IONIC LIQUIDS FOR THE DISSOLUTION AND REGENERATION OF CELLULOSE

Richard P. Swatloski, John D. Holbrey, Scott K. Spear, and Robin D. Rogers*

Department of Chemistry and Center for Green Manufacturing
The University of Alabama, Box 870336, Tuscaloosa, AL 35487-0336

ABSTRACT

There is an increasing willingness to develop new cellulose-based materials, particularly from homogeneous solution, due to the fact that cellulose is the earth’s most abundant biorenewable resource. The opportunity to use ionic liquids as solvents for clean extraction and processing of cellulose has been investigated. Cellulose can be dissolved in a number of ionic liquids and easily regenerated by contacting with water. This allows a simple, benign system for the processing of cellulose into fibers, monoliths, and films by forming into an aqueous phase. This has potential environmental and cost advantages over current processing methodologies which make use of volatile or hazardous solvents.

INTRODUCTION

In the past, society’s perceptions of chemistry and the chemical industry were centered on the discovery of new beneficial drugs, technology, and overall improvements in the quality of life. However, with the rapidly expanding chemical industry, societal perceptions of chemistry have become increasingly more negative. With the current desire to develop sustainable resources as alternatives to petroleum-based chemical feedstocks, there is a significant potential for growth and diversification in the applications of cellulose-based materials. The growing willingness to develop new cellulosic materials results from the fact that cellulose is a renewable resource, though many of the technologies currently used in cellulose processing are decidedly non-green (1). The chemical community is beginning to realize that sustained growth, revenue, and scientific development may be a direct result of taking into account how our production practices and technologies impact the health and safety of employees and the environment. Subsequently, the idea of “green chemistry” was established to promote the research, development, and implementation of innovative chemical technologies to achieve pollution prevention in a technologically and economically sound manner.

Based on the large amount of volatile organic compounds consumed, alternatives to their consumption appear as promising choices towards pollution prevention. We have been investigating ionic liquids (ILs) as alternatives to traditional organic solvents in industrial applications. In our research, we have focused on ILs incorporating the 1-alkyl-3-methylimidazolium ([C\text{\textsubscript{mim}}]+) cation, as shown in Figure 1. The alkyl group is usually an \( n \)-alkyl and increasing the length of the alkane chain affects the resulting properties (e.g., viscosity, hydrophobicity, and melting point). A wide range of anions...
including [PF$_6$], [BF$_4$], [NTf$_2$], Cl, Br, and SCN, can be used to form ILs applicable across a wide array of technologies. The choice of cation and anion, along with the type of substituent(s) on the cation, permits fine-tuning of the hydrophobicity, melting points, and other physical properties of the IL. The use of ILs as replacements for conventional organic solvents in chemical (2,3), biochemical (4), and separation (5,6,9) processes has been demonstrated.

![Figure 1](image1.png)

**Figure 1.** The 1-alkyl-3-methylimidazolium cation is used as the basis for many ILs.

Cellulose is one of nature’s most abundant biorenewable materials and cellulose-derived products have been used in all cultures from the most primitive to the most highly developed modern technological societies (10). Cellulose is a polydisperse polymer composed of linear glucose units (Figure 2) which form a range of supramolecular semi-crystalline structures (11,12), as a result of the highly ordered hydrogen-bonding between hydroxyl groups. Due to this extensive hydrogen-bonded network, cellulose is insoluble in water and most common organic solvents, without chemical derivatization of at least one of the hydroxyl functions.

![Figure 2](image2.png)

