

Dissolution of Wood in Ionic Liquids

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The present paper demonstrates that both hardwoods and softwoods are readily soluble in various imidazolium-based ionic liquids (ILs) under gentle conditions. More specifically, a variety of ionic liquids can only partially dissolve wood chips, whereas ionic liquids such as 1-butyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride have good solvating power for Norway spruce sawdust and Norway spruce and Southern pine thermomechanical pulp (TMP) fibers. Despite the fact that the obtained solutions were not fully clear, these ionic liquids provided solutions which permitted the complete acetylation of the wood. Alternatively, transparent amber solutions of wood could be obtained when the dissolution of the same lignocellulosic samples was attempted in 1-benzyl-3-methylimidazolium chloride. This realization was based on a designed augmented interaction of the aromatic character of the cation of the ionic liquid with the lignin in the wood. After dissolution, wood can be regenerated as an amorphous mixture of its original components. The cellulose of the regenerated wood can be efficiently digested to glucose by a cellulase enzymatic hydrolysis treatment. Furthermore, completely acetylated wood was found to be readily soluble in chloroform, allowing, for the first time, detailed proton nuclear magnetic resonance (NMR) spectra and NMR diffusion measurements to be made. It was thus demonstrated that the dissolution of wood in ionic liquids now offers a variety of new possibilities for its structural and macromolecular characterization, without the prior isolation of its individual components. Furthermore, considering the relatively wide solubility and compatibility of ionic liquids with many organic or inorganic functional chemicals or polymers, it is envisaged that this research could create a variety of new strategies for converting abundant woody biomass to valuable biofuels, chemicals, and novel functional composite biomaterials.

KEYWORDS: Wood; dissolution; derivatization; regeneration; characterization; cellulose; lignin; ionic liquids; cellulase digestion; NMR; diffusion studies

INTRODUCTION

The efficient utilization of biomass is becoming increasingly important due to diminishing resources of fossil fuels as well as global heating warnings caused by greenhouse gas emissions. To date, wood is mainly utilized for the production of paper from cellulose, and most of the other components of wood are simply incinerated to energy. Therefore, there is an increasing demand for new processes that could provide new means to use this resource in a more efficient manner, not only as a fuel but also as a starting material for our chemical industry with the aim of producing commodity and fine chemicals.

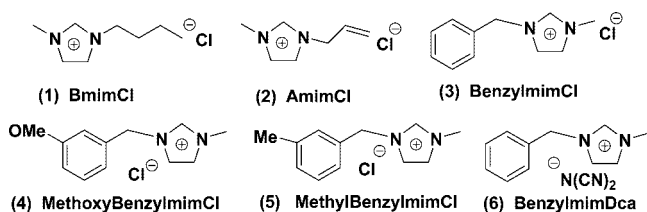
The main components of wood are cellulose, lignin, hemicellulose, and extractives. From these, lignin binds the plant cells together, providing wood with mechanical strength and rigidity to resist external forces, such as wind, and forming a barrier against microbial attack. According to the current view, lignin is an irregular, cross-linked polymer network, which is composed of randomly cross-linked phenylpropanoid units (1–3). Therefore, in general, it is thought that it is practically impossible to dissolve wood in its native form, because the three-dimensional lignin network binds the whole wood architecture together. In papermaking, the lignin network is fragmented under alkaline conditions, and cellulose is harvested as cellulose fibers. The insolubility of wood in common solvents has severely hampered the development of new methods for the efficient utilization of wood and its components.

Some time ago Lu and Ralph demonstrated that after extensive ball-milling, wood becomes soluble in dimethyl sulfoxide–tetrabutyl ammonium fluoride and dimethyl sulfoxide–

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Scheme 1. Structures and Abbreviations of the Examined Ionic Liquids

ide-imidazole binary solvent systems (4). However, it is well-known that the required extensive ball-milling causes degradation of both cellulose and lignin (4). Consequently, from both economic and environmental points of view, the magnitude of the wood conversion industries to paper and allied products imposes serious challenges in the development of green processing technologies for wood and other lignocellulosic materials. It has also been shown that some ionic liquids (ILs) (such as 1-butyl-3-methyl- and 1-allyl-3-methylimidazolium chloride, [bmim]Cl and [amim]Cl, respectively) can effectively dissolve biopolymers (5, 6). In our continuing work to characterize the structure of lignin, we have observed that both [bmim]Cl and [amim]Cl were also able to dissolve different types of lignin samples. Similar results were very recently reported by Pu et al. (7). These results have prompted us to examine the dissolution of wood and lignin in these solvents. This paper reports our initial findings that pertain to the various issues that determine the complete solubility of hardwoods and softwoods in ionic liquids.

