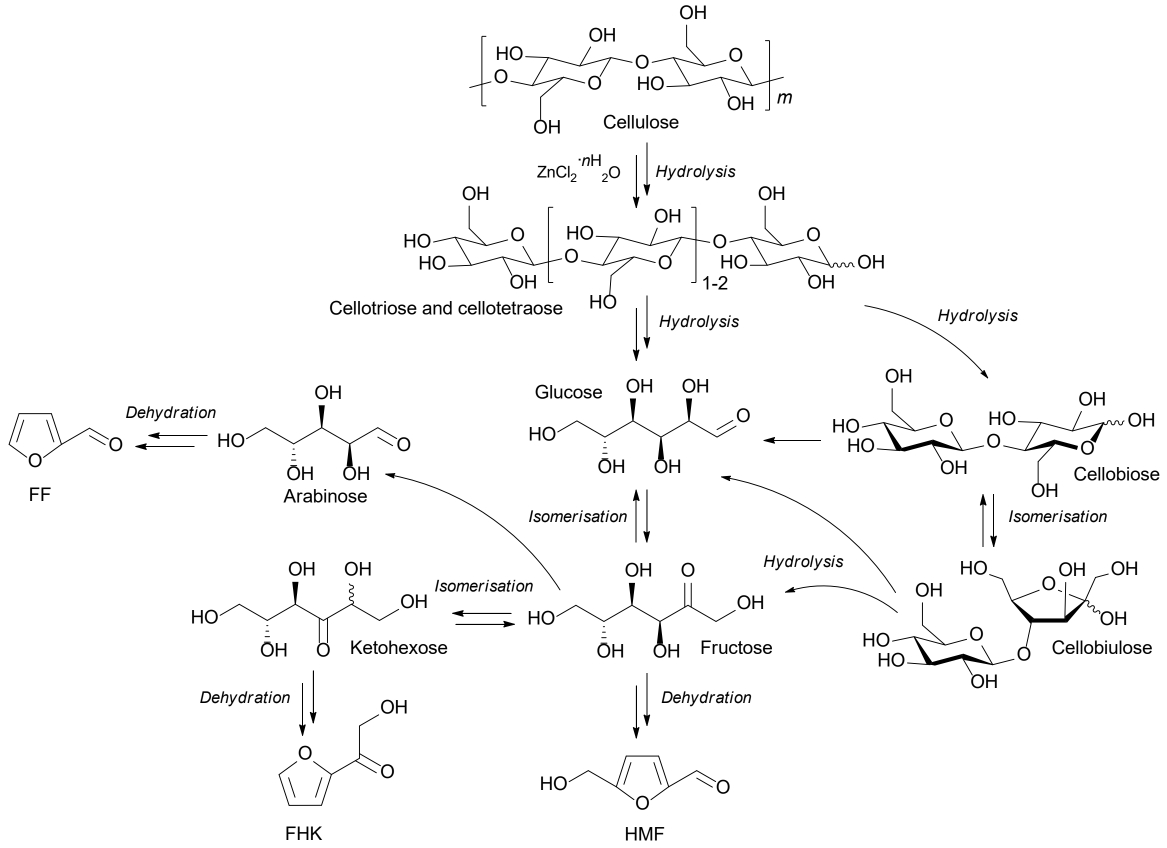
Results and discussion

To understand the role of the molecular formula of $ZnCl_2 \cdot nH_2O$ on the conversion of cellulose, $ZnCl_2 \cdot nH_2O$ with hydration number $n = 2.5–4.5$ was employed under various processing conditions. Firstly, we probed the dissolution of MCC in $ZnCl_2 \cdot 2.5–4.5H_2O$ (1 wt% of MCC, based on solvent, 80 °C, 2.5 h); dissolution is usually considered to be the first step of the conversion of cellulose in aqueous zinc chloride systems.[12,13] All of $ZnCl_2 \cdot 2.5–4.25H_2O$ permitted complete dissolution of MCC, while $ZnCl_2 \cdot 4.5H_2O$ formed a suspension thereof in the IL. Presumably, the most hydrated IL is unable to efficiently disrupt the extensive hydrogen bonding that characterises the macromolecular structure of cellulose, similar to water or to common organic solvents.[1,4,7] Note that this suspension became a homogeneous solution under our reaction conditions of 120 °C (see text below and Table 1). Regeneration of the dissolved cellulose from ILs by precipitation with 0.01 M aqueous hydrochloric acid, washing, and drying, revealed the extent to which the polysaccharide transforms in ionic media (ESI Table S2). There is no significant change of the mass with the cellulose regenerated from $ZnCl_2 \cdot 3.5–4.5H_2O$ (i.e. the weight of the loaded and recovered cellulose from the ILs was similar), implying that the substrate is stable to hydrolysis in such media under the applied conditions. In contrast, $ZnCl_2 \cdot 2.5–3.25H_2O$ initiates the conversion of cellulose during the dissolution, as evidenced by some mass losses (ESI Table S2). Possibly, the systems with lower hydration number possesses higher acidity, and therefore promote conversion of cellulose into water-soluble molecules. Analysis of the neutralised aqueous phases recovered from the zinc salts (as detailed above) identified only trace amounts of water-soluble saccharides (we detect mono-, di-, tri-, and tetrasaccharides) and furan derivatives (HMF, FHK, and FF). This suggests that cellulose likely converts into higher oligosaccharides (e.g., with five or six glucose units) under our conditions, a matter we are currently investigating. The dissolution and regeneration of MCC in/from $ZnCl_2 \cdot 2.5–4.5H_2O$ demonstrate that these media have differing influences on the cellulose, and it can be reasonably anticipated that this will affect the acid-catalysed transformation of polysaccharides at elevated temperatures.