**Figure 2.** Molecular structure of the cellulose polymer chain, $n$ is typically 400-1000.

Cellulose and cellulose derivatives, obtained from trees and cotton plants, can be used as a biorenewable source of chemicals, for example, to prepare polymers for applications in paints, plastics and for the formulation of other materials such as fiber, paper, and membranes. Physical and chemical processing methods for treating cellulosic resources are numerous. Chemical, enzymatic, microbiological, and macrobiological catalysts can be used to accelerate the process under conditions selected to be thermodynamically favorable to product formation. Chemical processes include oxidation, reduction, pyrolysis, hydrolysis, isomerization, esterification, alkoxylation, and copolymerization. Wood, paper, cotton, rayon, cellulose acetate, and other textiles are a few examples of the broad range of cellulosic materials. Some of the most important cellulose derivatives and their world wide production are shown in Table I. However, despite the extensive utilization of cellulosic materials, their full potential has not been fully exploited, partially due to the historical shift towards petroleum-based polymers from the 1940’s onwards, and also by the limited number of common solvents in which cellulose is readily soluble.
There are only a limited number of common solvents in which cellulose is soluble; such solvents include, carbon disulfide, \( N,N\)-dimethylacetamide/lithium chloride (DMAC/LiCl), concentrated inorganic salts (ZnCl\(_2\)/H\(_2\)O, Ca(SCN)\(_2\)/H\(_2\)O), and mineral acids (H\(_2\)SO\(_4\), H\(_3\)PO\(_4\)), or molten salt hydrates (including LiClO\(_4\)+3H\(_2\)O and NaSCN/KSCN/LiSCN/H\(_2\)O eutectics). A list showing the solvent classes that have been reported for the non-derivatizing dissolution of cellulose are shown in Table II. Among the limitations of many non-derivatizing cellulose solvents are high toxicity, high reactivity of the solvents leading to undesired side reactions, and the loss of solubility during reactions yielding inhomogeneous conditions by formation of gels and pastes. The efficiency of existing methods for dissolving and derivatizing cellulose can be significantly improved by the availability of suitable solvents for refined and natural cellulose; such an example is \( N\)-methylmorpholine-\( N\)-oxide (NMNO), used as a solvent for non-derivatizing dissolution of cellulose for the production of lyocell fibers (13). NMNO dissolves cellulose typically as the monohydrate (about 13% water) at about 100 °C.

### Table I. Examples of Cellulose Esters and Ethers Commercially Produced.

(Data from reference 14.)

| Product               | Global Production\(^a\) | Functional Group | \(D_f\)^\(^b\) | Examples of solubility        |
|-----------------------|--------------------------|------------------|----------------|-----------------------------|
| Cellulose acetate     | 900,000                  | -C(O)CH\(_3\)    | 0.6-0.9        | Water                      |
|                       |                          |                  | 1.2-1.8        | 2-methoxy ethanol           |
|                       |                          |                  | 2.2-2.7        | Acetone                    |
|                       |                          |                  | 2.8-3.0        | Chloroform                 |
| Cellulose acetopropionate | c                      | -C(O)CH\(_3\)CH\(_3\)  | 2.4/0.2 | acetone, ethyl acetate       |
| Cellulose acetobutyrate | c                      | -C(O)CH\(_3\)CH\(_2\)CH\(_3\) | 0.2/2.7 | acetone, DiBK               |
| Cellulose nitrate     | 200,000                  | -NO\(_2\)        | 1.8-2.0        | Ethanol, methanol, acetone, MEK |
|                       |                          |                  | 2.0-2.3        | Acetone                    |
|                       |                          |                  | 2.2-2.8        | acetone, MEK               |
| Cellulose xanthate    | 3,200,000                | -C(S)SNa         | 0.5-0.6        | aqueous NaOH               |
| Carboxymethyl cellulose | 300,000                 | -CH\(_2\)COONa   | 0.5-2.9        | Water                      |
| Methyl cellulose      | 150,000                  | -CH\(_3\)        | 0.4-0.6        | 4% aqueous NaOH          |
|                       |                          |                  | 1.3-2.6        | cold water                 |
|                       |                          |                  | 2.5-3.0        | organic solvents           |
| Ethyl cellulose       | 4,000                    | -CH\(_2\)CH\(_3\) | 0.5-0.7        | 4% aqueous NaOH            |
|                       |                          |                  | 0.8-1.7        | cold water                 |
|                       |                          |                  | 2.3-2.6        | organic solvents           |
| Hydroxyethyl cellulose | 50,000                   | -CH\(_2\)CH\(_2\)OH | 0.1-0.5 | 4% aqueous NaOH            |
|                       |                          |                  | 0.6-1.5        | water                      |

\(^a\)Tons/annum. \(^b\)\(D_f\) is degree of functionalization (0-3). \(^c\)No production number available.
In addition to bulk dissolution, solvents are needed for characterization of materials. The system DMAC/LiCl is used as a solvent for the analysis of cellulose and for the preparation of a wide variety of derivatives. Its usefulness in analysis is due to the fact that the solvent is colorless and dissolution succeeds without or at least with negligible degradation even in case of high molecular weight polysaccharides, e.g. cotton linters or bacterial cellulose.