EXPERIMENTAL PROCEDURES

Materials. Unbleached Norway spruce thermomechanical pulp (TMP) and pine TMP were sampled in a Swedish mill, ca. 38% dryness, 85 mL of CSF, standard newspaper quality; the mill has a one-stage refining and a subsequent reject refining (ca. 20%) stage. This pulp was taken at a press stage after the refined and refined reject pulps had been combined. Norway spruce sawdust was prepared in-house. All wood samples used (spruce TMP, spruce sawdust; particle size = 0.1–2 mm, pine TMP) were kept in a vacuum oven at 50 °C for 24 h prior to use. All reactions were carried out under argon atmosphere. Pyridine and acetic anhydride were purchased from Aldrich, Fluka, and J. T. Baker and used without further purification.

Synthesis of Ionic Liquids. Structure numbers in bold refer to those of **Scheme 1**. [Amim]Cl (2) was synthesized according to the general procedure provided by Zhang et al., (6) with slight modification; both allyl chloride (Aldrich) and 3-methylimidazole (Aldrich) were distilled prior to use. [Amim]Cl was further purified, to remove trace color, by dissolving the crude [amim]Cl mixture in water and refluxing with activated charcoal (18 h). The solution was filtered through a silica plug, and the water was removed by distillation and dried for 2 days in vacuo to yield [amim]Cl as a pale yellow crystalline solid, with a melting point of 52 °C: δ H (300 MHz, CDCl₃) 4.06 (3 H, s), 4.94 (2H, d), 5.40 (1H, d), 5.91–5.97 (1H, m), 7.42 (1H, s), 7.65 (1H, s), 10.44 (1H, s).

1-Methyl-3-benzylimidazolium Chloride (3). The ionic liquid, was prepared with benzyl chloride (0.25 mol) and 1-methylimidazole (0.23 mol) using CH₃CN as solvent in a 250 mL three-neck bottle. The mixture was refluxed for 48 h under an Ar atmosphere. After evaporation of the solvent and of the residual benzyl chloride, the pure ionic liquid was obtained. Drying of the materials took place at 120 °C under vacuum by stirring for 24 h. The product was of a solid gelatinous nature at room temperature; yield, 95%; δ H (300 MHz, CDCl₃) 4.02 (3H, s), 5.54 (2H, s), 7.27–7.34 (4H, m), 7.42–7.45 (2H, m), 7.47–7.50 (1H, t), 10.56 (1H, s).

1-Methyl-3-m-methoxybenzylimidazolium Chloride (4). The ionic liquid was synthesized using the same procedure as per ionic liquid (3); yield, 95%; T_m = δ H (300 MHz, CDCl₃), 3.76 (3H, s), 4.01 (3H,

s), 5.48 (2H, s), 6.81–6.82 (1H, d), 6.95–6.99 (2H, m), 7.22–7.24 (1H, m), 7.32 (1H, d), 7.45 (1H, s), 10.78 (1H, s).

1-Methyl-3-methylbenzylimidazolium Chloride (5). The ionic liquid was synthesized using the same procedure as per ionic liquid (3); yield, 96%; δ H (300 MHz, CDCl₃) δ 2.26 (3H, s), 4.01 (3H, s), 5.44 (2H, s), 7.10 (1H, d), 7.17–7.19 (3H, m), 7.25 (1H, d), 7.51 (1H, d), 10.72 (1H, s).

1-Methyl-3-benzyl-imidazolium Dicyanamide (6). The ionic liquid was prepared by the anion exchange reaction between 1-methyl-3-benzylimidazolium chloride (0.20 mol) and NaN(CN)₂ (0.21 mol) using H₂O as solvent. The homogenous mixture was stirred at room temperature for 12 h. After evaporation of the water, 50 mL of CH₂Cl₂ was added into the residua. The formed NaCl was filtered, and the organic solvent phase was dried with anhydrous MgSO₄. After filtration of the MgSO₄ and evaporation of the solvent, a yellow liquid ionic liquid was obtained: yield, 93%; δ H (300 MHz, CDCl₃) δ 3.98 (3H, s), 5.38 (2H, s), 7.25 (1H, d), 7.32 (1H, d), 7.38–7.43 (5H, m), 9.21 (1H, s).

All IL samples were dried using an oil pump vacuum at 80 °C for several days to remove all residual water and solvent traces. The water content of the used ILs was below 1% (according to ¹H NMR).

NMR Spin Diffusion Measurements. Such NMR spectra were acquired with a Varian Inova 500 MHz NMR spectrometer in CDCl₃ at 27 °C. The parameters for the diffusion-ordered spectra were as follows: gradient parameters selected for each gradient in bipolar gradient pair (BPPSTE sequence); gradient duration, 1.8 ms; gradient recovery delay, 200 μ s; diffusion delay, 200 ms; gradient strengths (G/cm), 4.6, 6.5, 7.9, 9.2, 10.2, 11.2, 12.1, 13.0, 13.7, 15.2, 16.5, 18.9, 20.0. The number of transients was 256 for each spectrum acquired with a recycling time of 2.1 s.