To test this proposal, we dissolved MCC in $ZnCl_2 \cdot 2.5–4.5H_2O$ (80 °C, 2.5 h) and then attempted the hydrolysis-conversion of cellulose at 120 °C for 1 h. Table 1 shows that less hydrated solvents, in particular $ZnCl_2 \cdot 2.5–3.0H_2O$, yielded predominantly furan derivatives, namely HMF, FHK, and FF (total yield up to 30 mol% based on anhydroglucose units present in cellulose), and only trace amounts of low molecular weight saccharides. The chemistry using MCC in $ZnCl_2 \cdot 3.0H_2O$ was repeated but employing highly purified doubly sublimed zinc chloride. A similar portfolio of products appeared, in which the total yield of furans was slightly lower (Table 1) but the results were otherwise unsurprising.[‡] Furan derivatives are considered to form by a cascade of acid-catalysed reactions, involving the *hydrolysis* of cellulose into glucose, aldose-ketose *isomerisation*, and *dehydration*, respectively, as pictorially represented in Scheme 1.[4,5,13,22,25] HMF is an anticipated dehydration product, while FHK and FF are less commonly obtained as major transformation products of carbohydrates.[4,13,22]
In our former study, the occurrence of FHK was attributed to the formation of the intermediate ketohexose (*isomerisation* product derived from fructose); FF was proposed to form from fructose via an intermediate pentose (e.g., arabinose).[13] In the present work, we identified that cellobiose, glucose, and fructose, which putatively appear during the conversion of cellulose (Scheme 1), fully convert into furanoids and humins[24] in $ZnCl_2 \cdot 2.5H_2O$ under the reaction conditions (120 °C, 1 h, total yield of furanoids up to 16 mol%, based on sugar substrate). This result evidences that low molecular weight saccharides are unstable in less hydrated solvents ($ZnCl_2 \cdot 2.5–3.0H_2O$), which mediate both the transformation of cellulose into furan derivatives and into by-product humins. In contrast, zinc chloride presented as higher hydrates, namely, $ZnCl_2 \cdot 3.25–4.5H_2O$, demonstrates improved conversion and selectivity towards HMF (the anticipated *dehydration* product) and low molecular weight carbohydrates (as *hydrolysis* products, namely, glucose, cellobiose, cellotriose, and

Table 1 Catalytic conversion of cellulose in $ZnCl_2\cdot nH_2O$ [a]

Solvent-catalyst	Conv (wt%)	Yield glucose (wt%)	Yield fructose (wt%)	Yield cellobiose (wt%)	Yield cellobiulose (wt%)	Yield cellotriose (wt%)	Yield cellotetraose (wt%)	Yield HMF (mol%)	Yield FHK (mol%)	Yield FF (mol%)
$ZnCl_2\cdot 2.5H_2O$	86	0	0	0	0	0	0	7	10	8
$ZnCl_2\cdot 2.75H_2O$	95	1	1	0	0	0	0	14	9	7
$ZnCl_2\cdot 3.0H_2O$	98 (97)[b]	1 (1)[b]	1 (0)[b]	0 (0)[b]	0 (0)[b]	0 (0)[b]	0 (0)[b]	15 (12)[b]	7 (4)[b]	6 (9)[b]
$ZnCl_2\cdot 3.25H_2O$	99	5	3	1	1	0	0	19	7	5
$ZnCl_2\cdot 3.5H_2O$	99	7	4	1	1	0	0	20	7	5
$ZnCl_2\cdot 3.75H_2O$	99	7	4	1	1	0	0	20	6	4
$ZnCl_2\cdot 4.0H_2O$	99	18	8	3	2	2	1	20	6	3
$ZnCl_2\cdot 4.25H_2O$	99	19	9	4	2	3	1	21	5	3
$ZnCl_2\cdot 4.5H_2O$	94 (99)[c]	21 (10)[c]	10 (1)[c]	7 (6)[c]	4 (1)[c]	5 (4)[c]	1 (6)[c]	16 (14)[c]	5 (5)[c]	2 (3)[c]

