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Ionic Liquids and Their Interaction with Cellulose

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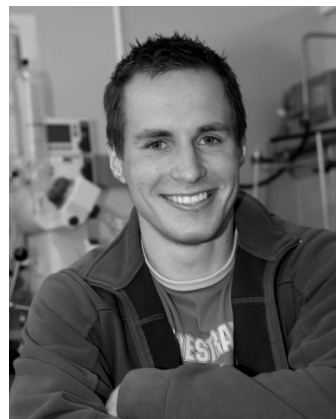
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1. Introduction

Sustainability, industrial ecology, eco-efficiency, and green chemistry are directing the development of the next generation of materials, products, and processes. Biodegradable plastics and biocompatible composites generated from renewable biomass feedstock are regarded as promising materials that could replace synthetic polymers and reduce global dependence on fossil fuel sources.¹ It is estimated that the world is currently consuming petroleum at a rate 100 000 times faster than nature can replace it.² The growing global environmental awareness and societal concern, high rate of depletion of petroleum resources, concepts of sustainability, and new environmental regulations have triggered the search for new products and processes that are more compatible with the environment.

The most abundant natural polymer in our environment is cellulose. It has an estimated annual biosphere production of 90×10^9 metric tons and, consequently, represents the most obvious renewable resource for producing biocomposites.³ Its highly ordered structure is responsible for its desirable mechanical properties but makes it a challenge to find suitable solvents for its dissolution.⁴



André Pinkert was born in Schwabach, Germany, in 1981. He studied Chemistry at the University of Erlangen-Nürnberg, Germany, and received his prediploma and diploma degrees in 2004 and 2008, respectively. During 2005, he joined the Marine Natural Products Group, lead by Murray H. Munro and John W. Blunt, at the University of Canterbury (UoC), New Zealand, working on the isolation and characterization of bioactive metabolites. In early 2006, he returned to Germany and resumed his studies at the University of Erlangen-Nürnberg, finishing his degree under the supervision of Rudi van Eldik. Associated with his studies, during 2007, he worked for AREVA NP on radio-nuclear chemistry and computer modeling. Since 2008, he is studying towards a Ph.D. degree at UoC under the supervision of Shusheng Pang, Ken Marsh, and Mark Staiger. His research focuses on biocomposites from natural fibers, processed via ionic liquids.

The first attempts to dissolve cellulose date back to the early 1920s.⁵ Several aqueous and nonaqueous cellulose solvents have been discovered since then, but all of these solvents suffer either from high environmental toxicity or from insufficient solvation power.⁶ In general, the traditional cellulose dissolution processes require relatively harsh conditions and the use of expensive and uncommon solvents, which usually cannot be recovered after the process.^{6–10}

However, a new class of solvents was opened to the cellulose research community, when in 2002 Swatloski et al. reported the use of an ionic liquid as solvent for cellulose both for the regeneration of cellulose and for the chemical modification of the polysaccharide.⁷ In 1934, Graenacher had discovered a solvent system with the ability to dissolve cellulose, but this was thought to be of little practical value at the time.^{11,12}

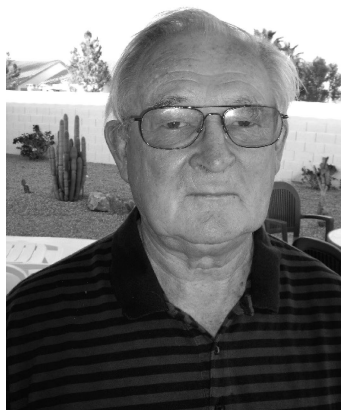
Ionic liquids are a group of salts that exist as liquids at relatively low temperatures (<100 °C). They have many attractive properties, including chemical and thermal stability, nonflammability, and immeasurably low vapor pressure.¹² First discovered in 1914 by Walden, their huge potential in industry and research was only realized within the last few decades.^{13,14}

This review aims to provide a summary of our current state of knowledge on the structural features of wood

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Ken Marsh was born in Melbourne, Australia, in 1939 and completed his B.Sc. (Hons) at the University of Melbourne, Australia, in 1960 and his Ph.D. in Physical Chemistry at the University of New England, Australia, in 1968 under Professor Robin H. Stokes. In 1966, he took an appointment at The University of New England and was promoted to Associate Professor in 1974. In 1983, he moved to Texas A&M University, initially as Associate Director of the Thermodynamics Research Center and then, in 1985, as Director. In addition he held appointments in both Chemical Engineering and Chemistry Departments at Texas A&M. In 1997, he retired as Director and took a position at the University of Canterbury, New Zealand, and he retired as Professor in 2005. He remains Editor in Chief of the Journal of Chemical and Engineering Data. His interests include thermodynamic and transport properties of nonelectrolyte solutions, gas hydrates, and ionic liquids and the development of new experimental techniques to measure thermophysical properties of fluids. He has also been active in database development, including the IUPAC ionic liquid database. He was awarded in 1969 the Nuffield Dominion Travelling Fellowship, in 1972 the Royal Australian Chemical Institute Rennie Memorial Medal, in 1988 a Texas Engineering Experiment Station Senior Fellow. In 1996, he was awarded an Honorary Medal by the Institute of Physical Chemistry, Polish Academy of Science, for significant contribution to the advancement of Physical Chemistry at the Polish Academy of Science. In 2007, he was awarded the Donald J. Katz award by the Gas Processors Association for outstanding accomplishments in gas processing research. He was chairman of the IUPAC Commission of Physicochemical Measurements and Standards, IUPAC representative to CODATA, Chairman, ASTM Subcommittee D03.03, and a member of the IUPAC Physical Chemistry Division Committee and Chairman of the CODATA Task Group on a World Data Depository. He is the author of over 180 research papers and an author, coauthor, or editor of 20 books.

cellulose, the influence of the ion type and ion structure on the physical properties of ionic liquids, the application of ionic liquids as solvents for cellulose, and possible routes for cellulose functionalization.

2. Cellulose

Cellulose is the most common organic polymer and is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products. Wood consists of up to 47 % cellulose, which is the main structural component of the primary cell walls of plants.¹⁵ Although wood pulp remains the most important raw material source for cellulose, it can also be extracted from algae, bacteria, and annual crops.¹⁶

Cellulose is a linear polymer of cellobiose that consists of two glucose sugar units that are linked by glucosidic linkages (C—O—C) at the C₁ and C₄ positions. Its structure is shown in Figure 1. The size of its chains depends on the degree of polymerization (DP), which is the number of repeating units of glucose. The DP can vary considerably, from about 20 in the case of laboratory-synthesized cellulose to about 10 000 or more for bacterial cellulose.^{16,17} Each glucose unit is rotated through 180° with respect to its



Shusheng Pang was born in Hebei, China, in 1958. He received B.E. and M.E. in Chemical Engineering from Hebei University of Technology in 1982 and 1987, respectively. He completed his Ph.D. thesis in 1994 in the Department of Chemical and Process Engineering, University of Canterbury, New Zealand, with Professor R. B. Keey on high-temperature drying of softwood. Prior to joining the University of Canterbury in 2002, Dr. Pang held a research position at the New Zealand Forest Research Institute on wood processing. Recently Professor Pang, working with Professor Ken Marsh and Dr. Mark Staiger, has been leading a research program at the University of Canterbury on development of new synthesis materials from renewable sources such as wood.



Mark P. Staiger trained as a materials engineer in the Department of Materials Engineering, Monash University, Australia, and subsequently received his Ph.D. degree from the same University in 2001. Dr. Staiger has worked on polymer-related research for the past 8 years in his current position as Senior Lecturer at the University of Canterbury, New Zealand. A major theme within his research group is the use of cellulose in nanocomposites, biocomposites, biofoams, electrospinning, and biomaterials. Currently, his research is concerned with viable manufacturing pathways for a new group of eco-materials known as all-cellulose composites, aided by funding from the New Zealand Foundation for Research, Science and Technology.

neighbor, so that the structure repeats itself every cellobiose unit. Wood cellulose contains about 10⁴ units, and reaches a length of about 5 μm in the highly crystalline regions.¹⁵ One chain end has a reducing hemiacetal group at the C₁ position while the other end has an alcoholic hydroxy (OH—) group on the C₄ carbon position.

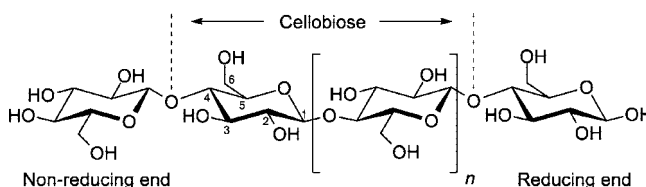


Figure 1. Cellulose polymer chain structure.

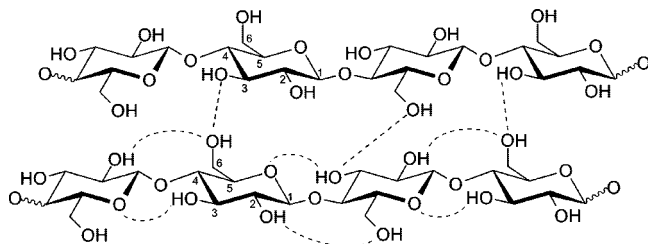


Figure 2. Intra- and intermolecular hydrogen bonds in cellulose.