Dissolution of Wood in Ionic Liquid. The ionic liquid was charged into a 50 mL dried flask equipped with a mechanical stirrer, under an inert atmosphere of argon. The temperature of the dissolution process was controlled by an oil bath at the specified temperature (**Table 1**). The wood sample (particle size = 0.1–2 mm) was then added into the ionic liquid quickly, and the dissolution proceeded at specified time intervals.

Wood Regeneration, Enzymatic Hydrolysis, Glucose Determination. The wood solution created by the treatment described previously was gradually added into an excess of rapidly stirred distilled water. The precipitated bulky material was then filtered using a Buchner funnel, washed thoroughly with distilled water. Finally, a small sample of it was taken to determine its solids content by oven-drying it at 110 °C overnight. The remaining material was then treated with cellulase (Iogen, Canada; filter paper activity = 130 FPU mL⁻¹) using a previously optimized (8) ratio of 40 FPU/g of wood. The enzymatic hydrolyses were carried out at 40 °C for 48 h using 50 mM citrate buffer (pH 4.5) at 5% consistency in an orbital water bath shaker. The filtrate from the enzymatic hydrolysis was then diluted to a volume of 250 mL using a volumetric flask. Using 100 mL of this solution subsequent dilutions were thus prepared containing 100–1000 μ L (in 100 μ L intervals) of this filtrate in distilled water. Four milliliters of each of these dilutions was then added into a test tube. A series of glucose standards with the following concentrations were also prepared: 1.28 $\times 10^{-6}$, 2.55 $\times 10^{-6}$, 3.83 $\times 10^{-6}$, 5.11 $\times 10^{-6}$, and 6.39 $\times 10^{-6}$ g/mL. In addition, the coloring reagent was prepared by mixing 1 part of reagent B with 50 parts of reagent A of BCA test kit (protein assay kit, Sigma). Reagent B is a copper solution, and reagent A is a BCA solution. The resulting solution is green in color, which should be freshly prepared for every analysis. The color was finally developed by adding to each of the 4 mL glucose standard solutions and diluted filtrates 1 mL of coloring reagent. In addition, a blank solution was also prepared by mixing 4 mL of distilled water and 1 mL of coloring reagent. The samples were then mixed using a Vortex mixer for few seconds. The samples were then allowed to react at 60 °C (protected from light by covering each tube with aluminum foil) and allowed to incubate for 2 h (stirring is not necessary). Samples containing glucose turned purple. The amount of glucose in the various samples was finally determined spectrophotometrically at 562 nm against a blank.

Determination of Solubilization Conditions and Solubility of Wood in Ionic Liquids. Ten grams of ionic liquid was charged into a

Table 1. Dissolution Behavior of Wood-Based Lignocellulosic Materials in Different Imidazolium-Based Ionic Liquids

entry	ionic liquid	wood sample form	solubilization conditions	solubility (wt %)
1	[bmim]Cl	wood chips	130 °C, 15 h	partially soluble
2	[amim]Cl	ball-milled Southern pine powder	80 °C, 8 h	8
3	[amim]Cl	Norway spruce sawdust	110 °C, 8 h	8%
3b	[amim]Cl	Norway spruce sawdust	80 °C, 24 h	5
4	[bmim]Cl	Norway spruce sawdust	110 °C, 8 h	8
5	[amim]Cl	Norway spruce TMP	130 °C, 8 h	7
6	[bmim]Cl	Norway spruce TMP	130 °C, 8 h	7
7	[amim]Cl	Southern pine TMP	110 °C, 8 h	2
8	[amim]Cl	Southern pine TMP	130 °C, 8 h	5
9	[bmim]Cl	Southern pine TMP	130 °C, 8 h	5
10	[bzim]Cl	Southern pine TMP	130 °C, 8 h	5
11	[bzim]Cl	Norway spruce TMP	130 °C, 8 h	5
12	[bz-ome-mim]Cl	Southern pine TMP	130 °C, 8 h	5
13	[bz-ome-mim]Cl	Southern pine TMP	130 °C, 8 h	2
14	BenzylmimDca	Southern pine TMP	130 °C, 8 h	2

100 mL dried three-neck flask under an inert atmosphere of argon, which was heated with a temperature-controlled oil bath at a given temperature. The wood powder (Norway spruce, particle size = 0.1–2 mm) or fiber was added in portions of only 1 wt % of ionic liquid each time with mechanical stirring. Additional sample was introduced until the solution became homogenous and somewhat clear or until the disappearance of fibers was evident.