[a] Conversion is specified in wt% based on cellulose input. Yields are specified in wt% based on cellulose input for carbohydrates and in mol% based on anhydroglucose units present in the substrate for furan derivatives (HMF, FHK, and FF). Reaction conditions: MCC (50 mg), solvent-catalyst (5.000 g), 80 °C, 2.5 h, then 120 °C, 1 h. [b] The processing was performed in the IL prepared from the double sublimed $ZnCl_2$.‡ [c] Reaction conditions: MCC (50 mg), $ZnCl_2\cdot 3.0H_2O$ (5.000 g), 80 °C, 2.5 h, addition of water (0.71 mL) to form $ZnCl_2\cdot 4.5H_2O$, then 120 °C, 1 h.



Scheme 1 Proposed acid-catalysed cascade of cellulose conversion into small molecules. *n* = 2.5–4.5. *m* = integer.

cellotetraose, and *isomerisation* products, namely, fructose and cellobiulose). Usefully, only small amounts of humins were noted. The yields of HMF (yield up to 21 mol%) and low molecular weight saccharides (total yield up to 48 wt% based on cellulose input) improve with increasing hydration number; however, HMF yield decreased with the most highly hydrated solvent ($ZnCl_2\cdot4.5H_2O$, Table 1). It is reasonable to posit that the dissolution of cellulose is the rate limiting step before the acid-catalysed transformations, and thus the overall conversion towards HMF is lower in $ZnCl_2\cdot4.5H_2O$ (recall that cellulose is less soluble in this IL, as discussed above, but dissolves at the reaction temperature). To assess whether solubility played a significant role, cellulose was dissolved in $ZnCl_2\cdot3.0H_2O$ (80 °C, 2.5 h), after which the reaction medium was diluted with water to form $ZnCl_2\cdot4.5H_2O$ and processed at 120 °C for 1 h under homogeneous conditions (Table 1).§ While there was some variability in the accumulation of low molecular weight saccharides under these conditions, yields and ratios of the furanoid products were essentially identical to the principal reaction directly employing $ZnCl_2\cdot4.5H_2O$. We also identified trace amounts of other oligosaccharides, likely to be the *isomerisation* products derived from cellotriose and cellotetraose (ESI Fig. S1). Model reactions with cellobiose as a substrate confirmed the conversion thereof into cellobiulose and glucose in 23% and 4% yield, respectively, in $ZnCl_2\cdot4.25H_2O$, when mild reaction conditions are employed (80 °C, 2h). This confirms that *isomerisation* can take place in zinc chloride hydrates at earlier stages of the catalytic cascade involving reducing oligosaccharides (Scheme 1). The isomerisation of aldo-oligosaccharides into keto-oligosaccharides has been identified in subcritical aqueous ethanol.[26,27]

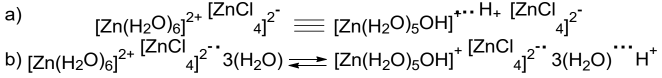
Table 2. The probe of acidity of neat $ZnCl_2\cdot nH_2O$

Solvent / Acid	pH [a]	$\Delta\delta$ [b]
$ZnCl_2\cdot2.5H_2O$	–0.5	44.7
$ZnCl_2\cdot2.75H_2O$	–0.4	43.7
$ZnCl_2\cdot3.0H_2O$	–0.2	42.7 (43.0)[c]
$ZnCl_2\cdot3.25H_2O$	0.0	41.9
$ZnCl_2\cdot3.5H_2O$	0.3	41.1
$ZnCl_2\cdot3.75H_2O$	0.5	40.4
$ZnCl_2\cdot4.0H_2O$	0.7	39.7
$ZnCl_2\cdot4.25H_2O$	0.9	39.1
$ZnCl_2\cdot4.5H_2O$	1.1	38.6
HCl (37 wt%)	–1.1[27]	–
H_2SO_4 (10 wt%)	–	37.6[32]