Native cellulose is a linear but semicrystalline polymer, consisting of highly structured crystalline regions (microfibrils) and amorphous parts. Other plant polysaccharides such as lignin and hemicellulose have branched structures.¹⁸ The very stable β -(1 \rightarrow 4)-link is reinforced by intrachain hydrogen bonds between the C₃ hydroxy group and the adjacent in-ring oxygen, as well as between the C₂ hydroxy group and the hydroxymethyl group oxygen on C₆ (Figure 2).¹⁹ In the natural state, about 40 to 70 cellulose chains are interconnected by obvious hydrogen bonds between the C₆ hydroxymethyl and the C₃ hydroxy groups of the adjacent chains to form a microfibril.²⁰ These microfibrils are extremely stiff, having an elastic modulus of about 220 GPa parallel and about 15 GPa perpendicular to the fiber direction.²¹ The high chemical and mechanical stability of cellulose and its hydrophobic nature is due to the strong glycosidic bonds and the huge degree of both intra- and intermolecular hydrogen bondings. They not only act as interconnections between the cellobiose units but are also responsible for the hydrophilic nature of the biopolymer.¹⁷

3. Ionic Liquids

3.1. Fundamentals

Molten salts with low melting temperatures (<100 °C), now referred to as ionic liquids (ILs), attracted first interest in the 1960s at the U.S. Air Force Academy as salt electrolytes for thermal batteries. These first-generation ILs, consisting of binary mixtures of 1-butylpyridinium chlorides ([BPy]Cl) and aluminum chlorides (AlCl₃), suffered from serious limitations like easy electrochemical reduction and air-sensitivity.²² These problems were overcome in the early 1990s with second-generation ionic liquids that were air- and water-stable.²³

The most common examples of these ILs include salts of organic cations, such as alkylimidazolium [R₁R₂IM]⁺, alkylpyridinium [RPy]⁺, tetraalkylammonium [NR₄]⁺, or tetraalkylphosphonium [PR₄]⁺, and anions, hexafluorophosphate [PF₆]⁻, tetrafluoroborate [BF₄]⁻, nitrate [NO₃]⁻, methanesulfonate (mesylate) [CH₃SO₃]⁻, trifluoromethanesulfonate (triflate) [CF₃SO₃]⁻, and bis-(trifluoromethanesulfonyl)amide [Tf₂N]⁻, as well as several low melting chloride, bromide, and iodide salts (Figure 3).²⁴

The number of potential ion combinations available reputedly equates to 10¹² ILs.²⁵ ILs are formed from bulky, unsymmetrical ions with a delocalized charge in order to achieve a low melting temperature. Room-temperature ionic liquids (RTILs) are ILs with a melting temperature below room temperature. The huge variety of possible ion combinations allows for tailoring ionic liquid solvents with specific properties for certain purposes, the so-called task-specific ionic liquids (TSILs).²⁶

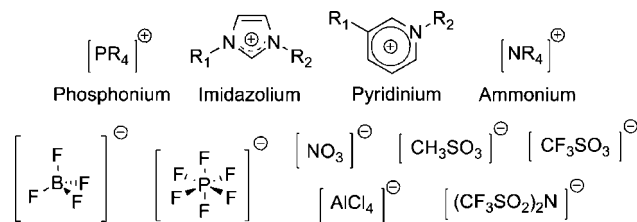


Figure 3. Commonly used cations and anions.

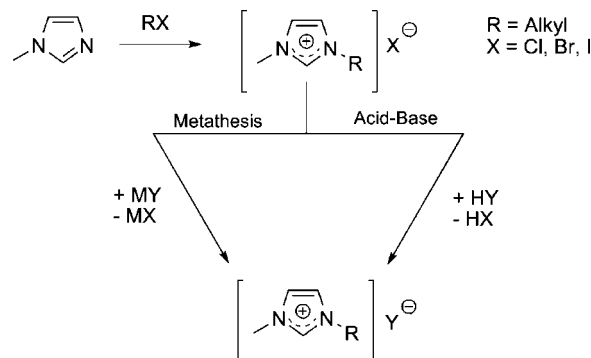


Figure 4. Typical synthesis paths for the preparation of ionic liquids.

3.2. Synthesis and Purification

The synthesis of imidazolium ionic liquids can generally be split into two steps: the formation of the desired cation and then the exchange of the anion to produce the final product according to the scheme shown in Figure 4. The most common ILs are prepared by quaternizing a nitrogen heterocycle with an alkyl halide (Mentschutkin reaction).²⁷ The anion exchange involves either the direct treatment of a halide salt with a strong Lewis acid to form complex anions or the formation of the ionic liquid by the addition of a metal salt to precipitate the unwanted ion (Finkelstein reaction).²⁸ Other synthesis routes have been developed that include solvent and halide free pathways, microwave or sonochemical methods, or using cheaply available industrial products as starting materials, such as, for example, the detergent sodium octylsulfate.²⁹

Depending on the method of synthesis, impurities in the IL can be tertiary amines, alkyl halides or alkyl sulfates or their side-reaction products, and, after metathesis, residual halide or sulfate. Methods of purification include extraction of the IL with polar solvents (e.g., ethyl acetate), extraction of the aqueous solution of IL with an immiscible organic solvent (e.g., dichloromethane), flash column chromatography of a solution of IL in an organic solvent, or treatment of the ionic liquid with activated charcoal.²⁸

3.3. Properties and Applications

ILs offer a variety of physical properties that make them attractive to a broad field of applications. Some of these properties are common to all ILs and as such are defining characteristics. ILs with quaternized nitrogen cations, for example, are nonflammable and were initially thought to have negligible vapor pressure, but Earle et al. showed that they can be distilled under low pressure and high temperature.³⁰ Nevertheless, these desired properties are significant as their negligible vapor pressure means solvent evaporation is limited, thus reducing the need for respiratory protection and exhaust systems. This property also enhances their recycling and is one reason for them often being called “green

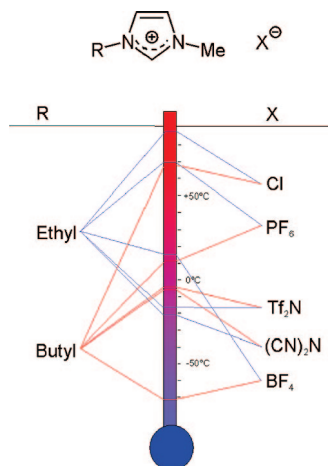


Figure 5. Melting temperatures of selected imidazolium-based ionic liquids depending on their ion composition (adapted from Laus et al.).³⁷

solvents". Recent studies have shown that they have a wide range of toxicity, and as a result, the use of the term "green solvents" has been questioned.^{31,32}

The diversity of ionic liquids makes them applicable to myriads of applications that include optical thermometers, biocatalysis and separation processes, polymer and catalytic chemistry, electrolytes, biosensors, analytic devices, lubricants, solvent replacement applications, and lunar telescopes.^{22,25,26,33,34}

Properties such as melting temperature, thermal stability, refractive index, acid–base character, hydrophilicity, polarity, density, and viscosity can be tailored to a certain degree. However, the presence of reactant impurities such as halide anions, organic bases, and absorbed water can considerably alter their properties, accounting for much of the variability of published property data.^{35,64}

3.3.1. Melting Temperature

The melting temperature and viscosity of ILs depend significantly on the anion type, although the cation does have a minor influence.³⁶ Most ionic liquids show a glass transition, which occurs when a supercooled liquid forms an amorphous solid. Solid ILs in the crystalline state may still contain some amorphous regions, thus showing both a glass transition temperature (T_g) and a melting temperature (T_{fus}). The thermal properties are governed by van der Waals forces and electrostatic interactions, which are primarily determined by the size, symmetry, H-bond interactions, and charge delocalization (Figure 5).^{37,38}

Symmetry. Low-symmetry cations like 1-butyl-3-methylimidazolium [BMIM]⁺ possess only C1 symmetry, and their salts melt at lower temperatures than analogous salts with higher symmetry, such as 1-butylpyridinium [BPy]⁺ salts with C_{2v} symmetry.¹⁴ Figure 6 shows a correlation between symmetry and melting temperature for a group of tetraalkyl phosphonium [P_{nmn}]⁺ ionic liquids. In the series [P_{666n}]PF₆, the melting temperature reaches a maximum for the symmetrical (T_d) cation [P₆₆₆₆]⁺ and decreases as one of the chains gets either longer or shorter, with concomitant symmetry lowering to C_{3v}.¹⁴

Alkyl Chain Length. The length of the alkyl chain also influences T_{fus} . Figure 7 shows an optimized structure of the 1-methyl-3-octadecylimidazolium [C₁₈MIM]⁺ cation. Such cations of the general formula [C_nMIM]⁺ possess a charge-

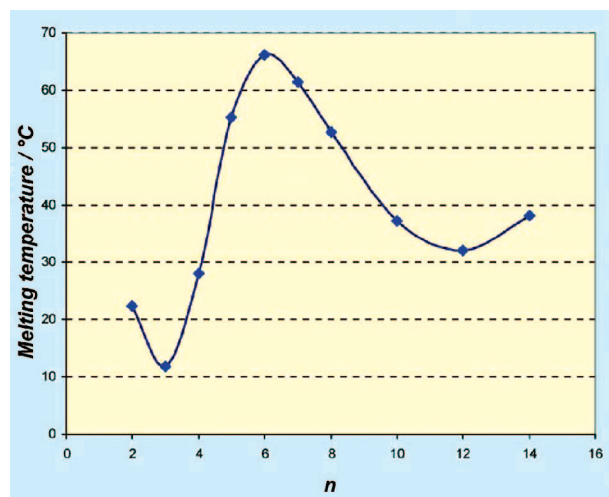


Figure 6. Melting temperatures of [P_{666n}]PF₆ as a function of n (modified from Plechkova and Seddon).¹⁴

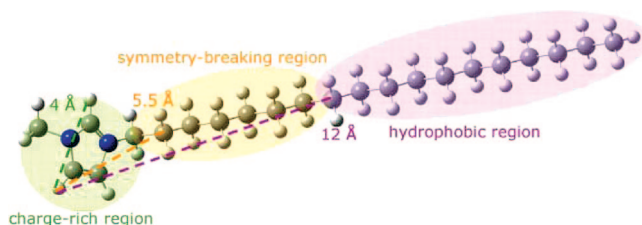


Figure 7. Optimized structure of [C₁₈MIM]⁺ showing structural important regions (adapted from Plechkova and Seddon).¹⁴

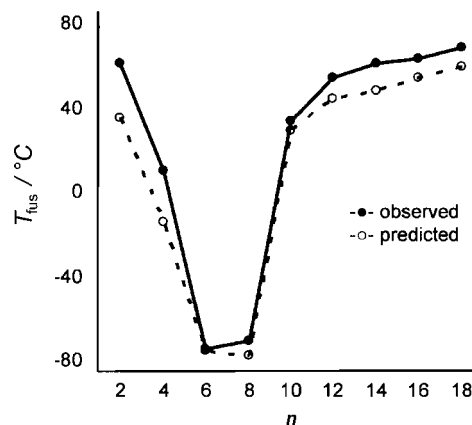


Figure 8. Predicted and observed melting temperatures for a series of [C_nMIM]PF₆ ILs (modified from Plechkova and Seddon).¹⁴

rich imidazolium core and a hydrophobic alkyl side chain. An increasing number of carbon atoms ($n < 7$) in the side chain result in a decrease of the melting temperature due to the lower overall symmetry of the cation (symmetry-breaking region). However, side chains with more than seven carbon atoms lead to an increase of the melting temperature, as attractive van der Waals interactions between the alkyl side chains start outweighing the symmetry effect (hydrophobic region).