RESULTS AND DISCUSSION

Dissolution of Wood into Ionic Liquids. Complete wood dissolution [up to 8% (w/w), **Figure 1**] can be carried out by simply mixing a dried wood sawdust sample with the ionic liquid ([amim]Cl or [bmim]Cl) and stirring the mixture mechanically at 80–120 °C. In a previous study, similar solvents were utilized, but it was claimed that the sample did not dissolve completely and that dissolution was limited, leading to partial fractionation of the sample (9). However, in that work, the researchers used wood chips for dissolution experiments. The two crucial parameters that define wood solubilization are as follows: First, the dissolution rate of wood is highly dependent on the particle size of the wood sample. This is because the complex and compact structure of the wood cell wall and between the lignin, cellulose and hemicellulose would essentially inhibit the diffusion of the ionic liquid into its interior, resulting in only a partial dissolution of wood chips.

During our work we discovered that the solubilization efficiency of the lignocellulosic materials in ILs was found to be of the order ball-milled wood powder > sawdust ≥ TMP fibers ≫ wood chips. The dissolution of fine sawdust (Norway spruce, particle size = 0.1–2 mm) in ILs takes place within a few hours, even under ambient conditions. Furthermore, thermomechanical pulp (TMP) samples readily dissolved in [bmim]Cl and/or [amim]Cl. However, we discovered that it takes several weeks for wood chips (size in excess of 5 mm × 5 mm × 1 mm) to completely dissolve at elevated temperatures. It has also been previously reported that wood dissolution into ILs is possible under microwave irradiation, which enhances the rate of dissolution (10). However, this also leads to delignification and to partial degradation of the wood components (11).

In addition to the particle size, the water content of a wood sample plays a key role in determining its solubility in ionic liquids. Overall, water was found to significantly reduce the solubility of wood in ILs. The mere fact that it is very difficult to remove water effectively from wood chips provides ample justification as to why the earlier efforts were unsuccessful in documenting the complete wood solubilization (9). A hot stage optical microscopy investigation of a Norway spruce sawdust sample in [amim]Cl clearly demonstrates the disappearance of fibrous material (**Figure 1**) over a period of several hours.

On a macroscopic scale, the appearance of [bmim]Cl and [amim]Cl wood solutions was not fully clear. Because the dissolution of cellulose, as well as various hemicelluloses (6, 12), has been demonstrated to produce clear viscous solutions in [bmim]Cl, the hazy appearance of wood solutions could be due to the presence of lignin. In the literature, the dissolution of cellulose in various solvent systems has been discussed in detail (5, 13–18). A common property for these solvents is their ability to break down the extensive inter- and intramolecular hydrogen bonding network of cellulose. In ILs, both the cation and anion of the salt play a crucial role in the dissolution of cellulose. In addition, the viscosity of the IL plays a role in the dissolution speed (12). For the efficient dissolution of cellulose in ILs, the cation is usually an imidazolium salt with a C2–C6 side chain. (5) From these, the butyl and allyl derivatives are the most efficient, and growing chain length has been found to decrease the solubility of cellulose (5, 6). From anions, the chloride is usually the most efficient due to its capability to participate in breaking down hydrogen bonds (5, 18). Notably, also various strong Lewis acid anions (such as aluminum chlorides) have the potential of being efficient solvents for cellulose. However, these often pose problems associated with solvent recycling, and their enhanced reactivity precludes them from a variety of applications.

Beyond the mass transfer and diffusion considerations outlined above aimed to rationalize the solubilization order already discussed previously (see **Table 1**), additional explanations are in order if one is to comprehend the reason for hazy

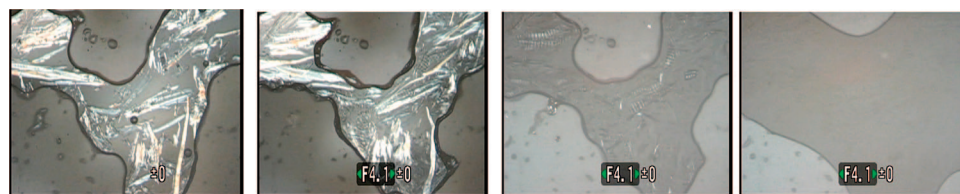


Figure 1. Optical photomicrographic images (magnification ×10) of Norway spruce fibers from sawdust in AmimCl as a function of time (from left to right: initial, 0.5 h, 2 h, 4 h at 120 °C).