[a] pH readings were performed in triplicate at room temperature. [b] Difference between the chemical shifts of α and β carbons of mesityl oxide (5 wt% based on IL) in $ZnCl_2\cdot nH_2O$ (0.5 g) with external lock DMSO-d_6 at 25 °C. [c] $\Delta\delta$ of $ZnCl_2\cdot3.0H_2O$ prepared from the double-sublimed anhydrous $ZnCl_2$‡

Evidently, the level of hydration plays a determinative role in the catalyst activity, most likely related to the acidity of the system. pH measurements§§ of $ZnCl_2\cdot nH_2O$ (Table 2) reveal the dramatic extent to which the molecular formula influences the acidity of the zinc chloride hydrate solvent system, and the very high acidity associated with lower hydration states. Table 2 shows a systematic decrease of acid strength from less hydrated (n = 2.5) media to more highly hydrated (n = 4.5) solvents. $ZnCl_2$ is commonly considered to be a Lewis acid, but clearly the hydrated form becomes a source of Brønsted acidity comparable to concentrated protic acids (e.g., the reported pH of 37 wt% aqueous HCl is –1.1).[28] This phenomenon is caused by Lewis acid assisted Brønsted acidity through binding of the metal centre to water and release of hydrogen cation.[25,29,30] We also probed the binding ability of zinc chloride hydrates with mesityl oxide using ^{13}C NMR spectroscopy to provide a deeper insight into the acidity of inorganic solvents.[20] Acids are known to form complexes with α,β-unsaturated carbonyl compounds, whose binding strength correlates to a difference between the chemical shifts of the α and β carbons ($\Delta\delta$), thereby providing a measure of acidity: the greater the $\Delta\delta$ value, the stronger the binding between the acid and the mesityl oxide and cooorespondingly the stronger the acid.[20,31,32] The $\Delta\delta$ values for $ZnCl_2\cdot2.5$–$4.5H_2O$ are equivalent to those of strong Brønsted acids (Table 2),[20,32] and there is a perfect correlation between pH and the $\Delta\delta$ values. The values obtained for $ZnCl_2\cdot3.0H_2O$ prepared from the anhydrous salt and separately from the double sublimed salt showed only marginal differences in $\Delta\delta$ values, implying that any residual impurities from the manufacturing process (e.g. HCl) play little or no role in this chemistry.‡ These data help to rationalise the experimental observations in the catalysed reactions of the saccharides.

The changes in acidity are most likely affected by the structure of ILs. It has been established that $ZnCl_2\cdot nH_2O$ comprises a hydrated zinc cation and a tetrachlorozincate anion, as pictorially presented in Scheme 2.[9,10,33] When n = 2–3, the hydrated water is present only in the inner coordination shell of zinc cation. With these entities, hydrogen cation H^+ is directly sourced from the metal aquo complex, accounting for the impressive acid strength (Table 2). With higher hydrates (n = 3.25–4.5), there is water present in excess of the inner coordination sphere, and available to hydrate the H^+ into the less active H_3O^+ cation or even more highly hydrated species.[34,35] This hydration effect is known to suppress the Brønsted acid activity,[35] and is consistent with our experimental results. The higher acidity with lower levels of water present would be consistent with the notion of a less well hydrated hydrogen cation. Nevertheless, discrete species of hydrated H^+ such as $H_{13}O_6^+$ may not exist within these concentrated ionic solvents, unlike in dilute aqueous solutions.[34,35] H^+ is presumably delocalised between the water molecules in the outer coordination sphere, remaining a part of the ionic system.



$$\text{a)}\ [Zn(H_2O)_6]^{2+}[ZnCl_4]^{2-} \equiv [Zn(H_2O)_5OH]^{+}\cdots H^{+}[ZnCl_4]^{2-}$$

$$\text{b)}\ [Zn(H_2O)_6]^{2+}[ZnCl_4]^{2-}\cdot 3(H_2O) \rightleftharpoons [Zn(H_2O)_5OH]^{+}[ZnCl_4]^{2-}\cdot 3(H_2O)\cdots H^{+}$$

Scheme 2. Proposed formation of hydrogen cation from zinc chloride hydrate. a) Hydrogen ion generation in the presence of a 'proton' acceptor. b) Sample provision of hydrated hydrogen ion for *n* = 4.5.