Figure 8 also illustrates the agreement between experimental results and a computational study using a QSPR (quantitative structure–property relationship) approach.³⁹

Hydrogen Bonds. The presence or absence of strong hydrogen bonds also influences the melting temperature. The existence of hydrogen bonds in imidazolium ILs was first reported in 1986.⁴⁰ Traditionally, the C–H...X (X = Cl, Br) interaction is characterized as a relatively weak interac-

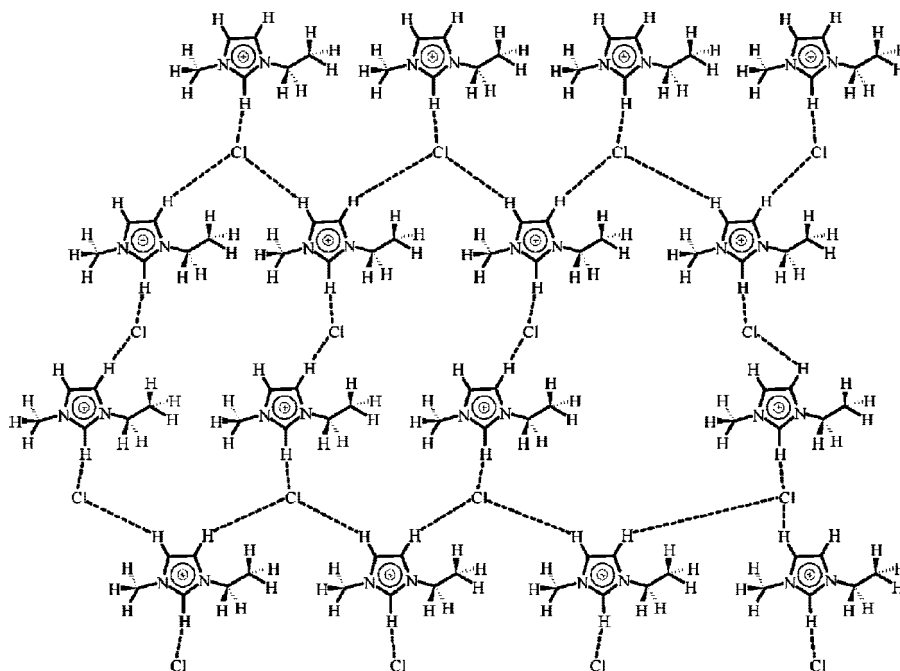


Figure 9. Schematic representation of H-bonding in [EMIM]Cl (adapted from Heinze et al.).²⁸

tion, but it becomes very strong in imidazolium-based halide ILs and can even possess some covalent character.⁴¹ These strong hydrogen bonds involve all three imidazolium ring protons resulting in a three-dimensional ion-network with aromatic π -stacking interactions between the imidazolium cores (Figure 9).⁴² $[\text{BF}_4]^-$ anions can also form H-bonds in imidazolium-based ionic liquids, although the H-bonds are considerably weaker than those of the corresponding halides, based on the much lower melting temperatures of the tetrafluoroborate.⁴¹ Hexafluorophosphate anions do not normally participate in hydrogen bonding.⁴³

Viscosity. The viscosity of ionic liquids is highly sensitive to contaminations. The presence of water decreases the viscosity, whereas chloride impurities have the opposite effect.^{35,44} The presence of cosolvents seems to decrease the aggregation of the ions in the liquid, resulting in a decrease of viscosity, although experimental results indicate that the nature of the cosolvent plays a more important role than its amount.⁴⁵

A major barrier to the commercial application of ILs arises from their high viscosity. The viscosity of ILs is higher than water and similar to oils, and the viscosity decreases with increasing temperature.⁴⁶ The temperature dependence of the viscosity with unsymmetric cations and no functional groups in the side chain can generally be described with the Arrhenius equation. For ILs with symmetrical cations and low molecular weight, the Vogel–Tammann–Fulcher (VTF) equation appears more suitable. For other ionic liquids, neither model can accurately describe the temperature dependence of viscosity.⁴⁶

Abbott predicted the viscosity behavior of ionic liquids by the application of the “hole theory”. For low viscosity, the ions must be relatively small and the liquid must contain large free spaces. It is suggested that ILs with a high surface tension possess these properties; these include imidazolium salts with C_4 – C_6 alkyl moieties.⁴⁷ Nitrate ($[\text{NO}_3]^-$) based ILs that have a low surface tension are an example of ILs with low viscosity and high electrical conductivity.⁴⁸ The same correlation between surface tension and viscosity was observed for $[\text{TF}_2\text{N}]^-$ and $[\text{PF}_6]^-$ ions.⁴⁹

Furthermore, branching of the alkyl chain in 1-alkyl-3-methylimidazolium salts reduces viscosity, as it reduces the intermolecular dipole–dipole interactions. The same reason accounts for the relatively low viscosity of most polyfluorinated anions.⁵⁰ Additional factors to be considered are H-bonding ability and symmetry (see section 3.3.1).^{49,51}

To conclude, the viscosity of ILs based on the most common anions decreases in the order $[\text{Cl}]^- > [\text{PF}_6]^- > [\text{BF}_4]^- > [\text{TF}_2\text{N}]^-$.

Density. Density is one of the most often reported properties of ILs, probably because nearly every application requires knowledge of density. In general, ionic liquids are denser than water. The molar mass of the anion significantly affects the overall density of ILs.⁵⁰ The bis(methanesulfonyl)amide $[\text{Ms}_2\text{N}]^-$ salts, for example, have lower densities than the $[\text{TF}_2\text{N}]^-$ salts. Given that the molar volumes of both anions are similar, this is due to the greater mass of the fluorinated $[\text{TF}_2\text{N}]^-$ anion.⁵¹ In addition, the packing may become more efficient as the alternating positive and negative ions are of similar size.⁵⁰

Surface Tension. Little data has been published on the surface tension of ILs.^{48,49} In general, the liquid/air surface tensions of ILs are somewhat higher than conventional solvents, except for water, and span an unusually wide range.⁵⁰ Surface tension values vary with temperature, and both the surface excess entropy and energy are affected by the alkyl chain length, decreasing with increasing chain length. For a specific cation, the compound with the larger anion has, in general, the higher surface tension.⁵² However, alkylimidazolium $[\text{PF}_6]^-$ salts have a higher surface tension than the corresponding $[\text{TF}_2\text{N}]^-$ salts.⁵⁰

Thermal Stability. Most ILs exhibit relatively high thermal stability, with onset decomposition temperatures (T_{onset}) of (300 to 400) °C. The decomposition appears to be independent of the cation but decreases as the hydrophilicity of the anion increases.⁵⁰ In general, it has been suggested that the stability dependence on the anion is $[\text{PF}_6]^- > [\text{TF}_2\text{N}]^- \approx [\text{BF}_4]^- > \text{X}^-$.⁵³ However other factors can affect the thermal stability. Fluorinated anions such as $[\text{PF}_6]^-$ and

[BF₄][−], for example, are unstable in the presence of water and decompose to produce HF.^{28,31,54} In thermogravimetric analysis (TGA), some metals catalyze decomposition; hence, it is advisable to use sample pans made of platinum rather than aluminum.^{53,55}

The thermal stability of ILs has been revised recently as it was shown that degradation occurs at much lower temperatures if the temperature is held at that elevated level for a longer period (≈10 h). On the basis of these observations, the introduction of a new parameter describing the maximum operating temperature without degradation is suggested.^{55,56}

The anions usually decompose via dealkylation, whereas the cations undergo primarily alkyl migration and elimination reactions.⁵⁵ In general, imidazolium salts tend to be more stable than tetraalkylammonium salts.⁵³

Polarity. For molecular solvents, the term “polarity” is often related to its ability to dissolve other compounds. The precise definition of “solvent polarity” is complex since this term encompasses many molecular properties responsible for interactions between solvent and solute molecules (e.g., Coulombic, directional, inductive, dispersion, hydrogen bonding, electron pair donor, and electron pair acceptor forces). Hence, the quantitative characterization of “solvent polarity” remains a problem not completely solved for molecular solvents.⁵⁰

The most common method to describe the polarity of ionic liquids is the solvatochromic determination of the Kamlet–Taft parameters. Fluorescence spectra, refractive indices, or organic reactions have been also used to determine polarity.^{57,58} The linear solvation-energy relationship (LSER) parameters are empirical and attempt to describe both H-bond basicity/acidity and polarity/polarizability. As a rule of thumb, ILs are polar solvents similar to short- to medium-chain alcohols.^{57,58} Water impurities do not greatly influence the polarity. Anions have the greatest effect on the H-bond basicity, and the polarity of ILs depend to some extent on the polarity of their environment.^{59,58}

Permittivity. The relative dielectric permittivity, previously known as dielectric constant ϵ_s , cannot be used for the quantitative characterization of solvent polarity as this property does not provide an adequate correlation with much of the experimental data of molecular solvents. Conventional methods for measurement of ϵ_s are not applicable due to the high electrical conductivity of ionic liquids, although measuring the permittivity at high frequencies ($f > 5$ GHz) and subsequent extrapolation to zero frequency provides an estimate of the relative permittivities.^{60–63} Huang and Weingaertner conclude that the relative permittivities of 1,3-dialkylimidazolium ILs at ambient temperature vary little ($\epsilon_s = 10$ to 15) compared to that of molecular solvents. Even though ϵ_s of ILs can range from about 11 to 57, ϵ_s of ILs are significantly lower than those of common polar solvents.^{60,61} The influence of the anion on ϵ_s appears to be minor, and H-bonding influences the permittivity, and hence the polarity, in very much the same way as in molecular liquids.⁶¹ Table 1 tests the relative dielectric permittivity and the cellulose dissolving power of some ILs. Molten salts with fluoride-containing anions are poor cellulose solvents and also have low permittivities. In contrast, 2-hydroxyethylammonium formate [HEA]Fmt displays the highest permittivity measured for an IL so far, and it also possesses high cellulose-dissolving ability.⁶¹ The relationship between per-

Table 1. Cellulose-Dissolving Capacity of Ionic Liquids in Mass Fraction (w) in Correlation to Their Relative Dielectric Permittivity

ionic liquid ^a	cellulose solubility 100 w	relative dielectric permittivity at 20 °C	references cellulose solubility/permittivity
[HEA]Fmt	30	57.3	Bical ⁶⁵ /Huang ⁶¹
[EMIM]EtOSO ₃	0	27.9	Zavrel ⁶⁶ /Weingaertner ⁶⁰
[EMIM]BF ₄	0	12.9	Zavrel ⁶⁶ /Weingaertner ⁶⁰
[EMIM]Tf ₂ N	0	12.3	Zavrel ⁶⁶ /Weingaertner ^{60,62}
[BMPyr]Tf ₂ N	0	11.7	Zavrel ⁶⁶ /Weingaertner ⁶³
[BMIM]BF ₄	0	11.7	Zavrel ⁶⁶ /Weingaertner ⁶⁰
[BMIM]PF ₆	0	11.4	Zavrel ⁶⁶ /Weingaertner ⁶⁰

^a Cations: [HEA] = 2-hydroxyethylammonium, [EMIM] = 1-ethyl-3-methylimidazolium, [BMIM] = 1-butyl-3-methylimidazolium, [BMPyr] = 1-butyl-3-methylpyrrolidinium. Anions: Fmt = formate, BF₄ = tetrafluoroborate, PF₆ = hexafluorophosphate, Tf₂N = bis(trifluoromethanesulfonyl)amide, EtOSO₃ = Ethylsulfate.

mittivity and cellulose-dissolving power of ionic liquids has yet to be systematically studied.

