The effect of the ionic liquid anion in the pretreatment of pine wood chips†

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The effect of the anion of ionic liquids on air-dried pine (*Pinus radiata*) has been investigated. All ionic liquids used in this study contained the 1-butyl-3-methylimidazolium cation; the anions were trifluoromethanesulfonate, methylsulfate, dimethylphosphate, dicyanamide, chloride and acetate. Using a protocol for assessing the ability to swell small wood blocks (10 × 10 × 5 mm), it was shown that the anion has a profound impact on the ability to promote both swelling and dissolution of biomass. Time course studies showed that viscosity, temperature and water content were also important parameters influencing the swelling process. We used Kamlet–Taft parameters to quantify the solvent polarity of the ionic liquids and found that the anion basicity described by the parameter β correlated with the ability to expand and dissolve pine lignocellulose. It is shown that 1-butyl-3-methylimidazolium dicyanamide dissolves neither cellulose nor lignocellulosic material.

Introduction

Lignocellulosic biomass has been identified as a suitable feedstock for future large-scale biorefineries.[1] Lignocellulose is widely distributed and can be grown and harvested on a billion ton scale.[2] Fuels and materials derived from biomass are potentially "carbon-neutral" or can even help to sequester carbon dioxide. The production cost of lignocellulosic biomass is less than for starch-based substrates, but more extensive pretreatment is required in order to release the carbohydrates and other components from the resistant cell wall matrix, adding significantly to process complexity and overall costs. Once released from the lignocellulose complex, the carbohydrates can be fermented to liquid fuels or chemicals. Several pretreatment options have been developed.[3] None is currently able to provide the optimal economic and environmental performance.[4]

Recently, attention has been drawn towards the application of ionic liquids in lignocellulose processing.[5,6] Ionic liquids are salts that are liquid at or near room temperature. Liquid salts have negligible vapour pressure under ambient conditions and are usually non-flammable. By modification of the cations and/or anions an enormous range of potential ionic liquids is possible, encompassing a wide variety of solvent properties. Treatment of lignocellulose with certain ionic liquids results in enhanced glucose yields.

Lignocellulose is a complex composite of polymeric carbohydrates (cellulose and hemicelluloses) and lignin. Cellulose is the most abundant component, consisting of 1→4-β linked glucopyranose. Only a few solvents are able to dissolve this crystalline polymer, such as *N*-methylmorpholine-*N*-oxide (NMO)[7] or concentrated phosphoric acid.[8] However, recently a range of ionic liquids based on the imidazolium cation have been shown to be effective cellulose solvents,[9–14] yielding clear viscous solutions of cellulose. The dissolved cellulose can subsequently be precipitated by adding water or protic organic solvents such as ethanol.[9] The crystallinity of the regenerated cellulose is reduced, which significantly accelerates subsequent hydrolysis with cellulases.[15]

The interaction of solvents with solutes can be described by empirical polarity scales. One has been devised by Kamlet and Taft with three polarity parameters. These quantify the general dipolarisability (π^*), the hydrogen bond acidity (α) and the hydrogen bond basicity (β). The methodology has been successfully applied to characterise molecular solvents[16–19] as well as ionic liquids.[20] It is possible to correlate Kamlet–Taft parameters with the rates of chemical reactions, *e.g.* in nucleophilic substitutions[21–23] and esterifications.[24]

It has been observed that for ionic liquids, the anion has an impact on the ability to dissolve cellulose.[9] NMR studies on ionic liquids that dissolved glucose and cellobiose showed that the anion strongly coordinates to the carbohydrates' hydroxyl groups.[25]

After initial studies focused on ionic liquids containing chloride as anion,[9] Fukaya *et al.* found cellulose solubility in other 1,3-dialkylimidazolium ionic liquids that contained anions such as formate,[11] acetate, phosphate or phosphonate anions,[12] and the concomitant measurement of Kamlet–Taft parameters confirmed that these ionic liquids are characterised by a high β parameter.

Ionic liquids have also been used to dissolve lignocellulosic material. So far, most literature reports only used ground or milled lignocellulose. The partial dissolution of wood shavings in 1-butyl-3-methylimidazolium chloride {[C_4C_1im]Cl} was first described by Rogers and co-workers,[5] with the dissolution of wood sawdust and thermomechanical wood pulp in 1-butyl-3-methylimidazolium chloride and in 1-allyl-3-methylimidazolium

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Table 1 Ionic liquids used in this study and their Kamlet–Taft parameters. Values with standard deviation were measured in triplicate. Measurements were taken at 25 °C unless stated otherwise.