In the present context, the $ZnCl_2{\cdot}nH_2O$ fulfils two roles. In the first, it acts as ionic liquid solvent for the cellulose. As is evident from the results presented above, some embodiments of $ZnCl_2{\cdot}nH_2O$ are less good than others, as solvents for cellulose (e.g. $ZnCl_2{\cdot}4.5H_2O$). The second role is the provision of an acid catalyst to cause the hydrolyisis of cellulose into low molecular weight saccharides and their further reaction into furanoid products. While the exact nature of the catalyst remains to be established, we have unambiguously established that the $ZnCl_2{\cdot}nH_2O$ provides acidity in differing degrees. Now with reference to the synthesis results and the acidity measurements (Tables 1 and 2), there are distinct experimental outcomes associated with the different reaction media. The high acidity of the less hydrated media (e.g., $ZnCl_2{\cdot}2.5H_2O$) leads the conversion of cellulose towards furan-type molecules but also promotes the production of large amounts of humins. In contrast, more highly hydrated ILs (e.g., $ZnCl_2{\cdot}4.0$–$4.5H_2O$) possess good activity for the hydrolysis-conversion into low molecular weight saccharides (glucose, fructose, cellobiose, cellobiulose, cellotriose, and cellotetraose) and HMF, avoiding the formation of humins.

Of the systems investigated, $ZnCl_2{\cdot}4.25H_2O$ is capable of dissolving cellulose *and* providing high yields of low molecular weight carbohydrates and HMF (Tables 1, S2). Accordingly, we conducted the hydrolytic processing of MCC in $ZnCl_2{\cdot}4.25H_2O$ under various reaction parameters. Firstly, the influence of the reaction temperature and time was surveyed. At 100 °C (Fig. 1a), reaction of MCC favours formation of cellotriose and cellotetraose (yields up to 13 wt% and 20 wt%, respectively) up to 160 min, but at 200 min disaccharides (cellobiose and cellobiulose, 9 wt% and 8 wt% yields, respectively), monosaccharides (glucose and fructose, 22 wt% and 9 wt% yield, respectively) and furanoids (HMF, FHK and FF, yields 15, 5 and 1 mol%, respectively) predominate. This suite of products perfectly exemplifies the acid-catalysed cascade of reaction portrayed in Scheme 1, namely *hydrolysis* of cellulose into low molecular weight glucans, aldose-ketose *isomerisation*, and *dehydration* into furan derivatives. It is evident (Fig. 1) that higher reaction temperatures accelerate the catalytic transformations leading to the rapid formation of monosaccharides (glucose and fructose yields up to 33 wt% and 15 wt%, respectively, 120 °C, 40 min) and ultimately dehydration products (HMF, FHK and FF, yields up 21, 5 and 3 mol%, respectively, 120 °C, 60 min) in shorter reaction times (Fig. 1b,c). However, extended reaction at elevated temperatures resulted in the formation of humins, diminishing the yields and selectivity of the target products. From these results, it can be concluded that shorter reaction times are preferred at elevated temperatures to ensure high yields of glucose and HMF (these molecules are commonly desirable products of the cellulose valorisation),[2,4,5] and minimal formation of humins.

Under certain conditions the addition of acids, usually hydrochloric acid, to zinc chloride hydrate improves the yields of saccharides or HMF,[11,12,36] although sulfated titania has been used to good effect in the depolymerisation of cellulose.[37] The added HCl would produce a system akin to Lucas's reagent.[38] To investigate whether this would equally apply to our circumstances, we employed a range of Brønsted acids (hydrochloric, phosphoric, sulfuric or *p*-toluenesulfonic acid) and Lewis acidic metal chlorides ($AlCl_3$, $InCl_3$, $LaCl_3$, $GdCl_3$, $YbCl_3$ or $HfCl_4$) in the hydrolytic processing of MCC in $ZnCl_2{\cdot}4.25H_2O$ at 120 °C for 1 h. The addition of Brønsted acids substantially improves yields of carbohydrates and provides more complete hydrolysis of cellulose into the monomer glucose (Table 3).