Miscibility with Water. The hydrophilic/hydrophobic nature of ILs determines their solvation properties, which determines the recovery of products by solvent extraction and environmental contamination through wastewater. A recent publication indicates a route for separating water-miscible ILs from the aqueous phase.⁶⁷ The miscibility of ILs with water depends mainly on the hydrophilic nature of the anion and the hydrophobic nature of the cation, which is primarily determined by the length of the alkyl chains.⁵⁰ In general, the solubility of water decreases with a decrease in temperature. All ILs are hygroscopic to some extent and absorb water from the atmosphere.

IR studies indicate that the water dissolved in ILs is mostly present in the “free” state, bonded via H-bonds to two anions. Cammarata et al. suggested that the degree of hydrophilicity of the IL can be used as an indicator for the strength of these H-bond interactions.⁶⁸ Nuclear magnetic resonance (NMR) studies suggest that water molecules prefer to interact with the H-2, H-4, and H-5 protons of the imidazolium core and that the three-dimensional ion network of the ionic liquid is weakened as a result.⁶⁹

Toxicity. Ionic liquids quickly gained attention as new solvents within the green chemistry community. Initially there were few environmental and ecological studies, and only within the last couple of years has the cytotoxic, environmental, and microbial toxicity of the most common ILs been studied.^{32,70–72} The effect of [BMIM]Cl, as the most widely used IL, on marine algae, *Vibrio fischeri*, luminescent bacteria, leukemia cell lines, or enzymes like acetylcholinesterase (which plays an essential role in the nervous system of all higher organisms) showed that the IL was not acutely toxic ($EC_{50} \approx 13 \mu\text{M}$).⁷⁰

However, the toxicity of ILs increases dramatically with increase in the length of the alkyl side chain, due to an increase in lipophilicity. The cation dominates the toxic effect of ILs, although some influence of the anion has been shown.⁷¹ In general, imidazolium ILs are more toxic than the more bulky phosphonium ILs, and it is recommended to work with the shorter methyl side chain on the cation core (instead of ethyl) wherever possible.^{72,73}

Currently there is a lack of in vivo investigations on IL biouptake. Life-cycle analysis of ILs with more emphasis on recycling has been proposed by the research community.^{71,72}

Access of Thermophysical Properties. Easy access to the exponentially increasing rate of publications on ILs

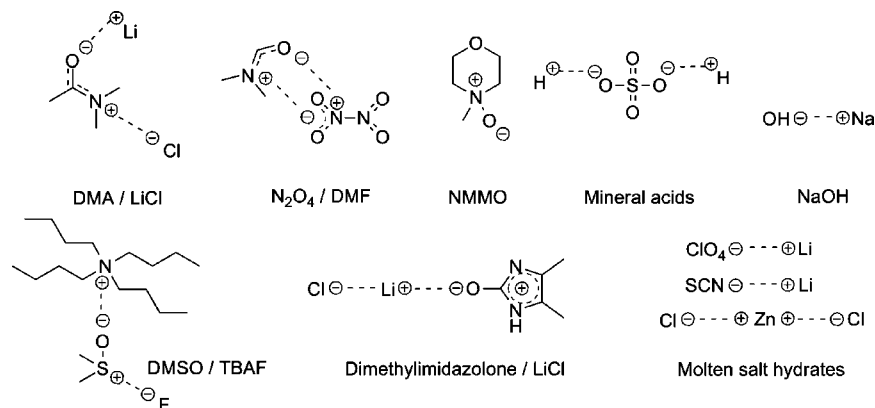


Figure 10. Traditional cellulose solvents: *N,N*-dimethylacetamide/lithium chloride (DMA/LiCl), dinitrogen tetroxide/dimethylformamide (N_2O_4 /DMF), *N*-methylmorpholine-*N*-oxide (NMMO), mineral acids, sodium hydroxide (NaOH), dimethylsulfoxide/tetrabutylammonium fluoride (DMSO/TBAF), dimethylimidazolone/lithium chloride, molten salt hydrates.

during the past decade requires a comprehensive data collection of as many properties as possible.²² The most comprehensive data collection (1984 to 2004) of IL properties with 1680 property data compound combinations was published by Zhang et al. in 2006, prior to the establishment of the IUPAC operated, freely accessible online database “IL Thermo”.⁷⁴ It is regularly updated and contains, at the time of writing, property data of 339 ionic liquids with a total number of 212 different ions and more than 20 000 property data points for pure ionic liquids.⁷⁵ Mixture data is also included.

4. Dissolution and Regenerating Cellulose

4.1. Introduction

Cost-effective and environmentally friendly dissolution of cellulose is crucial for advancing the use of the biopolymer in new materials such as wood composites. Ideally, all H-bonds within the cellulose microfibrils would be broken during the dissolution process. The dissolved polysaccharide could then be mixed with other biopolymers (lignin, hemicellulose, chitosan, keratin fibers, etc.) as reinforcements, before solvent recovery with the cellulose forming strong inter- and intramolecular H-bonds with itself and the other components. Molecular modeling of interfaces between cellulose and surrounding molecules suggest that the interfacial interactions are dominated by Coulomb interactions, predominantly by hydrogen bonds.²¹

In reality, it is difficult to dissolve cellulose because degradation of the glucosidic bonds of the single cellulose chains occurs under too drastic conditions, and sometimes the regenerated biopolymer does have a lower degree of polymerization (DP) than the initial starting material.⁷⁶

4.2. Cellulose Dissolution Using Conventional Methods

The efficient dissolution of cellulose is a long-standing goal in cellulose research and development and is still of great importance. Natural cellulose contains highly crystalline regions, and the highly branched H-bonding network makes it insoluble in water and many organic solvents. Figure 10 gives an overview of the most common traditional cellulose solvents.^{5,37,77–81} Depending on the interaction of the solvent molecules with the polysaccharide, these solvents are called derivatizing or nonderivatizing.⁸³ Derivatizing solvents interact chemically with the cellulose hydroxyl groups and

form intermediates. Nonderivatizing solvents do not. Commercial examples for derivatizing cellulose solvents are sodium hydroxide/carbon disulfide (Viscose) or sodium hydroxide/urea (CarbaCell) mixtures.^{16,83} *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) is used as a nonderivatizing solvent for direct dissolution of cellulose in industrial fiber-making (Lyocell process).⁸⁴ A wider range of products and synthesis paths is available with the application of *N,N*-dimethylacetamide/LiCl and dimethylsulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF), both nonderivatizing solvent systems.^{76,85} Recently, molten salt hydrates such as $\text{LiX} \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{I}^-, \text{NO}_3^-, \text{CH}_3\text{CO}_2^-, \text{ClO}_4^-$) have been reinvestigated and shown to be efficient nonderivatizing solvents for cellulose.⁷⁹ Studies on the chemical modification of the dissolved cellulose show that a rather large excess of reagent is necessary. This is due to the high water content of the salt hydrates, with the water being responsible for promoting unwanted side reactions.⁷⁶

But most obvious from Figure 10 is that the very high polarity of these cellulose solvents, if not even ionic character, is favorable for the breakdown of the cellulose network. Furthermore, the chloride ion seems to be one of the favorite cellulose-dissolving anions; and although various mechanisms of the chloride–cellulose interactions have been proposed, no specific data is available to support these speculations.⁸⁶

4.3. Dissolution with Ionic Liquids

Ionic liquids appear to be highly polar due to their ionic character, resulting in their enhanced biopolymer dissolving capacity. Table 2 gives an overview of the cellulose-dissolving capacity of ionic liquids reported in the literature.

A number of factors influence the cellulose dissolution, and it is important to note that Table 2 deals only with the dissolution capacity of these solvents, and not with the kinetics. Low viscosity ILs promote the dissolution process (mainly due to the higher mobility of the ions), and longer dissolution times (>12 h) do not always lead to better results, especially at higher temperatures.^{87–89} The risk of partial degradation at elevated temperatures may count for the fact that the favored dissolution temperature is very often 10 °C above the melting point of the IL.^{76,90}

Impressive results have been obtained when (3 to 5) s microwave pulses were used instead of thermal (external) heating. For example, the solubility of cellulose with a DP of 1000 could be increased by 150 %.⁷ Microwave heating

Table 2. Cellulose-Dissolving Capacity of Ionic Liquids and Other Solvents in Mass Fraction (*w*) for Different Degrees of Polymerization (DP)