Ionic liquid	Abbreviation	α	β	π^*
1-Butyl-3-methylimidazolium trifluoromethanesulfonate	$[C_4C_1im][OTf]$	0.634 (0.008)	0.483 (0.008)	0.974 (0.002)
	$[C_4C_1im][OTf]$	0.63[20]	0.46[20]	1.01[20]
1-Butyl-3-methylimidazolium dicyanamide	$[C_4C_1im][N(CN)_2]$	0.543 (0.002)	0.596 (0.004)	1.052 (0.003)
1-Butyl-3-methylimidazolium methylsulfate	$[C_4C_1im][MeSO_4]$	0.545 (0.006)	0.672 (0.009)	1.046 (0.002)
1-Butyl-3-methylimidazolium chloride	$[C_4C_1im]Cl$, 75 °C	0.49	0.83	1.03
	$[C_4C_1im]Cl$	0.44[11]	0.84[11]	1.14[11]
1-Butyl-3-methylimidazolium dimethylphosphate	$[C_4C_1im][Me_2PO_4]$	0.452 (0.003)	1.118 (0.012)	0.970 (0.006)
	$[C_4C_1im][Me_2PO_4]$, wet, 8 wt%	0.44	1.00	0.97
1-Ethyl-3-methylimidazolium dimethylphosphate	$[C_2C_1im][Me_2PO_4]$	0.51[12]	1.00[12]	1.06[12]
1-Butyl-3-methylimidazolium acetate	$[C_4C_1im][MeCO_2]$	0.470 (0.012)	1.201 (0.017)	0.971 (0.007)
	$[C_4C_1im][MeCO_2]$	0.43[29]	1.05[29]	1.04[29]

chloride being reported shortly afterwards.[6] Lee *et al.* reported partial delignification of 5 wt% maple wood flour with 1-ethyl-3-methylimidazolium acetate {$[C_2C_1im][MeCO_2]$},[26] while the observed wood solubility was very low (less than 0.5%). An attempt was made to link solvent properties of 1,3-dialkylimidazolium ionic liquids with the impact on lignocellulose, *e.g.* the extraction of lignin with the Hildebrand solubility parameter. Wood flour solubility was compared with β parameters taken from the literature. A clear correlation could not be confirmed due to lack of data. In contrast, Sun *et al.* were able to observe almost complete dissolution of 5 wt% southern yellow pine and red oak particles in $[C_2C_1im][MeCO_2]$.[27] The wood could be fractionated into a carbohydrate-rich fraction with reduced lignin content (75% of original lignin content) and pure lignin after the treatment. When catalytic amounts of acid were added to 1-butyl-3-methylimidazolium chloride {$[C_4C_1im]Cl$} the carbohydrates were hydrolysed to oligomers and monomers.[28] The sugars were partially transformed to degradation products such as furfurals, while the insoluble fraction comprised mainly lignin.

Herein, we investigate the behaviour of chip-sized wood specimens when brought into contact with a range of ionic liquids that contain the 1-butyl-3-methylimidazolium cation. We use Kamlet–Taft parameters to explain the exceptional solubility of cellulose and lignocellulose in some of these ionic liquids. We present evidence that the amount of water present in the biomass plays an important role in the swelling/dissolution process of lignocellulose.

Results and discussion

The ionic liquids that are reported to affect lignocellulose and its components often contain dialkylimidazolium cations. Based on this, we screened a selected range of ionic liquids (Table 1), containing the popular 1-butyl-3-methylimidazolium {$[C_4C_1im]^+$} cation and a variety of anions. We included anions that are known to dissolve cellulose, lignocellulose and/or lignin. All selected ionic liquids are miscible with water.

The pine wood was used in air-dried form and thus contained a substantial amount of water. We decided to use air-dried wood because rigorous drying requires additional energy input, which is undesirable for an energy-efficient pretreatment process. We were also interested in the impact that this water might have on the ionic liquid–wood interaction. The ionic liquids were all dried under vacuum; the moisture content of the individual ionic liquids is listed in the experimental section.

We set out to monitor the behaviour of chips of pine in ionic liquids at three different temperatures, 60 °C, 90 °C and 120 °C. The initial observation was that, under the conditions used, none of the ionic liquids investigated was able to completely disintegrate the wood specimens. Instead a more-or-less pronounced change of dimensions was observed. Hence we decided to measure the specimens' size changes.

Wood is an anisotropic and microstructured material. It is made up of elongated cell channels that are several micrometers long and are surrounded by lignified cell walls. The majority of cells are orientated in the axial direction. There are few longitudinal cells, restricting swelling in the radial direction. The cells are inter-connected *via* pits and perforation plates, creating long channels that enable transport of nutrients and water between roots and leaves. Wood from temperate regions forms annual rings (growth rings) while growing, due to seasonal change of growth conditions.

Due to the known anisotropy of wood expansion, the specimens were cut in a specific orientation to obtain consistent results (Fig. 1). The three dimensions were defined as: *a* tangential (parallel to growth ring), *b* radial (perpendicular to growth ring) and *c* axial (longitudinal).

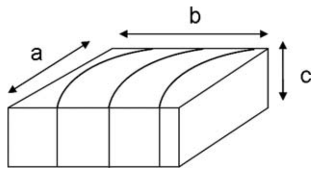

Fig. 1 Pine chip with growth rings. Definition of lengths *a* (tangential), *b* (radial) and *c* (axial) relative to growth rings.

Kamlet–Taft parameters

The abilities of the ionic liquids investigated to interact with solutes were measured using a set of three solvatochromic dyes. In accordance with previous measurements the dipolarity/polarisability expressed through π^* is high for all ionic liquids. The α value and the β value, which express the ability to donate and accept hydrogen bonds, respectively, depend on the ionic liquid composition.[20] The cation is responsible for the α value,[20] and in 1,3-dialkylimidazolium ionic liquids it largely arises due to the acidity of the proton that is attached to the carbon between the two ring nitrogen atoms. Our measurements show that the α values were between 0.45 and 0.64, a range that is typical of 1,3-dialkylimidazolium ionic liquids.[20] The anion is the most important determinant for β.[20] In our study, the β parameter varied between 0.5 and 1.2, which reflects the range of anions. $[C_4C_1im][OTf]$ was at the lower end of the scale, while $[C_4C_1im][Me_2PO_4]$ and $[C_4C_1im][MeCO_2]$ exhibited very high β values. This means that the acetate anion is a considerably stronger hydrogen bond acceptor than the chloride or the dimethylphosphate (Table 1).