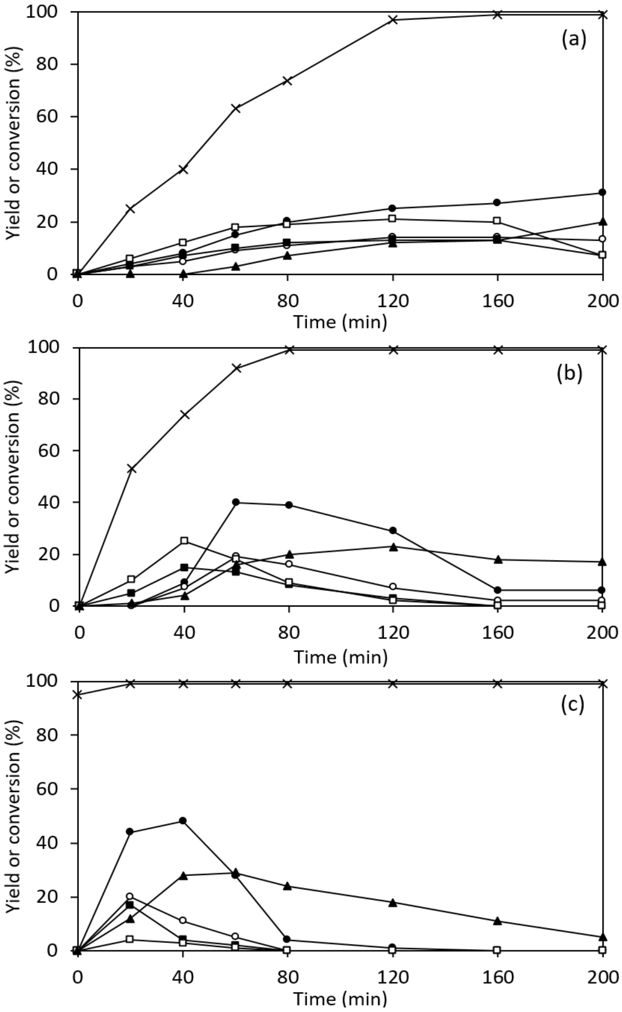


Fig. 1. Catalytic conversion of carbohydrates in $ZnCl_2{\cdot}4.25H_2O$ at various reaction conditions. a), b), c) T = 100, 110, 120 °C, respectively. Reaction conditions: MCC (50 mg), $ZnCl_2{\cdot}4.25H_2O$ (5.000 g). × = conversion. ● = yield of monosaccharides. ○ = yield of disaccharides. ■ = yield of cellotriose. □ = yield of cellotetraose. ▲ = yield of furanoids.

This is consistent with the general view that Brønsted acids promote the hydrolysis of polysaccharides.[4] With Brønsted acids, HMF remains the major furanoid product but the yield of this molecule reduces dramatically for reactions involving H_3PO_4 or, H_2SO_4. A drawback of H_3PO_4 and H_2SO_4 is the formation of insoluble salts in the reaction media, representing a potential hurdle if the recovery of the molten salt is considered. When Lewis acids were added, the reactions afforded lower yields of low molecular weight small

Table 3 Catalytic conversion of cellulose in $ZnCl_2 \cdot 4.25H_2O$ in the presence of additional Brønsted or Lewis acids[a]

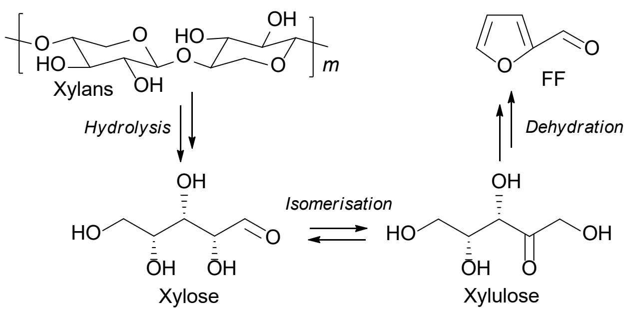
Co-catalyst	Conv (wt%)	Yield glucose (wt%)	Yield fructose (wt%)	Yield cellobiose (wt%)	Yield cellobiulose (wt%)	Yield cellotriose (wt%)	Yield cellotetraose (wt%)	Yield HMF (mol%)	Yield FHK (mol%)	Yield FF (mol%)
none	99	19	9	4	2	3	1	21	5	3
HCl	99	50	2	1	0	1	1	23	0	2
H_3PO_4	99	57	0	0	0	0	0	14	0	2
H_2SO_4	99	58	0	0	0	0	0	7	0	2
TsOH	99	30	2	1	0	1	0	22	1	3
$AlCl_3$	97	3	2	0	0	0	0	12	0	2
$InCl_3$	94	4	0	0	0	0	0	15	3	4
$LaCl_3$	95	7	0	2	1	4	1	15	4	3
$GdCl_3$	94	6	0	0	0	3	0	14	4	3
$YbCl_3$	93	8	0	2	1	5	1	13	5	3
$HfCl_4$	99	1	0	0	0	0	0	2	0	0

[a] Yields are specified in wt% based on input of cellulose for carbohydrates and in mol% based on anhydroglucose units present in the substrate for furan derivatives (HMF, FHK, and FF). Reaction conditions: MCC (50 mg), $ZnCl_2 \cdot 4.25H_2O$ (5.000 g), 80 °C, 2.5 h, then addition of acid co-catalyst (0.03 mmol), 120 °C, 1 h, maintaining the ratio of Zn/H_2O within ±1%.