ionic liquid	cellulose solubility 100 <i>w</i>	DP ^a (DP) ^b	solution conditions		reference
			<i>θ</i> /°C	<i>t</i> /h	
[BMIM]CF ₃ SO ₃	>50	Indulin AT (kraft lignin)	90	24	Lee ¹⁰¹
[MMIM]MeSO ₄	>50	Indulin AT (kraft lignin)	90	24	Lee ¹⁰¹
[BMPy]Cl	39	286 (172)	105	12	Heinze ^{76,103}
[BMPy]Cl	37	593 (412)	105	12	Heinze ^{76,103}
[BMPy]Cl	12	1198 (368)	105	12	Heinze ^{76,103}
[BMPy]Cl	>5	α-cellulose	105	12	Zavrel ⁶⁶
H ₃ PO ₄	38	cellulose	n.a.	n.a.	Boerstoe ⁷⁸
[HEA]Fmt	30	cellulose	n.a.	24	Bicak ⁶⁵
[IM] ₂ Al ₃ Cl ₃	25	wood	110	25 min	Xie ¹⁰⁴
[BMIM]Cl	25	1000	microwave heating		Swatloski ⁷
[BMIM]Cl	11–25	1175	n.a.	n.a.	Laus ³⁷
[BMIM]Cl	≈20	n.a.	100	2	Erdmenger ⁹¹
[BMIM]Cl	18	286 (307)	83	12	Heinze ^{76,103}
[BMIM]Cl	13.6	569	n.a.	n.a.	Kosan ⁹⁴
[BMIM]Cl	13.4	454	n.a.	n.a.	Kosan ⁹⁴
[BMIM]Cl	13	593 (544)	83	12	Heinze ^{76,103}
[BMIM]Cl	11	(wool keratin fibers)	130	10	Xie ¹⁰⁴
[BMIM]Cl	10	1198 (812)	83	12	Heinze ^{76,103}
[BMIM]Cl	10	cellulose	100	5 mg/h	Zhao ⁹²
[BMIM]Cl	10	1000	100	n.a.	Swatloski ⁷
[BMIM]Cl	>10	Indulin AT (kraft lignin)	90	24	Lee ¹⁰¹
[BMIM]Cl	8	Norway spruce sawdust	110	8	Kilpelainen ^{3,88}
[BMIM]Cl	8	(wool keratin fibers)	130	10	Xie ¹⁰⁵
[BMIM]Cl	7	Norway spruce TMP	130	8	Kilpelainen ^{3,88}
[BMIM]Cl	>5	α-cellulose	90	12	Zavrel ⁶⁶
[BMIM]Cl	5	Southern pine TMP	130	8	Kilpelainen ^{3,88}
[BMIM]Cl	5	1000	80	sonication	Swatloski ⁷
[BMIM]Cl	3	1000	70		Swatloski ⁷
[BMIM]Cl	3	1000	70		Swatloski ⁷
[BMIM]Cl	>3	maple wood flour	80	24	Lee ¹⁰¹
[BMIM]Cl	>3	wood chips	100–105		Kilpelainen ⁸⁸
[BMIM]Cl	partiallysoluble	wood chips	130	15	Kilpelainen ^{3,88}
[BMIM]Cl		n.a.	130	8	Aaltonen ⁸⁹
[BMIM]Cl		n.a.	130	27	Aaltonen ⁸⁹
[BMIM]Cl		n.a.	130	4	Aaltonen ⁸⁹
[BMIM]Cl		n.a.	130	4	Aaltonen ⁸⁹
[BMIM]Cl		wood	130	4.5	Aaltonen ⁸⁹
[BMIM]Cl		wood	130	10	Aaltonen ⁸⁹
[BMIM]Cl		wood	130	21	Aaltonen ⁸⁹
[BMIM]Cl		lignin	130	3	Aaltonen ⁸⁹
[BMIM]Cl		lignin	130	2	Aaltonen ⁸⁹
[BMIM]Cl		lignin	130	27	Aaltonen ⁸⁹
[BMIM]Cl		lignin	130	4	Aaltonen ⁸⁹
[BMIM]Cl		lignin	130	8	Aaltonen ⁸⁹
[BMIM]Cl		Southern yellow pine	110	16	Sun ¹⁰⁰
[BMIM]Cl		xylan	130	8	Aaltonen ⁸⁹
[BMIM]Fmt	<20	250	85	n.a.	Fukaya ¹⁰⁶
[BMIM]Fmt	8	225	110	n.a.	Zhao ⁹²
[AMIM]Fmt	20	250	80	n.a.	Fukaya ¹⁰⁶
NMMO	17	454 (444)	n.a.	n.a.	Kosan ⁹⁴
NMMO	14.4	569 (537)	n.a.	n.a.	Kosan ⁹⁴
[BMIM]Ac	13.2	569	n.a.	n.a.	Kosan ⁹⁴
[EMIM]Ac	>30	Indulin AT (kraft lignin)	90	24	Lee ¹⁰¹
[EMIM]Ac	15	225	110	n.a.	Zhao ⁹²
[EMIM]Ac	13.5	569	n.a.	n.a.	Kosan ⁹⁴
[EMIM]Ac	>5	α-cellulose	90	12	Zavrel ⁶⁶
[EMIM]Ac	>5	spruce, beech, chestnut	90	12	Zavrel ⁶⁶
[EMIM]Ac	<5	maple wood flour	80	24	Lee ¹⁰¹
[EMIM]Ac	4.9–5.0	red oak	110	16	Sun ¹⁰⁰
[EMIM]Ac	4.6–4.9	Southern yellow pine	110	16	Sun ¹⁰⁰
[EMIM]Cl	15.8	569	n.a.	n.a.	Kosan ⁹⁴
[EMIM]Cl	12	268 (329)	90	12	Barthel ^{90,103}
[EMIM]Cl	≈10	cellulose	100	2	Erdmenger ⁹¹
[EMIM]Cl	6	593 (580)	90	12	Barthel ^{90,103}
[EMIM]Cl	>5	α-cellulose	90	12	Zavrel ⁶⁶
[EMIM]Cl	4	1198 (1129)	90	12	Barthel ^{90,103}
[AMIM]Cl	>30	Indulin AT (kraft lignin)	90	24	Lee ¹⁰¹
[AMIM]Cl	14.5	220	80	<0.5	Zhang ⁹
[AMIM]Cl	14.5	650	80	<0.5	Zhang ⁹
[AMIM]Cl	12.5	1085	n.a.	n.a.	Laus ³⁷
[AMIM]Cl	11	250	100	n.a.	Fukaya ¹⁰⁷
[AMIM]Cl	10	250	100	n.a.	Fukaya ¹⁰⁶
[AMIM]Cl	10	1175	n.a.	n.a.	Laus ³⁷

Table 2. Continued

ionic liquid	cellulose solubility 100w	DP ^b (DP)	solution conditions		reference
			$\theta/^\circ\text{C}$	t/h	
[AMIM]Cl	8	1600	80	<0.5	Zhang ⁹
[AMIM]Cl	8	Southern pine powder	80	8	Kilpelainen ^{3,88}
[AMIM]Cl	8	Norway spruce sawdust	110	8	Kilpelainen ^{3,88}
[AMIM]Cl	7	Norway spruce TMP	130	8	Kilpelainen ^{3,88}
[AMIM]Cl	>5	α -cellulose	90	12	Zavrel ⁶⁶
[AMIM]Cl	>5	spruce, fir, beech, chestnut	90	12	Zavrel ⁶⁶
[AMIM]Cl	5	Norway spruce sawdust	80	24	Kilpelainen ^{3,88}
[AMIM]Cl	5	Southern pine TMP	130	8	Kilpelainen ^{3,88}
[AMIM]Cl	2	Southern pine TMP	110	8	Kilpelainen ^{3,88}
[AMIM]Cl	>3	maple wood flour	80	24	Lee ¹⁰¹
[AMIM]Cl	>3	1176	n.a.	n.a.	Laus ³⁷
[AMIM]Fmt	21.5	250	85	n.a.	Fukaya ¹⁰⁷
[BDMIM]Cl	12.8	569	n.a.	n.a.	Kosan ⁹⁴
[BDMIM]Cl	9	286 (377)	90	12	Barthel ^{90,103}
[BDMIM]Cl	6	593 (580)	90	12	Barthel ^{90,103}
[BDMIM]Cl	4	1198 (1129)	90	12	Barthel ^{90,103}
[BDMIM]Cl	≈ 3	1176	n.a.	n.a.	Laus ³⁷
[ADMIM]Br	12	286 (320)	80	12	Barthel ⁹⁰
[ADMIM]Br	4	593 (599)	80	12	Barthel ⁹⁰
[ADMIM]Br	4	1198 (1203)	80	12	Barthel ⁹⁰
[EMIM]MP	10	250	40–65	n.a.	Fukaya ¹⁰⁶
[HEMIM]Cl	6.8	cellulose	70	12	Luo ¹⁰⁸
ECOENG TM	>5	α -cellulose	90	12	Zavrel ⁶⁶
[Bu ₄ P]Fmt	6	225	110	n.a.	Zhao ⁹²
[(C ₆) ₃ C ₁₄ P]Dca	<0.5	225	110	n.a.	Zhao ⁹²
[BzDTA]Cl	5	286 (327)	62	12	Heinze ^{76,103}
[BzDTA]Cl	2	593 (527)	62	12	Heinze ^{76,103}
[BzDTA]Cl	1	1198 (966)	62	12	Heinze ^{76,103}
[Bu ₄ N]Fmt	1.5	225	110	n.a.	Zhao ⁹²
[Amm110]Cl	0.5	225	110	n.a.	Zhao ⁹²
[Amm110]Fmt	0.5	225	110	n.a.	Zhao ⁹²
[Amm110]Ac	0.5	225	110	n.a.	Zhao ⁹²
[Amm110]Dca	<0.5	225	110	n.a.	Zhao ⁹²
[BzMIM]Cl	>10	maple wood flour	80	24	Lee ¹⁰¹
[BzMIM]Cl	>10	Indulin AT (kraft lignin)	90	24	Lee ¹⁰¹
[BzMIM]Cl	5	Southern pine TMP	130	8	Kilpelainen ^{3,88}
[BzMIM]Cl	5	Norway spruce TMP	130	8	Kilpelainen ^{3,88}
[M(OEt) ₂ EtIM]Ac	12	225	110	n.a.	Zhao ⁹²
[M(OEt) ₃ EtIM]Ac	12	225	110	n.a.	Zhao ⁹²
[M(OEt) ₄ EtIM]Ac	10	225	110	n.a.	Zhao ⁹²
[M(OEt) ₂ Et ₃ N]Ac	10	225	110	n.a.	Zhao ⁹²
[M(OEt) ₃ Et ₃ N]Ac	10	225	110	n.a.	Zhao ⁹²
[H(OEt) ₂ MIM]Ac	5	225	110	n.a.	Zhao ⁹²
[M(OMe)BzIM]Cl	5	Southern pine TMP	130	8	Kilpelainen ^{3,88}
[M(OEt) ₇ EtIM]Ac	3	225	110	n.a.	Zhao ⁹²
[H(OEt) ₃ MIM]Ac	2	225	110	n.a.	Zhao ⁹²
[M(OMe)BzIM]Cl	2	Southern pine TMP	130	8	Kilpelainen ^{3,88}
[H(OEt) ₁ MIM]Cl	2	225	110	n.a.	Zhao ⁹²
[M(OEt) ₃ -MeOEtOMe-IM]Ac	0.5	225	110	n.a.	Zhao ⁹²
[M(OPr) ₃ EtIM]Ac	0.5	225	110	n.a.	Zhao ⁹²
[M(OEt) ₃ BuIM]Ac	<0.5	225	110	n.a.	Zhao ⁹²
[MM(EtOH)NH]Ac	<0.5	225	110	n.a.	Zhao ⁹²
[(MeOEt) ₂ NH ₂]Ac	<0.5	225	110	n.a.	Zhao ⁹²
[MM(MeOEt)NH]Ac	<0.5	225	110	n.a.	Zhao ⁹²
[M(MeOEt) ₂ NH]Ac	<0.5	225	110	n.a.	Zhao ⁹²
[BzMIM]Dca	2	Southern pine TMP	130	8	Kilpelainen ^{3,88}
[BMIM]Br	5–7	1000	microwave heating		Swatloski ⁷
[BMIM]Br		α -cellulose	90	12	Zavrel ⁶⁶
[BMIM]I		α -cellulose	90	12	Zavrel ⁶⁶
[BMIM]SCN	5–7	1000	microwave heating		Swatloski ⁷
[BMIM]BF ₄		1000	microwave heating		Swatloski ⁷
[BMIM]BF ₄		α -cellulose	90	12	Zavrel ⁶⁶
[BMIM]BF ₄	4	Indulin AT (kraft lignin)	90	24	Lee ¹⁰¹
[BMIM]PF ₆		1000	microwave heating		Swatloski ⁷
[BMIM]PF ₆		α -cellulose	90	12	Zavrel ⁶⁶
[BMIM]PF ₆	0.1	Indulin AT (kraft lignin)	90	24	Lee ¹⁰¹
[C ₆ MIM]BF ₄	5	1000	microwave heating		Swatloski ⁷
[C ₈ MIM]BF ₄	slightly soluble	1000	microwave heating		Swatloski ⁷
[C ₂ MIM]Cl	≈ 10	cellulose	100	2	Erdmenger ⁹¹
[C ₃ MIM]Cl	≈ 0.5	cellulose	100	2	Erdmenger ⁹¹
[C ₄ MIM]Cl	≈ 20	cellulose	100	2	Erdmenger ⁹¹
[C ₅ MIM]Cl	≈ 1.5	cellulose	100	2	Erdmenger ⁹¹
[C ₆ MIM]Cl	≈ 6.5	cellulose	100	2	Erdmenger ⁹¹
[C ₆ MIM]Cl		α -cellulose	90	12	Zavrel ⁶⁶