Table II. Solvent Classes for Non-Derivatizing Dissolution of Cellulose.

| Type of Solvent         | Example                                      |
|-------------------------|----------------------------------------------|
| Organics                |                                               |
| N-alkylpyridinium halogenides | N-ethylpyridinium chloride                  |
| oxides of tertiary amines | N-methylmorpholine-N-oxide                    |
| Bicomponent mixtures    |                                               |
| dimethyl sulfoxide (DMSO) containing solvents | DMSO/methylamine                           |
| liquid ammonia/sodium or ammonium salts | NH₃/NaSCN (NH₄SCN)                          |
| Dipolar aprotic solvents/LiCl | N,N-dimethylacetamide                     |
| Tricomponent mixtures   |                                               |
| amine/salt/polar solvent | NH₃/NaCl/DMSO                                |
| Metal/amine complexes   |                                               |
| Cadoxen                 | [Cd(H₂N(CH₂)₂NH₂)₃](OH)₂                     |
| Cuen                    | [Cu(H₂N(CH₂)₂NH₂)₂](OH)₂                     |
| Ammonium hydroxides     |                                               |
| Triton B                | trimethylbenzyl ammonium hydroxide           |
| Pure salts              |                                               |
| ZnCl₂•4H₂O, LiClO₄•3H₂O |                                               |
| Salt mixtures           |                                               |
| LiClO₄•3H₂O/MgCl₂•6H₂O  |                                               |
| LiClO₄•3H₂O/Mg(ClO₄)₂•H₂O |                                           |

Solvents are needed which will allow for homogeneous dissolution without prior derivatization (15,16). The dissolution of cellulose in molten organic salts was first described by Graenacher (17) in 1934. Molten N-ethylpyridinium chloride, in the presence of nitrogen-containing bases, was used as the solvent system, however, N-ethylpyridinium chloride has a relatively high melting point (118 °C) and the molten salt system was, at the time, a somewhat unusual and uncommon material. Also, this original work was undertaken at a time when ILs were essentially unknown and the application and value of ILs as a class of solvents had not been realized.
We have recently reported initial findings that indicate that cellulose can be dissolved in a series of ILs (18). The availability of a wide and varied range of ILs (19, 22), coupled with the current understanding of their solvent properties (23), is anticipated to allow flexibility and control in the processing methodology, with increased solution efficiency and reduction or elimination of undesirable solvents.

EXPERIMENTAL

A range of ILs containing the 1-butyl-3-methylimidazolium cation ([C₄mim]+) were screened. The anions used varied from small, hydrogen-bond acceptors (Cl⁻) to large, non-coordinating anions ([PF₆]⁻) also including Br⁻, [SCN]⁻, and [BF₄]⁻. In addition, the alkyl-chain substituent of the imidazolium cation was varied from butyl through octyl for the chloride salts. This has the effect of decreasing the melting point and lowering the operating temperature of the solvent ([C₄mim]Cl, for example, is a low melting, crystalline solid), but increases the viscosity of the resulting IL. The halide-containing ILs were prepared by alkylation of 1-methylimidazole with the corresponding haloalkane using literature methods (19). The remaining ILs ([C₄mim][PF₆], [C₄mim][BF₄], and [C₄mim][SCN]) were prepared from [C₄mim]Cl by metathesis.

The cellulose samples used included cellulose dissolving pulps (from International Papers' cellulose acetate, lyocell, and rayon production lines; degrees of polymerization from 487 to 1056). Fibrous cellulose (Aldrich), and Whatman cellulose filter papers were also examined. Samples were used as received, without any cellulose pretreatment. Screening studies were performed by placing a weighed sample of cellulose in a flat-bottomed vial, adding IL. The mixture was then heated without agitation in a thermostatted oven, or in a domestic microwave oven using short (3-5 s heating pulses). [C₄mim]Cl, which was a solid at room temperature, was pre-heated to above the melting point before adding to the cellulose samples. In each case, for the chloride ILs, on initial contact of the cellulose with the IL, the cellulose particles were observed to swell. Heating caused the cellulose to slowly dissolve in the IL, over a number of hours to give a viscous solution. Viscous pastes, containing over 25% by weight of cellulose could be prepared by mechanical working of the mixture combined with further heating.