versus transparent solutions. The highly crystalline character of cellulose in wood is driven by a set of regular intermolecular and intramolecular hydrogen-bonding interactions that when coupled with the three-dimensional network character of lignin and its possible covalent linkages with the carbohydrates are primarily responsible for the complex and compact structure of wood. Accounts of π - π interactions among the aromatic groups in lignin have also appeared in the literature, accounting for the conformationally stable supermolecular structure of lignin (19). Because significantly attractive interactions between π -systems have been known for over half a century (20), in recent years they have seen wide utility toward understanding crystal structure, self-assembly in nano-supermolecular structural chemistry, materials chemistry, etc. Ionic liquids have a more complex solvent behavior compared with traditional solvents. The various types of interactions between ILs with many solutes include dispersion, π - π , n - π , hydrogen bonding, dipolar, and ionic/charge-charge and have been investigated by Anderson et al. (21). This team has reported that although the Bmim cation does not have the analogous electron aromatic system, the chloride anion (with nonbonding electrons), in combination with the Bmim cation, forms an IL that exhibits the ability to interact with π -systems of probe molecules. In our case, conceivably the active chloride ions in the BmimCl ionic liquid would disrupt the hydrogen-bonding interactions present in wood, allowing it to diffuse into the interior of the wood and resulting in a viscous but hazy solution. Both, however, BmimCl and AmimCl still cannot effectively and fully interact and solvate the aromatic character of lignin, imparting a hazy characteristic to such solutions.

The Abraham solvation equation is an effective approach used to characterize the polymer solvation capacity of ILs (21). The various parameters involved in this equation include the ability of the ionic liquid to interact with π - and n -electrons of the solute, a measure of the dipolarity/polarizability of the ionic liquid, and the ionic liquid's hydrogen bond acidity and basicity. Upon close inspection of the Abraham solvation equation we concluded that for our work a cationic moiety with an electron-rich aromatic π -system may create stronger interactions (higher retention factors) for polymers capable of undergoing π - π and n - π interactions. With this in mind, we designed and synthesized a series of phenyl-containing ionic liquids and consequently examined their solubilization capabilities for various wood samples (entries 10–13, Table 1). The emerging data were found to be consistent with the above hypothesis as demonstrated by the fact that 1-benzyl-3-methylimidazolium chloride ([bmim]Cl) ionic liquids/wood solutions were completely transparent, amber colored, and viscous solutions. However, one major drawback of [bmim]Cl is its high viscosity. As such, efforts were directed to reduce it by decreasing the symmetry of the cation by synthesizing ILs 4 and 5 (Scheme 1) as well as altering the nature of the anion (IL 6, Scheme 1) within the structure of the ionic liquid. Although the obtained solutions were moderately clear (Table 1), their wood-dissolving abilities were not adequate as evidenced by the amount of residual fibrous material remaining when these structures were used. It is likely that any increase in the mass and bulk of the cation within a given ionic liquid may decrease the concentration of active chloride ion (5), thus reducing its solvating capacity for both cellulose and lignin. In addition, although $-N(CN)_2$ anion based ionic liquids have shown excellent solvating abilities for carbohydrates (22), IL 6 (Scheme 1), which was of significantly lower viscosity, even at room temperature, was only partially capable of dissolving Norway spruce TMP fibers (entry 14, Table 1). It

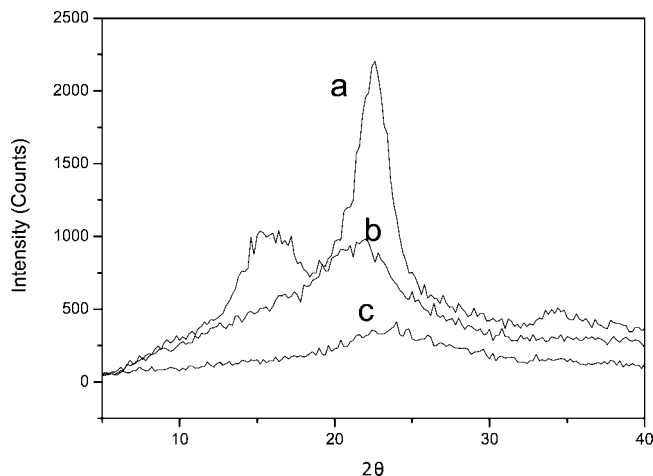


Figure 2. X-ray spectra of (a) spruce sawdust, (b) regenerated spruce from [amim]Cl using H₂O as the nonsolvent, and (c) 8% wt spruce sawdust in [bmim]Cl solution.

was also discovered that blending [benzylmim]Cl with [amim]Cl could effectively reduce the viscosity of [benzylmim]Cl, whereas a transparent solution of wood material could be obtained (entry 15, Table 1).

Furthermore, we have determined that the facility and the kinetics of the process of wood dissolution in ionic liquids are dependent on the applied temperature, which is consistent with the results in a previous publication related to the dissolution of wool keratin fibers (23). At higher temperatures (> 100 °C), all of the examined wood samples dissolved relatively rapidly. However, it was possible to dissolve up to 5% (w/w) of Norway spruce sawdust in [amim]Cl at 80 °C within 24 h. In fact, complete dissolution was also found to take place at ambient temperature. For example, when wood sawdust is gently homogenized with [amim]Cl in a mortar and the sample is subsequently transferred into a test tube (under argon), it slowly turns liquid over time. Among the examined ILs, the [amim]Cl was found to possess the lowest viscosity, which permits using somewhat lower temperatures. Alternatively, ILs with aromatic side chains (Scheme 1) required somewhat higher temperatures due to their higher melting points and viscosities (Table 1).