Table 2. Continued

ionic liquid	cellulose solubility 100w	DP ^b (DP)	solution conditions		reference
			$\theta/^\circ\text{C}$	t/h	
[C ₇ MIM]Cl	≈5	cellulose	100	2	Erdmenger ⁹¹
[C ₈ MIM]Cl	≈4	cellulose	100	2	Erdmenger ⁹¹
[C ₈ MIM]Cl		α-cellulose	90	12	Zavrel ⁶⁶
[C ₈ MIM]Dca	<1	225	110	n.a.	Zhao ⁹¹
[C ₉ MIM]Cl	≈2.5	cellulose	100	2	Erdmenger ⁹¹
[C ₁₀ MIM]Cl	≈0.5	cellulose	100	2	Erdmenger ⁹¹
[ABIM]Cl	>3	1176	n.a.	n.a.	Laus ³⁷
[DAIM]Cl	>3	1176	n.a.	n.a.	Laus ³⁷
[APIM]Cl	<3	1176	n.a.	n.a.	Laus ³⁷
[BMIM]Tf ₂ N	<0.5	225	110	n.a.	Zhao ⁹²
[BMIM]Sac		1176	n.a.	n.a.	Laus ³⁷
[BMIM]Ts		1176	n.a.	n.a.	Laus ³⁷
[BMIM]Ts		1176	n.a.	n.a.	Laus ³⁷
[BMIM]EtOSO ₃		α-cellulose	90	12	Zavrel ⁶⁶
[BMIM]HSO ₄		1176	n.a.	n.a.	Laus ³⁷
[BMIM]Dca		1176	n.a.	n.a.	Laus ³⁷
[BMIM]Dca	1	225	110	n.a.	Zhao ⁹²
[BDMIM]SCN		1176	n.a.	n.a.	Laus ³⁷
[ABIM]Dca		1176	n.a.	n.a.	Laus ³⁷
[AOMIM]Dca		1176	n.a.	n.a.	Laus ³⁷
[AOMIM]Cl		1176	n.a.	n.a.	Laus ³⁷
Ch/urea		1176	n.a.	n.a.	Laus ³⁷
[BMPyr]Cl		α-cellulose	90	12	Zavrel ⁶⁶
[BMPyr]Tf ₂ N		α-cellulose	90	12	Zavrel ⁶⁶
[EMIM]Tf ₂ N		α-cellulose	90	12	Zavrel ⁶⁶
[EMIM]EtOSO ₃		α-cellulose	90	12	Zavrel ⁶⁶
[EMIM]BF ₄		α-cellulose	90	12	Zavrel ⁶⁶
[HMIM]BF ₄		α-cellulose	90	12	Zavrel ⁶⁶
[HEMIM]BF ₄		α-cellulose	90	12	Zavrel ⁶⁶
[TBPM]Cl		α-cellulose	90	12	Zavrel ⁶⁶

^a Before regeneration. ^b After regeneration. n.a. = Not known by the author, TMP = thermomechanical pulp; **Cations:** [ABIM] = 1-allyl-3-butylimidazolium, [ADMIM] = 1-allyl-2,3-dimethylimidazolium, [AMIM] = 1-allyl-3-methylimidazolium, [Amm110]Cl = AMMOENGTM, [AOMIM] = 1-allyloxy-3-methylimidazolium, [APIM] = 1-allyl-3-propargylimidazolium, [BMIM] = 1-butyl-3-methylimidazolium, [BDMIM] = 1-butyl-2,3-dimethylimidazolium, [BzDTA] = benzyl dimethyl(tetradecyl)ammonium, [BMPyr] = 1-butyl-3-methylpyrrolidinium, [BMPy] = 3-methyl-*N*-butylpyridinium, [DAIM] = 1,3-diallylimidazolium, ECOENG = 1,3-dimethylimidazolium-dimethylphosphate, [EMIM] = 1-ethyl-3-methylimidazolium, [HEA] = 2-hydroxyethylammonium, [HEMIM] = 1-(2-hydroxymethyl)-3-methylimidazolium, [IM]₂ = imidazolium dication, [BzMIM] = 1-methyl-3-benzylimidazolium, [MMIM] = 1-methyl-3-methylimidazolium, [M(OMe)BzIM] = 1-methyl-3-m-methoxybenzylimidazolium, [TBPM] = tetrabutylphosphonium; **Anions:** Ac = acetate, Al_xCl_y = chloroaluminates, BF₄ = tetrafluoroborate, CF₃SO₃ = trifluoromethanesulfonate, Cl = chloride, Dca = dicyanamide, EtOSO₃ = ethylsulfate, Fmt = formate, MeSO₄ = methanesulfate, MP = methylphosphonates, PF₆ = hexafluorophosphate, Sac = saccharinate, SCN = thiocyanate, Tf₂N = bis-(trifluoromethanesulfonyl)amide, Ts = tosylate; **Other solvents:** Ch/urea = choline:urea (1:2 mixture), NMMO = *N*-methylmorpholine-*N*-oxide.

is characterized by an internal heating process due to the direct absorption of energy by polar molecules and differs significantly from conventional heating methods that are based on heat transfer. This internal heating may be responsible for the more effective breakdown of the H-bond network between the microfibrils, although care must be taken because heating occurs rapidly and can easily lead to biopolymer pyrolysis.⁸⁰ Sonication-assisted dissolution, however, seems only to have little benign influence on the dissolution.⁷ Additional influencing factors are definitely the degree of polymerization of the biopolymer, as well as the structure of the ionic liquid.⁸⁸

The most successful cations for cellulose dissolution are based on the methylimidazolium and methylpyridinium cores, with allyl-, ethyl-, or butyl- side chains. Even numbers of carbon atoms in the side chain show high cellulose dissolution in the series C₂ to C₂₀ compared with odd numbers.⁹¹ The maximum dissolution power is reached with the C₄ side chain, and incorporated hydroxy atoms seem to enhance cellulose solubility.⁸⁰ This could be due to the additional polarity in the heteroatomic substituents on the imidazolium ring. Double bond containing side chain reduce the viscosity of the IL. The same effect was observed if one of the alkyl chain carbon atoms was replaced by an oxygen atom, although those ILs do not tend to dissolve cellulose.^{29a,37}

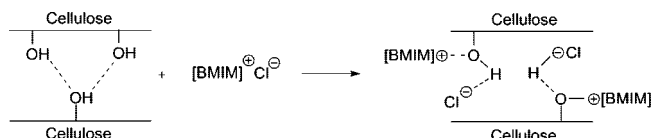


Figure 11. Proposed dissolution mechanism of cellulose in [BMIM]Cl (redrawn from Feng and Chen).⁸⁰

The most promising anions are chloride, acetate, and formate.¹³ ¹³C and ^{35/37}Cl NMR relaxation studies indicate there is a stoichiometric interaction between the chloride anions and the cellulose hydroxyl groups.⁹³

It is thought that both anions and cations are involved in the dissolution process. Figure 11 shows the proposed dissolution mechanism of cellulose in ionic liquids. The oxygen and hydrogen atoms of the cellulose form electron donor–electron acceptor (EDA) complexes with the charged species of the IL. It has been suggested that this occurs primarily between the C-6 and C-3 hydroxyl groups of neighbored cellulose chains.⁹⁴ This interaction results in the separation of the hydroxyl groups of the different cellulose chains leading to dissolution of the cellulose in the ionic liquid.^{9,80}

Heinze et al. investigated the interactions of IL cations using simple cellulose model systems (cellooligomers, DP 6 to 10). On the basis of his NMR studies, he suggests that

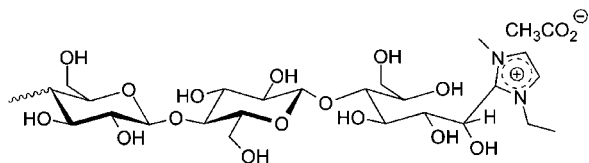


Figure 12. Structure proposed for a covalent binding of [EMIM]Ac to celooligomer (DP 6 to 10).²⁸

[EMIM]Ac forms a covalent bond between the C-1 carbon of the glucose unit and the C-2 of the imidazolium core (Figure 12). This suggestion was based on the fact that the C-1 carbon signal of the glucose unit disappeared after dissolution in [EMIM]Ac. Ebner et al. verified this hypothesis by means of ^{13}C -isotopic labeling and fluorescence labeling experiments that indicated the formation of a covalent bond between the C-2 carbon of 1-alkyl-3-methyl-imidazolium ILs and the reducing end of cellulose.⁹⁵ Surprisingly, this is not the case when the oligomer was dissolved in [EMIM]Cl.²⁸ Thus, bond formation is strongly catalyzed by bases. One explanation for this dichotomy could be found in possible residual imidazolium impurities in the [BMIM]Ac, as opposed to a possible base-free [EMIM]Cl. Another reason for this phenomenon might be a H-bond network within [EMIM]Cl (see Figure 9).²⁸ According to Leipner et al., who investigated the dissolution of cellulose on molten salt hydrates, an unsaturated coordination sphere of the cation is necessary to interact successfully with the cellulose.⁸¹ But even assuming that the cation in [EMIM]Cl would have a saturated coordination sphere, this would not explain their similar cellulose dissolution power (Table 2). It has been suggested that dissolved cellulose can exist in many different degrees of polymerization that depend, among other factors, on the solvent.^{16,94} This may account for the different reactivity of the IL cation toward the biopolymer.