The rate of cellulose dissolution was significantly improved using a microwave oven for heating. A 10 wt% solution was prepared by the following procedure: 0.5-1.0 g fibrous cellulose was placed in a glass vial and [C₄mim]Cl (10 g) was added as a liquid at 70 °C. The loosely capped vial was then placed in a domestic microwave oven and heated with 3-5 second pulses at full power. The vial was removed from the microwave oven between pulses, shaken or vortexed, and replaced in the oven. This procedure was repeated until a clear, colorless, viscous solution was obtained. ILs are heated with exceptional efficiency by microwaves (24) and care must be taken to avoid excessive heating that induces cellulose pyrolysis. The decomposition appears to be more rapid in contact with the ILs than for isolated cellulose under equivalent conditions.

Samples were regenerated by contacting the solutions of cellulose in IL with water. Threads were prepared by extruding the solution from a disposable syringe into a...
beaker of water. Cellulose films were obtained by coating a glass microscope slide with an even layer of the IL solution (approximately 1-2 mm thick). The slide was then immersed in a water bath. Initial, regenerated cellulose samples were flexible and apparently very porous. On drying, significant shrinkage occurred to form hard, resilient materials. The regenerated materials were then characterized by differential scanning calorimetry (DSC, TA 2620 DSC equipped with cryostat cooling; 5-20 mg samples; 5 °C min⁻¹ heating and cooling rates), thermogravimetric analysis (TGA, TA 2950, 10 °C min⁻¹ heating rate under nitrogen), and size exclusion chromatography (SEC). Scanning Electron Microscopy (SEM) was used to observe the bulk structure.

RESULTS AND DISCUSSION

The results obtained from screening high MW dissolving pulp (DP ~1000) in a range of ILs under thermal and microwave heating are summarized in Table III. The cellulose did not appear to dissolve in any of the ILs under ambient conditions at room temperature, although the cellulose fibers were wetted by the ILs. On heating to 100-110 °C, the cellulose fibers started to swell. Increasingly viscous solutions formed as cellulose slowly dissolved in the Cl⁻, Br⁻, and [SCN]⁻ containing ILs.

Table III. Solubility of High MW Dissolving Pulp (DP ~1000) in ILs Under Thermal and Microwave Heating (18).

| IL       | Method       | Solubility (wt%) |
|----------|--------------|------------------|
| [C₄mim]Cl | heat (100 °C) | 10%              |
|          | heat (70 °C)  | 3%               |
| [C₄mim]Cl | heat (80 °C) +| sonication       | 5%               |
|          | microwave heating | 25%, clear viscous 3-5 s pulses solution |
| [C₄mim]Br | Microwave    | 5-7%             |
| [C₄mim][SCN] | Microwave     | 5-7%             |
| [C₄mim][BF₄] | Microwave     | Insoluble        |
| [C₄mim][PF₆] | Microwave    | Insoluble        |
| [C₄mim]Cl | heat (100 °C) | 5%               |
|          | heat (100 °C) | slightly soluble  |

Cellulose dissolution is most efficient in ILs containing halide anions, in particular chlorides. The most dramatic effect was observed when samples of cellulose were heated in halide and pseudohalide ILs in a microwave oven. The greatest solubility of cellulose was obtained using [C₄mim]Cl. All the cellulose samples tested rapidly dissolved in [C₄mim]Cl to produce clear solutions in a matter of minutes. Cellulose concentration in the ILs can be up to about 25-30 wt%, producing viscous liquids or gels at high concentration. Compositions between 5-10 wt% cellulose are more easily prepared for the ILs screened. The viscous solutions obtained were optically anisotropic between crossed polarizing filters and displayed birefringence when high concentrations of cellulose (> 10 wt%) were dissolved in [C₄mim]Cl. This is indicative of a liquid crystalline phase. Solutions of cellulose that exhibit liquid crystalline behavior may have
useful applications for the generation of new, advanced materials (25). High strength materials that conserve anisotropy in the solid phase are especially desirable, yielding enhanced mechanical properties.

The key to non-derivatizing dissolution of cellulose is the ability to break the extensive hydrogen-bonding network present. Non-derivatizing solvents for cellulose effect dissolution by disrupting and breaking the intramolecular hydrogen-bonding network, for example, in dimethylacetamide/lithium chloride (DMAC/LiCl), complexation of lithium ions by DMAC mobilizes the chloride ions which interact with the cellulose hydroxyl-groups. In a typical 10 wt% LiCl/DMAC solution used for dissolving cellulose, free chloride ion concentration is about 6.7 mol%. In contrast, [C₄mim]Cl has a chloride concentration almost 3 times as high, (ca. 20 mol%). In both DMAC/LiCl and [C₄mim]Cl, the chloride ions are non-hydrated. It seems likely that the high concentration of non-hydrated chloride ions in [C₄mim]Cl is responsible for breaking the extensive hydrogen-bonding network present, which allows for much quicker dissolution times, and the ability to dissolve higher concentrations of cellulose.