saccharides and furan type molecules. The metal chlorides presumably coordinated to the excess of water in the outer coordination shell of zinc chloride hydrate, reducing the effective amount of free water present. This would tend to induce a strongly acidic environment, as shown in Table 1 for the less hydrated zinc chloride hydrate solvents, which is conducive to the formation of humins. Hard Lewis acids ($AlCl_3$, $InCl_3$, and $HfCl_4$), which are more likely to bind strongly to the 'hard' Lewis base O atom of H_2O, or to hydrolyse to [M]-OH + HCl, afforded very low yields of valuable molecules.[39,40] This effect is less prominent with soft Lewis acids ($LaCl_3$, $GdCl_3$, $YbCl_4$), even though the yields of desirable products were lower. Both sets of observations are consistent with the notion of Lewis acid-assisted Brønsted acidity,[29,30,41–43] which these Lewis acids would introduce (in the form of $[MX_3—OH]\cdots H$) in addition to existing effects contributed by the zinc chloride hydrate system. Such Lewis acid-assisted Brønsted acids have been demonstrated to possess very high acidity in some instances.[25,42] Overall, the conversion of cellulose in the presence of HCl is more efficient, compared to the processes with other added catalysts or in the neat inorganic solvent. Therefore, the conversion in $ZnCl_2 \cdot 4.25H_2O$ with added HCl remains the best process to this stage (Table 3).

We turned our attention to the conversion of other substrates, including starch, hemicellulose, and polysaccharides extracted from the macroalga *Ulva lactuca* in $ZnCl_2 \cdot 4.25H_2O$ + HCl (Table 4). These polysaccharides are fully soluble in the molten salt hydrate (no added HCl) at lower temperature (80 °C). Once dissolved, the HCl is added and the temperature raised to 120 °C. The $ZnCl_2 \cdot 4.25H_2O$ + HCl system is capable of converting the various polysaccharides into monomer sugars and furan derivatives. Other products, such as oligosaccharides, fructose, or FHK, were identified in trace amounts only. While the conversion of starch and algal saccharides, consisting of glucans (ESI Table S1), delivered somewhat similar portfolios of products to that obtained from MCC (Table 4, entries 1–3), the transformation of hemicellulose (Table 4, entry 4) provided mostly the dehydration product FF (28 wt%) and a little xylose (5 wt%). This suggests that xylans, a major component of hemicellulose,[15] are more amenable to conversion into furfural, relative to glucans. The transformation of xylans occurs through *hydrolysis* into xylose, xylose-xylulose *isomerisation* and then *dehydration* into FF, as demonstrated in Scheme 3.[44] Pleasingly, FF can be obtained in impressive yields when performing the catalytic reaction in the biphasic solvent system $ZnCl_2 \cdot 2.5H_2O$/anisole[13] (Table 4, entry 5, FF 52 wt% yield; as shown above in Table 1, this solvent system afforded good selectivity to furfural during the transformation of cellulose). The given outcomes evidence that the functionality of zinc chloride hydrate solvent can be tuned to promote the conversion of target substrate into a defined product.

Finally, we probed the transformation of lignocellulose and algal biomass in zinc chloride solvent. To do this, we conducted the dissolution of biomass in $ZnCl_2 \cdot 4.25H_2O$ under mild conditions (80 °C, 5 h), followed by the catalytic conversion of the substrates at elevated temperature (120 °C, 1 h) with added hydrochloric acid (Table 4). The dissolution of the biomass required extended times compared with the purified saccharides. Even after lengthy processing under mild conditions, softwood and algal biomass remained insoluble. Apparently, the rigid molecular structure of the native biomass resists complete dissolution in zinc chloride hydrate solvent, in contrast to refined saccharides.[45] This solubility issue likely affected the processing at elevated temperature affording low yields of glucose from the given substrates (Table 4, entries 5, 7, 9, 11). A method to overcome this hurdle is to add hydrochloric acid from the start, at low temperature. This approach substantially improved the conversion of corncob and algal substrates into glucose (yields up to 61 wt%, based on the glucan content in the biomass), HMF (up to 35 mol% yield, based on glucan content in the biomass) and FF (up to 29 wt% yield, based on total carbohydrate in the biomass). The processing of wood chips was less efficient, compared to other cellulosic materials, likely due to the more recalcitrant molecular structure and concomitant difficulties during depolymerisation (Table 4, entries 7, 8). Wood biomass remains one of the most challenging substrates for chemical processing.[4,45] Nonetheless, it is worth mentioning that processing of lignocellulose in zinc chloride hydrate enabled the recovery of lignin (so-called acid insoluble lignin) as an unreacted portion of substrate (ESI Fig. S2 and Table S3). This macromolecule is known to be somewhat stable in zinc chloride solvent,[46,47] and is another raw material holding promise to deliver a range of useful bio-based chemicals.[2,48] This set of reactions presents an efficient transformation of native cellulosic materials directly into glucose, HMF and FF, together with the simultaneous extraction of lignin.