Contaminations in the solvent can also influence the dissolution capacity of an IL. It has been shown that a mass fraction w of water of 0.01 in [BMIM]Cl is sufficient to prevent biopolymer dissolution.⁷ Elevated pressures of (0.2 to 0.9) MPa can assist the dissolution process while the addition of cosolvents can either reduce the rate (carbon disulfide) or have no effect on the solubility at all, although they can decrease the viscosity of the mixture (DMSO- d_6 , CH_3Cl , DMF).^{87,96–99}

However, the main source for processing cellulose remains wood, and the 120-year-old Kraft process still represents the main industrial method for extracting wood cellulose.¹⁰⁰ Ionic liquids are capable of dissolving lignin as well as cellulose.^{100,101} Sun et al. dissolved wood powder in [EMIM]Ac or [BMIM]Cl and partially separated lignin by choosing a reconstitution mixture of acetone and water (1:1). Carbohydrate-free lignin can be easily dissolved in this mixture, while cellulose and cellulose-rich materials dissolved in an IL are being reconstituted. It may be even possible to improve the delignification process by using choline-based ILs. They are not only more biocompatible than imidazolium-derived ILs but are also expected to be poor solvents for cellulose. At the same time, cholinium salts are good solvents for the lignin-like suberin, which is the main substituent of cork.¹⁰²

4.4. Regeneration of Cellulose

Independent of the solvent type used for dissolving cellulose, its regeneration is based on the same concept. The biopolymer solution is precipitated with the addition of an

excess of a polar solvent like water, acetone, dichloromethane, acetonitrile, or mixtures of them.^{7,12,37,87,88,103,109} Deionized water is often preferred when precipitated from NMMO solvent systems as the coagulated fibers show a higher degree of crystallinity, resulting in higher strength of the regenerated matrix.^{110,111}

The opposite behavior is testified when cellulose is recovered from ionic liquids, resulting in a 50 % to 75 % lower degree of polymerization than the initial biopolymer.¹¹² Although low-resolution proton NMR studies on regenerated cellulose fibers in the hydrated state have shown a rapid proton exchange between the surface hydroxyl groups of the biopolymer and the surrounding water, this interaction is not sufficient to fully reestablish the stiff H-bond network of microcrystalline cellulose.¹¹³ Recent studies indicate that the final hydrogel is free of ionic liquid residues that may count for the lower degree of crystallinity.¹¹⁴ Although X-ray photoelectron spectroscopy (XPS) is usually used to analyze the surface of materials, it has been used to determine changes in the H-bond network of cellulose after treatment with ionic liquids.¹¹⁵

The shape of the regenerated material varies according to the regeneration method and conditions. Thin films of (0.1 to 0.2) mm are obtained by casting the cellulose solution on glass plates prior to leaching with water.¹¹⁶ Other groups sprayed water on the surface of the gel in order to fix the shape of the final sample prior to immersion in water for several days.¹¹⁷ Duchemin et al. characterized all-cellulose composites and investigated the influence of process parameters, such as dissolution time, precipitation rate, or the initial cellulose concentration of the solvent, on the resulting material properties.¹¹⁷ All these parameters were shown to affect the mechanical properties of all-cellulose composites through their influence on crystallinity, void formation, and laminated microstructure. The stiffest gels were obtained following a slow and gentle precipitation. However, if the order of adding the solutions is reversed and the coagulation solvent is added to the cellulose solution, instead of the other way around, the cellulose can be recovered in the form of flocs that can be easily separated by filtration.¹¹²

Kosan et al. shaped cellulose dopes via a dry–wet spinning process by spinning the fiber directly into a coagulation bath.⁹⁴ Results indicate that the cellulose exists in different solution states, depending on the type of solvent, thus directly affecting the properties of the regenerated polymer.

Finally, nanofibrillar cellulose aerogels can be prepared if the regenerated gel is washed with liquid carbon dioxide prior to drying under supercritical conditions. The released carbon dioxide leaves a porous polymer structure resulting in an aerogel.⁸⁹ Similar methods can be applied to obtain hydro- and methanogels.¹¹⁸

5. Functionalizing of Cellulose

Chemical modification of natural fibers aims at altering its physicochemical properties to the desired need. Cellulose esters of inorganic and organic acids as well as cellulose ethers were pioneer compounds of cellulose chemistry and remain the most important technical derivatives of cellulose. They are used in coatings, membranes, binders, fillers, composites, drilling fluids, explosives, optical films, or separation media, as well as in medical applications (dialysis, tissue and bone engineering, wound dressing, joint replacement), in the food industry, or for the sorption of heavy metals.^{16,119–121} These derivatives can be acetates, carboxymethylates, benzoy-

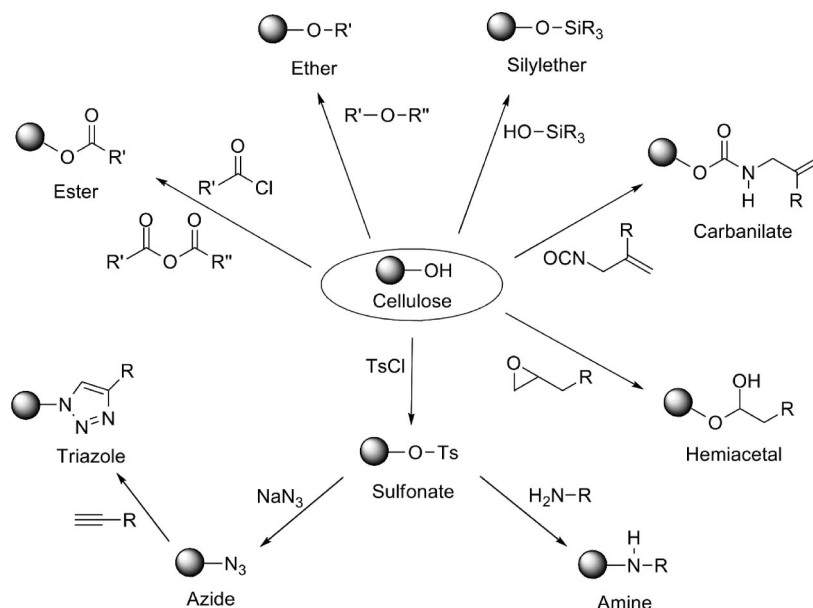


Figure 13. Functionalization routes for cellulose.

lates, urethanes (carbamates), (meth)acrylates, carbonates, sulfates, sulfonates, phthalates, tritylates, furorates, maleated esters, or ester resins.^{6,10,16,34,76,91,99,116,119,122–128}

Ionic liquids have been used as solvent for a wide range of cellulose modifications. Acylate, benzoylate, and carbamate derivatives of the biopolymer were successfully prepared in [BMPy]Cl, [BMIM]Cl, [BDMIM]Cl, [AMIM]Cl, [ADMIM]Br, [BnMIM]Cl, [EMIM]Cl, and [EMIM]Ac.^{1,10,76,90,116,123,129} The degree of substitution (DS) can be influenced by the choice of acylating agent, the reaction time, and the mole ratios of the reagents but is also dependent on the dissolution state of the cellulose.^{80,90,128} In the case of acylations, acyl chlorides tend to be more effective than the corresponding anhydrides for the modification.¹ The presence of bases such as pyridine or 1-methylimidazolium can increase the efficiency of the cellulose modification.^{76,98} Moreover, the different reactivity of the three hydroxyl groups on the glucose monomer unit ($C_6 > C_3 > C_2$) allows the regioselective introduction of protecting groups such as ethers, for example.^{6,130} Granström et al. selectively protected cellulose with 4-methoxytrityl in [AMIM]Cl, resulting in an increased reactivity of the modified cellulose.¹³¹ Such regioselective functionalizations of cellulose are a key factor for the controlled formation of colloidal suprastructures.¹⁶

Figure 13 provides a simplified overview about some cellulose functionalization routes. The hydroxy group offers a broad spectrum of possible reactions with other functional groups. Apart from ethers and esters, literature data can be found on sulfates, sulfonates, deoxyderivatives, silylates, amines, carbanilates, tritylates, hemiacetals, or azides.^{6,16,91,98,130,132,133} Koehler et al. synthesized trimethylsilylcellulose in [BMIM]Cl, [EMIM]Cl, and [EMIM]Ac.⁹⁸ Phthalated cellulose has been prepared in [AMIM]Cl, and furorates have been obtained through homogeneous modification of cellulose in [BMIM]Cl.^{127,128} The hydroxy group reacts with isocyanates to carbanilates, oxiranes react to hemiacetals, and sulfonate halides are converted into sulfonates like tosylates or mesylates, for example.^{16,134} These sulfonates are easily removed and are a favored intermediate to form 6-deoxy-cellulose derivatives like amides or azides.^{16,132} Cellulose azides can act as precursors for triazole derivatives. In addition, water-soluble cellulose sulfates have been prepared

with different sulfating agents in [BMIM]Cl, [AMIM]Cl, and [AMIM]Ac.⁹⁹ This is the first report of a nonderivatizing cellulose solvent that allows direct sulfation of the biopolymer under completely homogeneous reaction conditions.

An interesting approach is the introduction of molecules with functional groups on both ends of the chain. Hattori et al. immobilized carbamates via silane coupling on cellulose and copolymerized them with methacrylic acid or ethylene glycol dimethacrylate upon UV radiation.¹²² The concept of grafting molecules with tertiary halides suitable for forming radicals to react with polymerizable double bonds to composites has been exploited by others.^{124,135} Ring-opening graft polymerization and radiation-induced grafting of cellulose was reported using [BMIM]Cl.^{136,137} Meng et al. synthesized a cellulose-based macroinitiator, cellulose 2-bromoisobutyrylate, for atom transfer radical polymerization by direct homogeneous acylation of cellulose in [AMIM]Cl, without using any catalysts and protecting group chemistry.¹³⁸ Another group reacted the cellulose hydroxyl groups with 2-bromoisobutyryl bromide and copolymerized it with methacrylate or styrene via atom-transfer-radical-polymerization (ATRP), obtaining living polymers that were still active even after one year.¹³⁹ Meng et al. activated the cellulose surface with allylbromide or divinylsulfone prior to ATRP grafting with polymethyl methacrylate (PMMA) or polystyrene (PS).¹⁴⁰ Moreover, chemical grafting can also be done by direct condensation with, e.g., silane hydroxyls, resulting in surface compatibilization with hydrophobic moieties. The opportunities inherent in bifunctional groups have not been properly exploited since the modified fibers were introduced to inert matrices.¹⁴¹

Some more interesting and noteworthy biopolymer modifications include the use of dendrons, boronic acid derivatives, or *Acetobacter xylinum* bacteria. Within the past few years, several groups successfully introduced dendritic macromolecules, up to their fourth generation, onto the cellulose surfaces.^{116,134,142–144} Dendritic immobilized materials are currently used for enhanced separations in high-resolution capillary gas chromatography and capillary microextractions.¹³⁴ Liebert, for example, exploited the affinity of boric and boronic acid to react with polyols in ionic liquids and showed that interactions may occur at C-2 and C-3 of