Properties of Regenerated Wood. After dissolution of the lignocellulosic material into ILs, it is possible to recover the sample by simply pouring the solution into an excess of a nonsolvent, that is, water. If the regeneration is carried out under rapid mechanical stirring, fully amorphous material is obtained. This is clearly visible in the X-ray spectra of the regenerated material (Figure 2), because the X-ray diffraction signals from the crystalline regions of spruce sawdust have disappeared after the dissolution-regeneration process. The data of Figure 2 show that spruce sawdust/[amim]Cl displays a slight broad amorphous diffraction peak centered around 2θ of 25°, in the absence of the characteristic diffraction pattern of wood cellulose, which usually displays a prominent sharp peak near 15° and 23°. In an earlier work, Wei et al. (24) were investigating the structural differences between cellulose regenerated from [bmim]Cl and untreated cellulose, using Fourier transform IR (FT-IR) spectroscopy, X-ray diffraction, and thermogravimetric (TG) measurements. The data of this team showed that the crystalline form of wood pulp cellulose was transformed completely from cellulose I to cellulose II after regeneration from [bmim]Cl solution. However, the material regenerated from dissolved wood does not show any signs for cellulose II. This may be explained by the presence of lignin and other wood components, as well as by the regeneration method, which may contribute to the crystallinity of

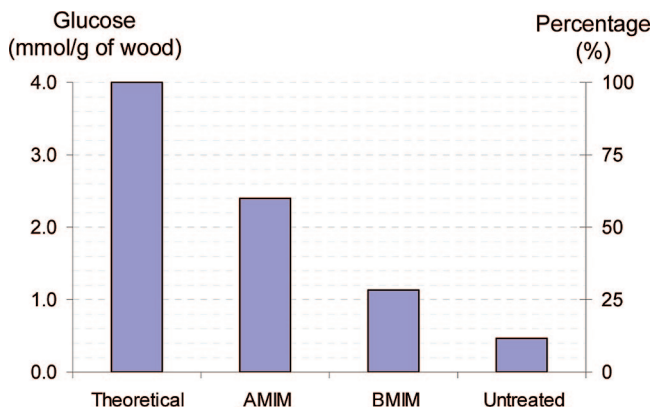


Figure 3. Amount of glucose released during enzymatic hydrolysis with the IL pretreatment (in [amim]Cl or [bmim]Cl), in millimoles per gram of wood and in percentage terms compared with the theoretical maximum and with a control experiment (spruce wood sawdust without pretreatment). The effect of galactoglucomannan.hemicellulose is not taken into account.

the sample. In the present study, the material was regenerated with vigorous stirring, which may partially inhibit the induction of crystalline ordering within the regenerated sample.

As demonstrated in **Figure 2**, the crystallinity of the cellulose in the wood was eliminated with the IL dissolution–regeneration treatment. Such a transformation is anticipated to allow a greater accessibility for the hydrolytic enzymes to rapidly penetrate and hydrolyze the wood (25). In an effort to further investigate the reactivity of regenerated materials toward cellulolytic enzymes, the pretreated lignocellulosic material in the IL was then submitted to an enzymatic hydrolysis (26). Our initial, and completely nonoptimized experiments, showed that about 60% of the theoretical amount of glucose was enzymatically released from the wood when predissolved in [amim]Cl and regenerated by precipitation in water. This compared to only 12% of glucose units being released from the untreated control wood sample (**Figure 3**). Similar pretreatments in [bmim]Cl were also found to improve the release of glucose unit but to a significantly lower degree compared to [amim]Cl. The use of ILs on straw as the raw material prior to cellulolytic hydrolysis has also been documented recently with somewhat less impressive results (27).

Acetylation of Wood Dissolved in Ionic Liquids. One of the major advantages of ILs is that they allow the use of a wide range of chemical reactions to be performed in them with significant alterations in the reaction rates and the stabilization of the various transition state complexes (28, 29). In the literature, the acetylation of cellulose has been studied for many ILs (6, 30, 31). By subjecting fully dissolved wood in [amim]Cl (entry 3b, **Table 1**) to an incremental addition of a 1:1 mixture of acetic anhydride/pyridine it became possible to essentially completely acetylate wood. This is evident from the complete disappearance of the hydroxyl IR stretch band located at 3500 cm^{-1} (**Figure 4**) as well as from the appearance of strong $\text{C}=\text{O}$ stretching band at 1750 cm^{-1} . The rigid and compact nature of wood is known to be attributed to an intricate hydrogen-bonded network that precludes its solubility in common molecular solvents. In this light, the demonstration of complete acetylation depicted in **Figure 4** is rather compelling. The complete derivatization of all of the hydroxyl functionalities also emphasizes that the obtained wood solutions are true solutions, and they are not simply gels or larger aggregates.