It is noteworthy that we observed a significant decrease of the α value when β was high. This has been noticed previously for other ionic liquids and ascribed to the strong hydrogen bonding of the anion to the cation in these cases.[20] This results in reduced hydrogen bond donation from the cation to the dye probe.

For $[C_4C_1im][MeCO_2]$ and $[C_4C_1im][Me_2PO_4]$, we found significantly higher β values than previously reported in the literature (Table 1). We suspected that the moisture content of the ionic liquids might influence the Kamlet–Taft values, as these ionic liquids are known to be very hygroscopic. We deliberately left a $[C_4C_1im][Me_2PO_4]$ sample to equilibrate with air and determined the Kamlet–Taft values. We found that, while α and π^* remain relatively unaffected by the water, β was significantly lower. This might explain the lower β values found in the literature.

Swelling and dissolution of pine wood

Pine, a softwood, was chosen as the substrate because it is a widely cultivated, fast-growing tree. Softwood is also regarded as particularly recalcitrant to many pretreatment methods, due to its high lignin content.[4]

The specimens with a mass of 0.15–0.20 g were immersed in 1.5–2.0 g of ionic liquid (10% by weight). The ionic liquid was added under vacuum. This preparation method enabled the rapid filling of all the wood voids in the specimens, maximising surface contact of the ionic liquid which resulted in a more uniform swelling across all orientations and more consistent results.

Correlation of anion basicity and the impact on wood specimens

Distinct differences were observed in the maximal swelling of the wood specimen, depending in which ionic liquid it had been placed. Expansion in the tangential direction (*a* in Fig. 1) was chosen as the principal indicator for swelling, because the swelling was most pronounced in this direction (Fig. 7).

The ionic liquid $[C_4C_1im][OTf]$ with a β value of 0.49 was a very poor swelling agent at all three temperatures, inducing some slow swelling only at 120 °C (Fig. 2). The ionic liquids with midrange β values, $[C_4C_1im][N(CN)_2]$ and $[C_4C_1im][MeSO_4]$ (0.60 and 0.69 respectively), were able to swell the wood up to 8%. This exceeds the swelling ability of water, which expanded air-dried pine chips by 5% at 60 °C and 90 °C. The swelling in these ionic liquids was not affected by temperature. The swelling in the ionic liquids $[C_4C_1im][Me_2PO_4]$ and $[C_4C_1im][MeCO_2]$ and $[C_4C_1im]Cl$ exceeded 8%, correlating well with their high β values of 1.12, 1.20 and 0.83. The swelling in these ionic liquids was temperature-dependent. $[C_4C_1im][MeCO_2]$ swelled the specimens by 15% at 90 °C and more than 20% at 120 °C (Fig. 2b and c).