The ILs with longer-chain substituents ([C₆mim]Cl and [C₇mim]Cl) appear to be less efficient at dissolving cellulose than [C₄mim]Cl. This may be due to the reduced effective chloride concentration within these liquids. A choice of IL has to be made, based on a set of criteria including solubilizing power and rheological properties; when cooled to room temperature, solutions of cellulose in [C₇mim]Cl form a viscous liquid, whereas solutions with [C₄mim]Cl crystallize.

The presence of water in the IL was shown to significantly decrease the solubility of cellulose, presumably through competitive hydrogen-bonding to the cellulose microfibrils which inhibits solubilization. When water was added to the IL at concentrations greater than ca. 1 wt% (approximately 0.5 mole fraction H₂O) the solvent properties were significantly impaired and cellulose was no longer soluble. Hydrogen-bonding properties are important in solvents for the dissolution of cellulose, for example anhydrous and monohydrated NMNO are good solvents, however, when completely hydrated by two or more waters, NMNO is no longer a good solvent for cellulose (26). Similarly, the ability of molten inorganic salt hydrates (27) to dissolve cellulose depends on the degree of ion hydration and is thought to occur via coordinating the cellulose hydroxyl groups to the metal-cation (when deficient in water).

Cellulose could be precipitated from the IL solution by the addition of water, or other precipitating solutions including ethanol and acetone. The macroscopic morphology of the regenerated cellulose varied depending on how contact of the IL solution and the regeneration liquid was achieved. To explore the scope for processing of cellulose from ILs, we prepared monoliths, fibers, and films by forming into an aqueous phase. Rapid mixing of the IL solution with an aqueous stream results in precipitation of cellulose as a powdery floc. By extrusion of the IL/cellulose solution into water, thin fibers and rods were prepared.

Scanning electron micrographs of fibrous cellulose before treatment, and after regeneration from [C₄mim]Cl are shown in Figure 3 at 300x magnification and a zoomed close-up, at higher magnification for the regenerated material. The original fibrous material has distinct strands, whereas after regeneration, the sample was largely
amorphous and showed a relatively smooth, homogeneous texture. The close-up picture, under high magnification (7000×) shows clearly that the initial fibers are no longer present, and that the cellulose has been regenerated as a single bulk macrostructure. SEC indicated that the dissolving pulp could be solubilized in [C₄mim]Cl and regenerated from water without significant change in the degree of polymerization or polydispersity.

Figure 3. SEM micrographs of fibrous cellulose showing the sample fibers (A), and the same materials after dissolution in [C₄mim]Cl and regeneration from water (B). Both A and B are at the same magnification (300×). The higher magnification (7000×) image of regenerated cellulose (C) shows the fused, homogeneous form with no residual fibers.

TGA curves are shown in Figure 4 for dissolving pulp after microwave induced dissolution in [C₄mim]Cl, and regeneration into a water bath. Rapid decomposition in a narrow temperature range from 350-360 °C is observed for the initial, untreated cellulose sample. The regenerated and dried material exhibits a lower onset temperature for decomposition, but gives a higher char yield (non-volatile carbonaceous material) on pyrolysis, indicated by the high residual masses after the decomposition step.

Figure 4. Thermal decomposition profiles of cellulose regenerated from [C₄mim]Cl IL into water (i) and of the original untreated dissolving pulp (ii). Samples were heated in platinum sample containers under a nitrogen atmosphere at 10 °C min⁻¹.
CONCLUSIONS

This research has shown that ILs can be used as non-derivatizing solvents for cellulose. Chloride containing ILs appear to be the most effective solvents and are the most strongly hydrogen-bonding. The ability of the ILs to dissolve cellulose varies significantly with the size and polarizability of the anion present, and also the nature of the cation, presumably solubilizing cellulose through hydrogen-bonding from hydroxyl functions to the anions of the solvent. Cellulose can be regenerated from the IL solution in a range of structural forms by simply contacting the cellulosic solution with water providing a simple system for the processing of cellulose into fibers, monoliths, and films. Thus, ILs have potential environmental and cost advantages over current processing methodologies, which make use of volatile and/or hazardous solvents.

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