Another significant manifestation of our work with fully acetylated wood is its solubility in chloroform. This allowed the recording, for the first time, of solution state ^1H NMR spectra

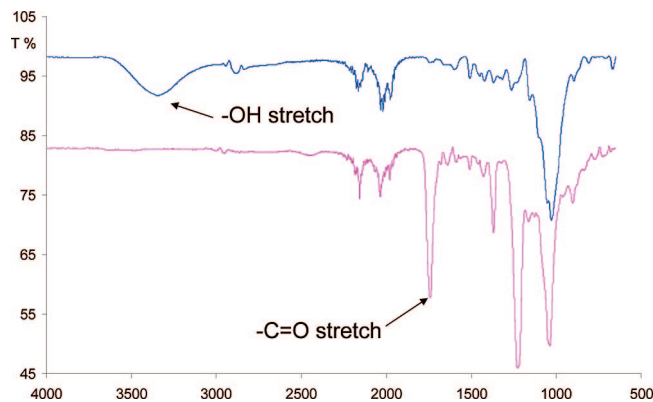


Figure 4. IR spectra (ATR) of vacuum-dried ($50\text{ }^\circ\text{C}$) spruce wood sawdust (top spectrum) and acetylated sample regenerated from [amim]Cl (bottom spectrum; entry 3b, **Table 1**). The signals for the —OH and —C=O stretching bands are indicated.

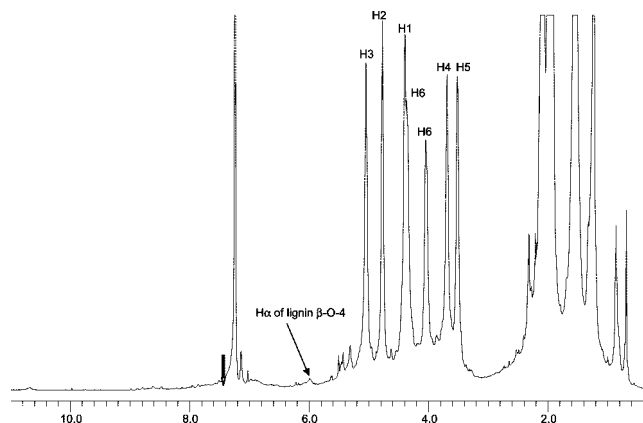


Figure 5. ^1H NMR spectrum (500 MHz) of acetylated Norway spruce sawdust sample dissolved in CDCl_3 . The assignments for acetylated cellulose signals are shown according to ref 35. In addition, the H_α signal due to the lignin $\beta\text{—O—4}$ structures is also shown.

of intact acetylated wood (**Figure 5**). However, the amount of material that could actually be incorporated in chloroform solutions (as well as DMSO, DMF, or acetone) was rather limited, and this limited our attempts to collect more informative two-dimensional correlation data (such as ^1H – ^{13}C HSQC) from the whole sample. Our continuing efforts, however, in the direction of synthesis new wood derivatives and ionic liquids may eventually allow us to overcome these limitations.

At first sight, the ^1H spectrum of acetylated wood seems somewhat surprising, because the signals from lignin are of rather low intensity as compared to the signals from cellulose, which are seen to dominate the spectrum. There are, however, two parameters that need to be carefully considered at this point. Because cellulose is a highly homogenous polymer, all of its signals are anticipated to show a similar proton chemical shift (i.e., the H-1 resonating at about δ 5.1). Lignin, on the other hand, is a highly irregular polymer. The lignin polymer is composed of different types of subunits, and even the signals from certain types of subunits will have a larger chemical shift dispersion caused by the neighboring structures (3). From the subunits of lignin, the signal from the α proton in $\beta\text{—O—4}$ substructures is known to possess a unique chemical shift at 6.0 ppm (3). Furthermore, during our work we determined the amounts of cellulose and lignin in the examined Norway spruce. This was found to be approximately 50% cellulose and 26% lignin. On the basis of the 26% lignin content, only about 20% of these are known to belong to $\beta\text{—O—4}$ subunits (1, 2). Therefore,

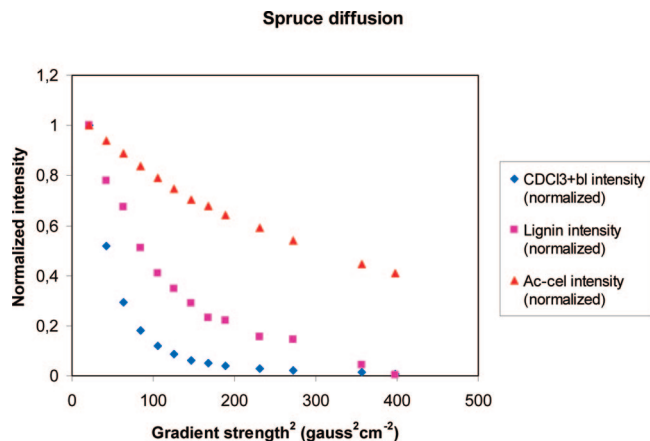


Figure 6. Diffusion measurements on acetylated Norway spruce sample dissolved in CDCl_3 ; diffusion rates of CDCl_3 (\blacklozenge), lignin β -O-4 α proton (\blacksquare), and cellulose H-1 (\blacktriangle).