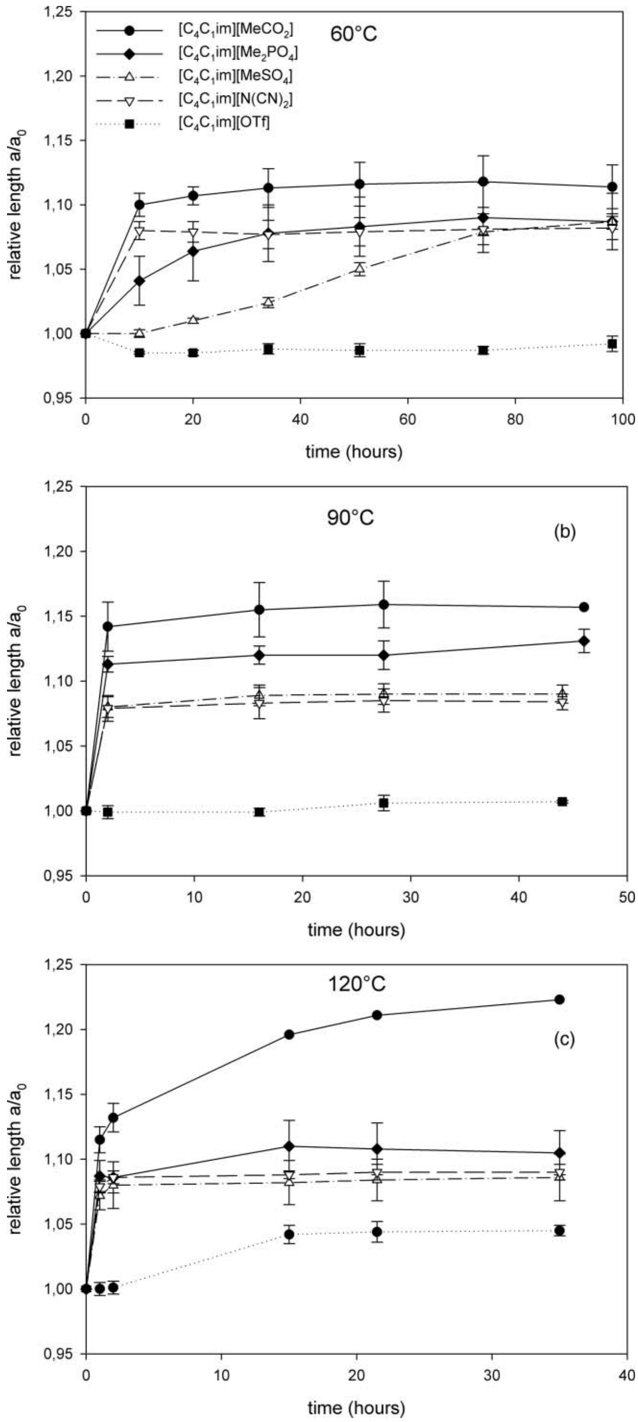

Fig. 2 Swelling in the tangential direction of pine specimens at different temperatures. Each time point was averaged over three samples, except for some of the $[C_4C_1im][MeCO_2]$ time points. Only one specimen survived to the end of the experiment; the other two split in half between the 2 h and 15 h measurements.

Several specimens incubated in $[C_4C_1im][MeCO_2]$ at 90 °C or 120 °C cracked along the growth ring. We suggest that the strong swelling exerted considerable tension on the tissue structure of the wood, which ultimately led to breaking.

Lignocellulosic components, particularly the carbohydrate polymers, are rich in hydroxyl groups. Ionic liquid anions that can strongly coordinate these hydroxyl groups (high β) are able to weaken the hydrogen-bonding interactions in the wood matrix and allow the chips to expand. Ionic liquids with low hydrogen-bond basicity, such as $[C_4C_1im][OTf]$, are not able to break the hydrogen bonds in the matrix and therefore do not expand it at all or only minimally, as observed for $[C_4C_1im][OTf]$ at 120 °C (Fig. 2c). Since these ionic liquids cannot dissolve the cellulose fibres, the wooden ultrastructure is preserved and no extraction is observed.

Fig. 3 displays the relationship between β and a, as well as the b and c dimensions. The greatest dependency on β is observed for the dimensions a and c, while length b was hardly susceptible to variations in β. We ascribe the different behaviour of b compared to a to the presence of radial pores (ray cells), which restrict swelling in length b. Length a was more susceptible to expansion due to the lack of radial cells. The data show that the swelling in dimension a can be correlated with the β values of the ionic liquids (Fig. 3a). Therefore we conclude that, when the cation is 1-butyl-3-methylimidazolium, an anion with high hydrogen-basicity allows stronger expansion of the wood matrix.

For the c dimension, we also observed a dependency on β. The less basic ionic liquids caused expansion of c, with a slight β dependency. For the ionic liquids $[C_4C_1im][Me_2PO_4]$ and $[C_4C_1im][MeCO_2]$, a reduction in c over time was observed, which we ascribe to dissolution of cell wall material.