Scheme 3. Proposed acid-catalysed transformation of xylans into furfural in zinc chloride hydrate. *m* = integer.

Table 4. Catalytic conversion of polysaccharides in zinc chloride hydrate solvent[a]

Entry	Substrate	Conv (wt%)	Yield glucose (wt%)	Yield HMF (mol%)	Yield FF (wt%)
1	MCC	99	50	23	1
2	Starch	99	46	21	2
3	*Ulva lactuca* saccharides	99	55	18	8
4	Hemicellulose	99	–	–	28
5[b]		99	–	–	52
6	Corncob	81	26	23	15
7[c]		85	61	30	22
8	Softwood chips	70	22	18	10
9[c]		74	26	22	11
10	*Ulva lactuca*	85	38	22	10
11[c]		90	52	25	15
12	*P. cruentum*	88	13	33	11
13[c]		94	49	35	29

[a] Conversion is specified in wt% based on substrate input. Yields are specified in wt% for carbohydrates, based on glucan content in the substrate, and in mol% for HMF, based on anhydroglucose units present. Yields are specified in wt% for FF, based on the total carbohydrate content in substrate because both glucans and xylans are convertible into FF. Reaction conditions: polysaccharide (50 mg), solvent-catalyst (5.000 g), 80 °C, 5 h, then addition of HCl (0.03 mmol) 120 °C, 1 h, maintaining the ratio of Zn/H_2O within ±1%. [b] Reaction conditions: hemicellulose (50 mg), solvent-catalyst (5.000 g), 80 °C, 2.5 h, then addition of anisole (40.0 mL), 120 °C, 1 h.[13] [c] Reaction conditions: polysaccharide (50 mg), solvent-catalyst (5.000 g), HCl (0.03 mmol), 80 °C, 5 h, then 120 °C, 1 h.

Conclusions

The present work provides an improved understanding of $ZnCl_2{\cdot}nH_2O$ (n = 2.5–4.5) as reaction media for the catalytic transformation of cellulosic substrates into value added products. The molecular formula for the IL solvent is critical to determining the acidity of the mixture, which has a defining role on the outcomes of the transformations. It shows that the amount of water present in inorganic molten salt and the processing conditions significantly influence the course of catalytic reactions enabling selectivity towards furyl hydroxymethyl ketone and furfural, or 5-(hydroxymethyl)furfural and low molecular weight reducing saccharides. The optimised methods enable the direct processing of lignocellulose and algal biomass into significantly value added chemicals under mild processing conditions and in high yields. This work improves our fundamental knowledge of the $ZnCl_2{\cdot}nH_2O$ system but there remain some fundamental questions to be answered before firm conclusions about the causality within the system can be fully ascribed. There also remain technical problems to be solved. One in particular is the efficient recovery of ionic liquids and products, which represents a challenge to be solved before practical application of the methods. If this challenge can be overcome, then substantial industrial progress will potentially have been made.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ The authors of the work cited in reference 9 used highly purified sublimed $ZnCl_2$ when determining the structure of zinc chloride

trihydrate to be $[Zn(OH_2)_6][ZnCl_4]$. The same authors employed dried anhydrous $ZnCl_2$ without sublimation to assess the solubility of cellulose at 25 °C in zinc chloride hydrate (reference 10). No specific rationale is provided in either case. Accordingly, we followed the method described in reference 10 to prepare the zinc chloride hydrate ionic liquids, employing dried anhydrous $ZnCl_2$ without prior sublimation as a practical approach to our work. Nevertheless, we used double-sublimed $ZnCl_2$ in selected instances for comparative purposes, as indicated in the main text and Table 1.

[§] Cellulose fully dissolves in $ZnCl_2{\cdot}3.0H_2O$ and remains soluble after dilution with water to a net of $n = 9$.[10]

[§§] pH measurements in concentrated systems are workable in both concentrated alkaline[49] and acidic media,[50] but subject to error, requiring corrections if accurate data are sought. Our pH measurements provide qualitative uncorrected data, supplemented by quantitative data using the mesityl oxide probe as determined by NMR spectrometry.

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