the intensity of the β -O-4 signals for lignin should be approximately 8% of the proton signal intensity of cellulose. Careful integration of the ^1H spectrum depicted in **Figure 6** yielded a value of 7.3%, which is in good agreement with the anticipated value.

The spectroscopic NMR characterization of acetylated intact wood in deuterated chloroform offers additional opportunities for addressing remaining questions related to the macromolecular and connectivity issues among the various wood components. To demonstrate this, we subjected the acetylated sample to NMR diffusion measurements (30). Such diffusion data provide ideal mobility information of the various molecules present in solution. Small molecules usually show characteristic large diffusion rates (such as the solvent present in an NMR sample), whereas larger molecules and macromolecules show smaller diffusion rates. Furthermore, it needs to be emphasized that the diffusion rates of all molecules are dependent on their hydrodynamic volume, which is related to the molecular weight, providing direct information about chemical bonding between molecules. In a diffusion experiment, the sample magnetization is first excited by a normal RF pulse, which is followed by a gradient pulse. Then follows a diffusion period (τ), which is a period when molecules are allowed to diffuse in the NMR tube. After τ , another gradient pulse with the opposite sign to the first one is applied to refocus the residual magnetization, and the spectrum (otherwise normal ^1H spectrum, but attenuated proportionally to the diffusion speed of the molecule in question) is collected. If a molecule has high diffusion speed (small molecules), its signal decays more quickly than those of molecules with small diffusion speed (large molecules). Therefore, the decay speed of the signals provides direct information of the mobility of the molecules in solution; covalently attached molecules should display exactly similar diffusion speeds. In practice, the diffusion measurements are usually carried out by varying the strength of the gradient pulses instead of varying the diffusion delay τ . The outcome of such experiments is similar to varying the diffusion delay but avoids the influence of relaxation during the experiment (32). Such diffusion measurements carried out on a sample of completely acetylated Norway spruce sawdust are shown in **Figure 6**. Notably, the diffusion rates of lignin (α signal of the β -O-4 subunits) and cellulose (H-1 protons) are clearly smaller than that of the solvent (i.e., the decay rate of the signal). Most significant, however, is the fact that cellulose and lignin have clearly different diffusion rates. Cellulose has a much lower overall diffusion constant as compared to lignin. The decay of the

cellulose and lignin signals (as well as chloroform) follows essentially single exponential behavior. The implications of these measurements suggest that there are no covalent linkages between cellulose and lignin in native wood. On the basis of the present data it seems probable that if there are covalent lignin-carbohydrate linkages in wood, they are more likely to exist between hemicelluloses and lignin rather than cellulose and lignin. Alternatively, the situation may be different between different species of wood, and this remains to be explored in detail. The possible linkage between lignin and carbohydrates is a question that has been puzzling researchers for a long time. It is practically impossible to isolate completely carbohydrate-free lignin samples from wood, but it has been very difficult to obtain precise structural information from intact wood.

In the present article, we have demonstrated that wood is fully soluble into certain ionic liquids. More specifically, we have discovered that most ionic liquids can only partially dissolve wood chips, whereas ionic liquids such as [Bmim]Cl and [Amim]Cl have good solvating power for Norway spruce sawdust, Norway spruce, and southern pine TMP fibers. Transparent amber solutions of wood could be obtained when the dissolution of the same lignocellulosic materials was attempted in [benzylmim]Cl. The fact that it became possible to fully acetylate wood is testimony to the complete accessibility of the various wood components to the chemical reagents, providing additional evidence supporting its total solubilization. During the dissolution, the components of wood remained intact, which opens a whole range of possibilities to utilize wood in an efficient manner. From these solutions wood can be readily regenerated as an amorphous material. After this dissolution-regeneration treatment, wood cellulose can be efficiently digested to glucose, which could be processed to various commodity chemicals (and fuels) (25). Considering the relatively wide solubility characteristics and compatibility of ionic liquids with many organic or inorganic functional chemicals or polymers, one may envisage that this research could create a variety of new strategies for converting our abundant woody biomass to valuable chemicals and novel functional composite biomaterials (33, 34). A variety of such promising technology platforms are currently under investigation in our laboratories aimed at further augmenting and exploring the full potential of the described research, details of which will be published in due course.

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