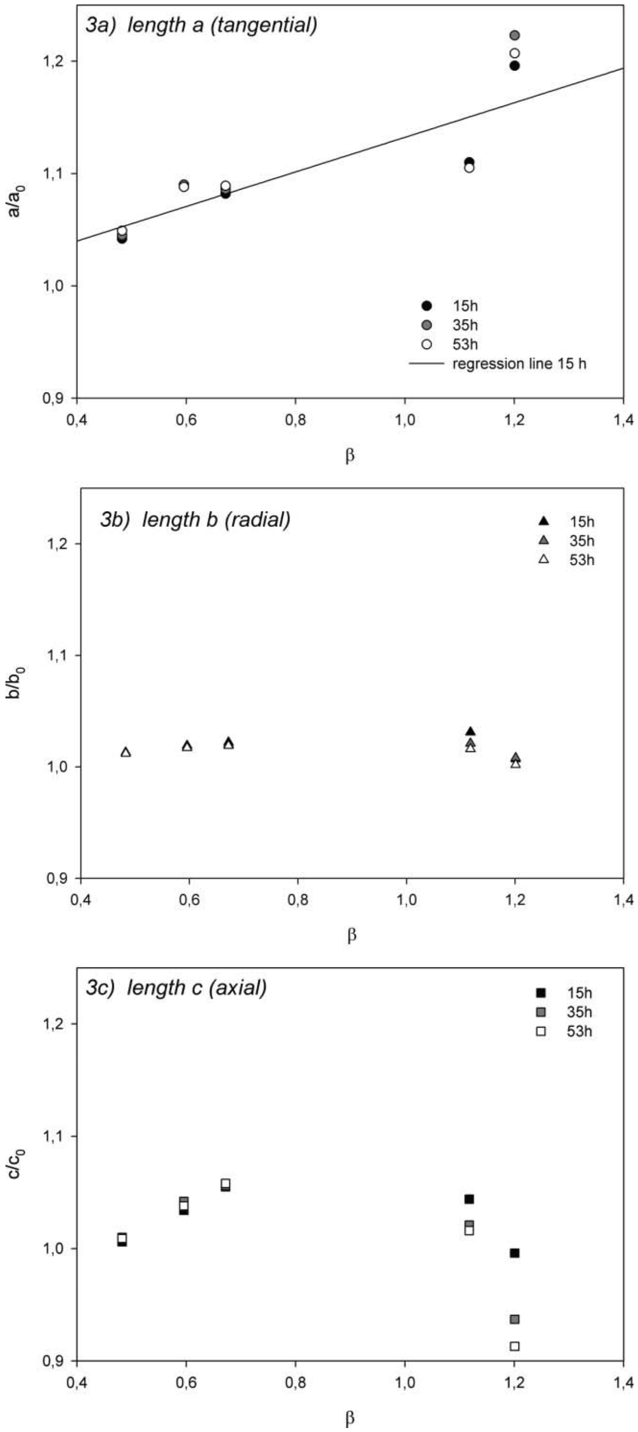

Fig. 3 Correlation between the relative cube dimensions a, b and c and Kamlet Taft parameter β. The pine chips were pretreated at 120 °C. A regression line is shown for the 15 h data points ($a/a_0 = 0.154\beta + 0.978$, $p = 0.054$). Error bars have been omitted for clarity.

Rate of swelling

At 60 °C, the lowest temperature investigated, different rates for the initial swelling were observed. The swelling was particularly slow with $[C_4C_1im][MeSO_4]$ and $[C_4C_1im][Me_2PO_4]$ (Fig. 2). In contrast, the ionic liquid $[C_4C_1im][N(CN)_2]$ acted quickly on lignocellulose even at this relatively low temperature.

We ascribe this behaviour to the relatively high viscosity of ionic liquids, compared to molecular solvents. $[C_4C_1im][N(CN)_2]$ has the lowest viscosity at room temperature of the ionic liquids tested (29.3 cP at 298 K[30]). Viscosity is temperature-dependent and, in the case of ionic liquids, the relationship follows the Vogel–Tammann–Fulcher (VTF) equation.[31] The viscosity is greatest close to the melting point and decreases exponentially with increasing temperature. 120 °C is more than 100 °C above the melting point for the ionic liquids shown in Fig. 2. Therefore viscosity differences between different ionic liquids at 90 °C will be small, and even less at 120 °C. This explains, at least partially, why the observed swelling rates are similar for $[C_4C_1im][N(CN)_2]$, $[C_4C_1im][MeSO_4]$, $[C_4C_1im][Me_2PO_4]$ and $[C_4C_1im][MeCO_2]$ at 90 °C and 120 °C.

Comparison of $[C_4C_1im][Me_2PO_4]$ and $[C_4C_1im][MeCO_2]$

We observed dissolution of pine cubes in the ionic liquids $[C_4C_1im][MeCO_2]$ (Fig. 4a) and $[C_4C_1im]Cl$ (see ESI), and to a lesser extent in $[C_4C_1im][Me_2PO_4]$ (Fig. 4b). The three dimensions (a, b and c in Fig. 1) were affected differently by the presence of hot ionic liquid. For dimension a, swelling is the dominant process, as discussed earlier. $[C_4C_1im][MeCO_2]$ was exceptionally capable of expanding the a dimension.

The profile for $[C_4C_1im][Me_2PO_4]$ was similar to that of $[C_4C_1im][MeCO_2]$, but swelling and dissolution were much less pronounced (Fig. 4b). An explanation could be the lower β value of $[C_4C_1im][Me_2PO_4]$. It is possible that the size of the anion may

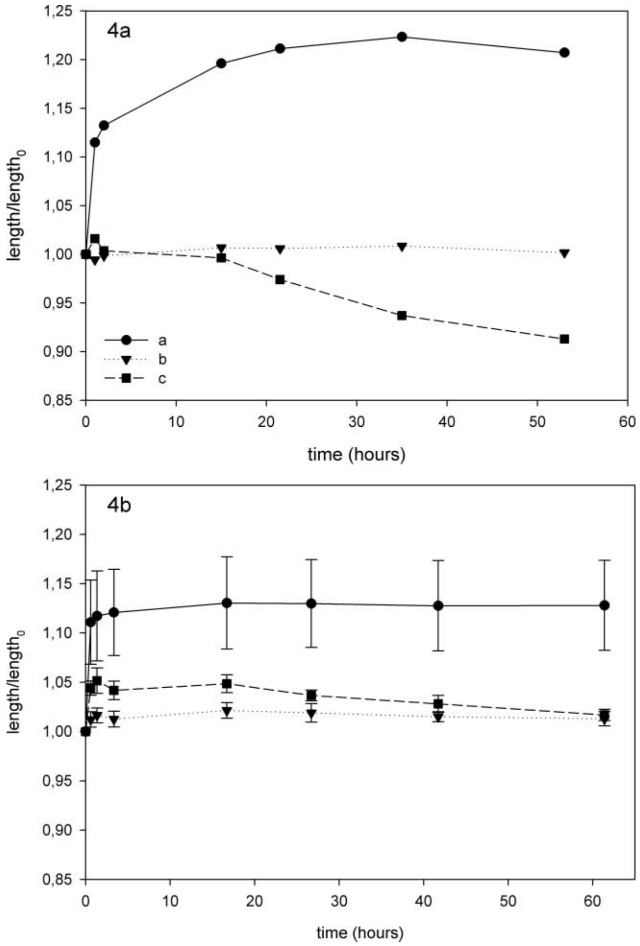

Fig. 4 Swelling profile of a pine chip in [C_4C_1im][$MeCO_2$] and in [C_4C_1im][Me_2PO_4] at 120 °C. Only one out of three replicates in [C_4C_1im][$MeCO_2$] remained intact during the treatment.

also play a role, a smaller ion being able to diffuse faster within the cell wall matrix.