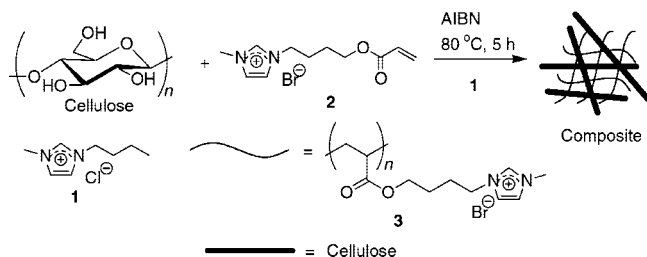


Figure 14. Mixture of two ionic liquids (1 + 2) is used to form a cellulose/IL-polymer composite. The IL-polymer 3 is made by radical polymerization of IL-monomer 2 (adapted from Kadokawa et al.).¹⁴⁹

glucose derivatives. The formation of a seven-membered ring was confirmed leading to the assumption that a comparable structure might be formed in the glucose based macromolecules cellulose and starch.⁸² Finally, Pommet et al. modified natural cellulose by utilizing bacteria to deposit nanosized bacterial cellulose around the fibers, which enhanced their adhesion to renewable polymers like cellulose acetate butyrate (CAB) or polylactic acid (PLA).¹⁴⁵

In general, the ILs can be successfully recovered after their use.^{76,90} However, one has to be aware that ionic liquids are not inert and that they can also react with the biopolymer.^{95,129}

6. Wood-Based Composites

A long-term goal should be to develop wood-based composites with similar or better properties than the current petroleum-based composite materials. Natural fibers offer advantages over manmade fibers that include low density, recyclability, and biodegradability.¹²⁶ Lu et al. proposed to group methods for forming composites into four main categories: compounding, blending, soaking, and spraying.¹⁴⁶ The majority of cellulose-containing composites have been prepared either by mixing with a water-compatible materials or by extrusion with a water-immiscible plastic matrix material.¹²⁴ Independent of the processing method, it is important to distinguish between two general types of wood composites: blended-wood composites, composed of wood and of synthetic components, and all-wood composites.

6.1. Polymer Blends

Most natural polymers are hydrophilic since they contain either hydroxyl or polar groups. Wood sawdust and recycled plastics such as high-density polyethylene (HDPE) have been used to make blended composites. The feedstock is based on cheap “waste-materials”. Adhikary et al., for example, compounded dried wood flour with HDPE granulates by extrusion, and pressurized (1 to 5) MPa hot and cold pressing to form a blended composite. The use of a coupling agent (maleated polypropylene), as well as an increase of polymer content, improved both the stability and the mechanical strength of the composite.¹⁴⁷

A different route for making biopolymer blends is possible using dissolved cellulose. The concept is to form interwoven networks between the cellulose chains and synthetic polymer strands during the regeneration process, as illustrated in Figure 14.

Cellulose is dissolved in a mixture of two ionic liquids. IL 1 acts as the cellulose solvent, and IL 2 (with an incorporated acrylate group in the side chain) acts as the monomer for the polymerization. The resulting composite consisted of cellulose with interlaced IL polymer strands.¹⁴⁸

This approach was further developed by using only one ionic liquid for both purposes. The two side chains of the imidazolium IL consisted of one vinyl and one styrene group, enabling the IL to act as both the cellulose solvent and the monomer.¹⁴⁹

A similar study has been made using branched polyamidoamine (PAMAM) dendrons to serve as molecular hooks for the cellulose chains. Cellulose was dissolved in [BMIM]Cl and either mixed with PAMAM directly, or pretreated with 1,3-phenylenediisocyanate under microwave irradiation. The obtained films were either a composite of cellulose and PAMAM dendrimers, or consisted of covalently bonded cellulose–PAMAM, connected via the diisocyanate linker.¹¹⁶ Another type of cellulose–PAMAM dendron has been prepared by exploiting the copper-catalyzed Huisgen reaction. An azido derivative of cellulose was dissolved in [EMIM]Ac and coupled with propargyl-containing dendrons, resulting in an triazolo linkage between the cellulose and the PAMAM dendron.¹⁵⁰

In blended composites, the matrix can consist of so-called binders, usually low-viscosity resins based on isocyanate, (poly)phenol formaldehyde, melamine urea, or melamine formaldehyde.^{151,152} The composite product *Vintorg*, for example, is made by modifying wood with high-intensity microwave energy and subsequent impregnation with commercial binders.¹⁵¹ Furthermore, microfibrillated cellulose (MFC) composites have been prepared by impregnating dried MFC films with melamine formaldehyde resin. The matrix was polymerized during hot pressing at elevated pressure and temperature.¹⁵² Plasticizers can be added to reduce the brittleness of the blend-composites. Most common are water and glycols, but urea and formamide are also used.¹⁵³

6.2. All-Wood Composites

All-wood composites consist only of wood components (cellulose, hemicellulose, lignin, etc.) and are, therefore, biocompatible. Such composites with properties similar to petroleum-based composites are highly desirable and would most certainly open up a new era if they could replace existing, petroleum-based materials. All-wood composites have been prepared in forms of fibers, gels, and films, but a persisting problem is the insufficient adhesion between the reinforcement and the matrix, mainly due to differential shrinking during the regeneration process.¹¹⁰

Electrospinning is a common method to produce composite nanofibers. Examples are cocontinuous cellulose acetate/polyurethane composite nanofibers made by multiple-jet electrospinning (ES), or the dry-jet wet spinning of cellulose solutions with dispersed magnetite particles (Fe_3O_4) to form fibers with magnetic properties.¹⁵⁴ Those fibers could find applications in protective clothing or tissue engineering.¹⁵⁴ In addition, spin-coating techniques can be exploited to form ionic liquid dispersed cellulose films with enhanced electromechanical behavior.¹⁵⁵

Micro- and nanoporous cellulose composites have been prepared as hydro- or ionic- or methano- or aerogels. Figure 15 shows a transparent cellulose gel, consisting of a 0.15 mass fraction cellulose solution in ionic liquid and absorbed water. Depending on the water content, it may be described as ionogel or hydrogel. Upon heating to 150 °C, the gel liquefied, but was regenerated after two days at room temperature.¹⁵⁶

If the gel is regeneration in methanol, it is called a methanogel. Aerogels however, need an additional process

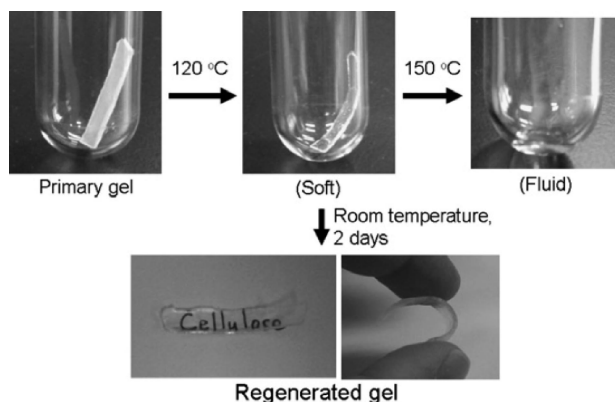


Figure 15. Photographs of a composite gel (consisting of cellulose, [BMIM]Cl, and absorbed water) after heating and after subsequent regeneration after two days at room temperature (adapted from Kadokawa et al.).¹⁵⁶

step, as the regeneration solvent has to be replaced with a gaseous component. This can be done by supercritical drying with carbon dioxide (scCO₂). The advantages of replacing the coagulation solvent with scCO₂ is the lack of surface tension under these conditions, thus preventing the voids in the gel collapsing. Aerogels possess high porosity, low density, low thermal conductivity, and transparency. Possible applications may be found in superthermal and sound isolators, in electronics, or in space and particle research.¹¹⁸

Very recently, lignocellulosic aerogels were prepared from cellulose, sodalignin, xylan, spruced wood, or combinations thereof.⁸⁹ Supercritical drying with CO₂ resulted in aerogels with bulk densities of (25 to 114) g·L⁻¹ and internal surface areas of (108 to 539) m²·g⁻¹.

Tsiopstias et al. investigated the preparation of porous gels using a new approach, called hydrogel foaming.¹¹⁸ The method is adapted from polymer foaming and is based on rapid depressurization of hydrogels. The pore-size distribution can be influenced by controlling pressure and temperature, except when hydrogels freeze during expansion. In the latter case, pore interconnection can be enhanced by a second foaming.¹¹⁸

Other ways to produce nanoporous cellulose foams from ionic liquid solutions can be achieved by oven drying, normal freeze-drying, or liquid nitrogen-assisted freeze-drying. The foam structure is not only affected by the drying method but also depends on the concentration of the cellulose solution.¹⁵⁷

Further ways to make all-cellulose composites are to impregnate wood fibers with dissolved cellulose or to penetrate wood fibers with a dissolving agent in order to generate the matrix from the partially dissolved fibers.¹¹⁰ Depending on the processing method, fibers with a tensile strength of (300 to 500) MPa (in fiber direction) and a storage modulus of up to 45 GPa (in fiber direction) can be obtained.¹⁵⁸

In addition, cellulose nanofibrils are used as reinforcement in the production of porous cellulose nanopaper of remarkably high toughness, exceeding the mechanical performance of plant fibers currently used in commercial products.⁴ The high toughness of the nanocomposite film is related to the nanofibrillar network structure and high mechanical performance of the cellulose fibrils. There exists a correlation between the molar mass of the microfibrils and the tensile strength, indicating that the ultimate strength of the composite is controlled by the mechanical strength of the microfibrils.⁴

The application of ionic liquids in the field of all-wood composites is yet to be fully exploited.

7. Conclusions and Remarks

Our knowledge of ionic liquids has advanced significantly during the past decade, and the steadily growing interest in ionic liquids as solvents is not expected to cease in the near future. A thorough understanding of the influence of the ion type and ion structure on the physical behavior of the IL is the key to unlocking the potential of this solvent class. The maintenance of a well-managed and freely accessible database to store, share, and compare experimental results is the most promising tool to achieve this understanding. Such a database allows the development of new structure–property relationships and comparison with results from molecular mechanics based calculations.

The solubility of cellulose in ILs is determined primarily by the effective polarity and the hydrogen bonding capacity of the IL, but it is also influenced by the melting temperature and the viscosity. Hence, a comprehensive collection of the effective polarity of ILs and their ability to dissolve biopolymers will assist in the search for the most effective cellulose solvents. This information will help modelers to predict interactions between biopolymers and ionic liquids more accurately; and is likely to result in a more straightforward search for ILs with good cellulose dissolving power.

In terms of activating the cellulose surface, the hydroxy group is fortunately one of the most versatile functional groups. Until recently, the limiting factor in functionalization was the solubility of the biopolymer in aqueous systems. Ionic liquids represent a new solvent class with properties different to molecular liquids. The high cellulose solubility in some ionic liquids could open up new functionalization pathways that are not accessible in traditional solvents.

8. Acknowledgments

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9. Note Added after ASAP Publication

In Table 2, the compound [ADMIM]Br was incorrectly identified as [ADMIM]Cl. In the footnote for Table 2, the correct definition for [BMPy] is now provided. The paper originally posted to the Web on September 16, 2009, and will be reposted on December 9, 2009.

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