The exact amount of wood material that was solubilised cannot be estimated from this profile, because swelling and dissolution take place simultaneously. While reduction of the specimen's size is probably due to solubilisation, the swelling caused by continued disintegration of the cell wall structure counteracts this effect. Interestingly, the dissolution of air-dried wood specimens under the chosen conditions was incomplete even after 2 days. This could be due to saturation of the ionic liquid with solutes. However, this is inconsistent with a linear decrease of length *c*, suggesting that the solubility limit had not been reached in our experiment. While dissolution of particles up to 1 mm appears to give good yields,[27] the yield from larger wood chips seems to be impaired. Slow dissolution of chip-sized lignocellulose has been previously reported.[5,6] This suggests that particle size is an important factor for lignocellulose dissolution in ionic liquids.

The influence of water

We hypothesised that the lignocellulose dissolution may be inhibited by water, as noted by others for cellulose dissolution.[32] Moisture can be introduced by the biomass and/or by the ionic liquid. All ionic liquids are more or less hygroscopic. For a given cation the amount of water that can be taken up by the ionic liquid increases with increasing hydrogen bond basicity of the anion.[33] We found that [C_4C_1im][Me_2PO_4] can take up more than 24 wt% (>400 mol%) water if allowed to equilibrate with the air in the laboratory. [C_4C_1im][$MeCO_2$] could take up 17 wt% (>200 mol%) water. Therefore, the ionic liquids needed to be dried thoroughly before use in order to allow comparison. Our drying procedure brought the water content to below 0.3 wt%. For example, Karl Fisher titration of dried [C_4C_1im][Me_2PO_4] and [C_4C_1im][$MeCO_2$] showed that 1.5 ml of ionic liquid contained 2.1 mg and 2.5 mg water, respectively. The pine chips used in this study contained 9 wt% water compared to the oven-dry weight. A typical wood specimen of 150 mg therefore contained 14 mg water. Hence, in our experiments the air-dried biomass introduced the greater part of the water into the system.

In order to test this hypothesis, we conducted an experiment with thoroughly dried wood specimens and handled the samples under a nitrogen atmosphere at all times. The pine cubes were dried under high vacuum at room temperature and immersed in the dried ionic liquids. The pretreatment temperature was set to 120 °C.

Interestingly, the performance of [C_4C_1im][$MeCO_2$] improved greatly under these conditions, resulting in softening and disintegration of the pine specimen at 120 °C in less than 15 h (Fig. 5). When exposing the [C_4C_1im][$MeCO_2$] treated wood to air, the structure re-hardened. We hypothesise that this was due to the uptake of atmospheric moisture. However, dry pine specimens treated with [C_4C_1im][Me_2PO_4] and [C_4C_1im]Cl remained intact and no softening was observed.

We suggest that the differences in moisture content of ionic liquids and/or biomass is a likely explanation for the contradicting observations for wood solubility in [C_2C_1im][$MeCO_2$] reported in the literature,[26,27] and that researchers must carefully monitor the water content in their systems when using ionic liquids for lignocellulose treatment.

The observed water-sensitivity is also of particular significance for the practical application of ionic liquids in biomass processing, as the feedstock will, under normal circumstances, have a proportion of bound water (8 to 15% compared to oven-dry biomass) and, when freshly harvested, appreciable quantities of free water. An industrial process that is based on dissolving lignocellulose with a dry ionic liquid will have to deal with additional energy requirements for thoroughly drying the substrate as well as the ionic liquid.

The choice of ionic liquid anion in combination with water content may have a profound impact on the dissolution process. This is shown in Fig. 6. Pine flour, either air-dried or vacuum-dried, was immersed in [C_4C_1im][$MeCO_2$] and [C_4C_1im]Cl and incubated at 90 °C under a nitrogen atmosphere. The [C_4C_1im][$MeCO_2$] was slightly yellow, while the [C_4C_1im]Cl was a white powder at room temperature. [C_4C_1im]Cl is very hygroscopic, attracting large amounts of water until it becomes a liquid, if it is not stored well sealed and under a dry atmosphere.

We observed that the [C_4C_1im][$MeCO_2$] liquor became more coloured when vacuum-dried pine powder was used. Conversely, the liquor of [C_4C_1im]Cl with vacuum-dried pine remained colourless during the 15 h treatment. The [C_4C_1im]Cl resolidified

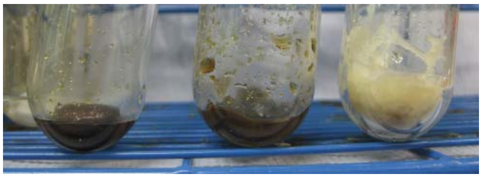

Fig. 5 Dry pine specimens treated at 120 °C for 15 h with $[C_4C_1im][Me_2PO_4]$ (left), $[C_4C_1im][MeCO_2]$ (middle) and $[C_4C_1im]Cl$ (right).

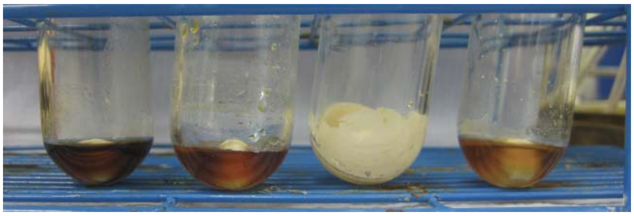

Fig. 6 IL solutions after treating pine flour at 90 °C. From left to right: vacuum-dried and air-dried flour in $[C_4C_1im][MeCO_2]$ and vacuum-dried and air-dried flour in $[C_4C_1im]Cl$.

upon cooling, confirming that water uptake had been prevented during the treatment.

This observation suggests that a certain amount of water seems to be necessary to promote lignin solubilisation in $[C_4C_1im]Cl$, while this does not seem to be true if the anion is acetate. Miyafuji *et al.* report that, at lower temperatures (<100 °C), the carbohydrate fraction of Japanese beech is preferentially solubilized in $[C_2C_1im]Cl$.[34] Other researchers have noted that high lignocellulose loading influences the ratio of carbohydrate/lignin solubilisation.[27] Using these findings and our own, there might be interesting opportunities for selective extraction of the cellulose fraction from biomass. The influence of the water content on the yield remains to be investigated.

The inability of $[C_4C_1im][N(CN)_2]$ to dissolve cellulose

We could not find evidence for dissolution of significant amounts of wood into $[C_4C_1im][N(CN)_2]$ (Fig. 7). Earlier reports claim that imidazolium-based ionic liquids with dicyanamide anions can dissolve cellulose in large amounts.[35] It was also reported that 1-benzyl-3-methylimidazolium dicyanamide $\{[BzC_1im][N(CN)_2]\}$ dissolved 2 wt% of Southern Pine thermo-mechanical pulp.[6] However, doubts have already been raised by others.[36] We investigated this claim by adding 2% dry cellulose to rigorously dried $[C_4C_1im][N(CN)_2]$. No dissolution was observed either at room temperature or at 100 °C. We speculated that chloride ions, a common contaminant of dicyanamide ionic liquids, could bring about cellulose dissolution, as it is known that $[C_4C_1im]Cl$ is a potent cellulose solvent. Therefore, increasing amounts $[C_4C_1im]Cl$ were added. However, a mixture of $[C_4C_1im][N(CN)_2]$ and $[C_4C_1im]Cl$ containing 7 mol% $[C_4C_1im]Cl$ did not dissolve 2 wt% cellulose. Also, 20 mol% and 30 mol% solutions were not able to dissolve cellulose.

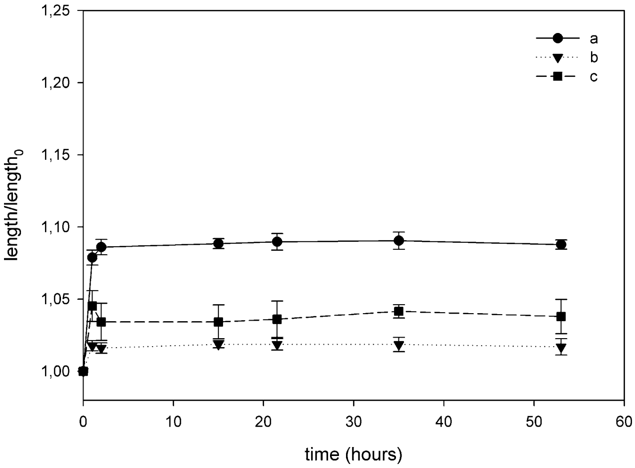

Fig. 7 Swelling profile of pine specimens in $[C_4C_1im][N(CN)_2]$ at 120 °C.

A β value of 0.60 was measured for the pure ionic liquid (Table 1). This is significantly lower than the β values of other known cellulose-dissolving ionic liquids, such as $[C_4C_1im]Cl$, $[C_4C_1im][Me_2PO_4]$ or $[C_4C_1im][MeCO_2]$. We therefore conclude that the dicyanamide anion is not capable of forming sufficiently strong hydrogen bonds to disrupt the hydrogen bonds in cellulose.

Conclusions

In agreement with Zavrel *et al.*,[37] we have found that ionic liquids that dissolve cellulose also dissolve lignocellulose. When paired with the 1-butyl-3-methylimidazolium cation, the hydrogen-bond basicity of the anion, expressed by the Kamlet–Taft parameter β, can be correlated with the swelling and dissolution of lignocellulose. Ionic liquids with β >0.80 exhibited swelling, followed by reduction of chip size. The swelling and dissolution in these ionic liquids is temperature-dependent, being better at temperatures larger than 100 °C. Swelling of wood blocks was most pronounced in the tangential direction, while dissolution seems to take place mainly in the axial direction of the wood blocks. Out of the investigated ionic liquids, $[C_4C_1im][MeCO_2]$ was identified as most effective swelling and dissolution agent, in agreement with its high β value. The dissolution of air-dried wood chips was slow and incomplete after 2 days at 120 °C. We have also shown that the amount of water present within the system is important for the swelling and dissolution of biomass.

Our results cast doubt that ionic liquids containing the dicyanamide anion can dissolve significant amounts of wood as well as cellulose. A significant amount of chloride impurities does not improve the solubility of cellulose.

Experimental

Materials

Cellulose (fibrous, long) was obtained from Sigma. 1-Methylimidazole (Acros Organics) and 1-butylimidazole (Aldrich) were distilled under vacuum from potassium hydroxide. 1-Chlorobutane and 1-bromobutane were distilled over P_2O_5. Dimethylsulfate (Aldrich) was distilled over CaO. Trimethylphosphate (Aldrich), silver acetate, sodium dicyanamide and silver nitrate (Aldrich) were used as received. Ethyl acetate and acetonitrile were dried over CaH_2. Toluene was distilled over sodium (with benzophenone as moisture indicator).

All ionic liquids were prepared using literature procedures (see ESI).[24,38,39] 1-Butyl-3-methylimidazolium dicyanamide and 1-butyl-3-methylimidazolium acetate were synthesised using 1-butyl-3-methylimidazolium bromide[24] and the silver salts of the respective anions.[40]

Preparation of wood chips

Pine (*Pinus radiata*) sapwood was obtained from a 15 year old tree harvested at Silwood Park, Ascot, in June 2008. All wood was taken from material sawn from the main trunk. Pine sapwood specimens of dimensions 10 mm × 10 mm × 5 mm were prepared. Specimens were stored air-dried at normal temperature and room humidity in the laboratory. The moisture content of the pine wood was 9% on oven-dry basis.

Swelling experiments

Pyrex culture tubes (Ø = 25 mm) with screw caps and Teflon linings were used as reaction vessels. The weight of dry wood specimens chips was determined using a precision balance (±0.0001 g). Lengths were measured with a calliper with an accuracy of ±0.01 mm. Experiments were performed in triplicate to account for sample heterogeneity. The ionic liquids were thoroughly dried before use at 40 °C under vacuum and overnight, except for $[C_4C_1im][MeCO_2]$ and $[C_4C_1im][Me_2PO_4]$, which were dried at 50 °C and 100 °C, respectively. The residual water content was 200 ppm for $[C_4C_1im][OTf]$, 400 ppm for $[C_4C_1im][MeSO_4]$, 3100 ppm for $[C_4C_1im][N(CN)_2]$, 1200 ppm for $[C_4C_1im][Me_2PO_4]$ and 1600 ppm for $[C_4C_1im][MeCO_2]$, according to Karl Fisher titration. A Schlenk flask was used as a soaking apparatus. The culture tube containing a wood sample was inserted into the Schlenk flask and the Schlenk sealed with a rubber septum. The flask was evacuated for 60 s and 1.5 ml ionic liquid injected through the septum with a syringe. The vacuum was applied until the chip appeared to be fully soaked. The tube was tightly sealed and the sample kept at 4 °C up for to 5 h until preparation of the remaining samples was finished. Samples were heated in an oven to the desired temperature. For measurements they were taken out and left to cool. The timing was stopped while samples were outside the oven. The wood specimens were removed from the ionic liquid and their surface wiped dry with a paper towel. The lengths were determined and samples placed in the glass tubes as quickly as possible.

For swelling under anhydrous conditions the pine specimens (10 × 10 × 5 mm) were dried under reduced pressure for 5 days, resulting in a mass loss of 9%. Oven-drying resulted in a comparable mass loss. The samples were handled in a glove box or under nitrogen atmosphere at all times. 2 g of $[C_4C_1im]Cl$ or 1.5 ml of dry $[C_4C_1im][Me_2PO_4]$ and $[C_4C_1im][MeCO_2]$ were transferred into Schlenk flasks, the pine specimens added and the Schlenk flask evacuated to allow filling of the wood pores. The samples were heated to 120 °C for 15 h.

Ionic liquid stability

Thermogravimetric analysis (TGA) did not show noticeable decomposition for $[C_4C_1im]Cl$, $[C_4C_1im][N(CN)_2]$, $[C_4C_1im][MeSO_4]$ and $[C_4C_1im][Me_2PO_4]$ at 120 °C over a period of 60 h. For $[C_4C_1im][MeCO_2]$, we observed a 12% weight loss within 60 h. We could not detect any decomposition products in the respective ^1H NMR spectrum.

Dissolution of pine flour

Pine wood was ground for 5 min in a water-cooled bench-top grinding machine. Part of the flour was dried under vacuum at 50 °C for 5 h. The dried pine flour was transferred into the glove box for storage. 30 mg of wet or dried flour was mixed with 1.0 g of $[C_4C_1im][MeCO_2]$ or $[C_4C_1im]Cl$. The flasks were kept under nitrogen atmosphere at all times. The mixtures were heated to 90 °C while stirring.

Measurement of Kamlet–Taft parameters

Stock solutions of the Kamlet–Taft dyes (Reichhardt's dye, 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline) were prepared in dichloromethane. The solution was transferred by syringe into a cuvette of 1 mm thickness under nitrogen atmosphere. The solvent was evaporated, the vacuum-dried ionic liquid added and the solution carefully mixed with shaking or a syringe needle. A spectrum was recorded using a PC-controlled Perkin Elmer Lambda 2 spectrometer with thermostatted sample holder. The measurements were conducted at 25 °C, except for $[C_4C_1im]Cl$, for which the spectra were recorded at 75 °C. The maximum of the absorption peak was determined using Origin 7. A Gaussian function was fitted to a 40 nm wide region with the peak maximum in the centre.

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