IONIC LIQUIDS: CURRENT DEVELOPMENTS, POTENTIAL AND
DRAWBACKS FOR INDUSTRIAL APPLICATIONS

Gerhard Laus,1,* Gino Bentivoglio,1,2 Herwig Schottenberger,1,* Volker Kahlenberg,3
Holger Kopacka,1 Thomas Röder,4 Herbert Sixta 4

1 Faculty of Chemistry and Pharmacy, University of Innsbruck, Innrain 52a, 6020 Innsbruck, Austria; Phone: +43 512 507 5118; Fax: +43 512 507 2934; E-mail: herwig.schottenberger@uibk.ac.at
2 Competence Centre for Wood Composites and Wood Chemistry K-Plus, St.-Peter-Str. 25, 4021 Linz, Austria
3 Institute of Mineralogy and Petrography, University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria
4 Lenzing AG, Department of Pulp Research, Werkstrasse 1, 4860 Lenzing, Austria

Dedicated to the memory of Prof. Josef S. Gratzl [1]

There is an increasing willingness to develop new cellulose-based materials due to the fact that cellulose is the earth’s most abundant biorenewable macromolecular resource. The efficient dissolution of cellulose is a long-standing goal in cellulose research and is still of great importance. This article gives a short survey of the relevant literature with respect to historical developments and potential industrial uses of ionic liquids and then proceeds to the latest results in cellulose/ionic liquid chemistry. Cellulose can be dissolved in several ionic liquids and can easily be regenerated by contacting with water. Dissolution and reconstitution experiments, fiber characteristics and molecular mass distribution data are described. The single crystal X-ray structure determination of the cellulose solvent 1-allyl-3-methylimidazolium chloride is presented. 162 references are given.

Keywords: cellulose, ionic liquids, 1-allyl-3-methylimidazolium chloride, X-ray diffraction

Introduction

Definition and properties

An ionic liquid (IL) is a liquid that contains only ions. In the broad sense, this term includes all the molten salts, for instance, sodium chloride at temperatures higher than 800°C. Today, however, the term "ionic liquid" is used for the salts whose melting point is relatively low (below 100°C) [2]. In particular, the salts that melt at room temperature are called "room-temperature ionic liquids" (RTILs).

Room temperature ionic liquids consist of bulky and asymmetric organic cations such as 1-alkyl-3-methylimidazolium, 1-alkylpyrrolidinium, 1-methyl-1-alkylpyrrolidinium or ammonium ions. A wide range of anions is employed, from simple halides which inflict high melting points, to inorganic anions such as tetrafluoroborate and hexafluorophosphate and to large organic anions like bis(trifluorosulfonyl)amide, triflate or tosylate (Figure 1). As one example, the melting point of 1-butyl-3-methylimidazolium tetrafluoroborate [BuImMe][BF₄] with an imidazole skeleton is about –80°C, and it is a colorless liquid with high viscosity at room temperature.

The notable characteristics of ionic liquids are their non-measurable vapor pressure, thermal stability, wide liquid range, and solvating properties for diverse kinds of materials. Another important feature of ionic liquids is their designability: miscibility with water or organic solvents can be tuned through sidechain lengths on the cation and choice of anion. Furthermore, they can be functionalised to act as acids, bases or ligands.

Because of their properties, ionic liquids attract great attention in many fields, including organic chemistry, electrochemistry, physical chemistry, and engineering. In addition, their non-volatility results in low impact on the environment and human health, and they are recognised as solvents for "green chemistry."
However, it remains to be seen how "environmentally-friendly" ILs will be once widely used by industry. Research into IL aquatic toxicity has shown them to be as toxic or more so than many current solvents already in use. Balancing between zero Volatile Organic Compounds (VOC) emissions, and avoiding spills into waterways (via waste ponds/streams, etc.) should become a top priority. That said, with the enormous diversity of substituents available to make useful ILs, they ought to be designed with the foresight of having useful physical properties and less toxic chemical properties [3].

![Cations](image)

**Figure 1.** The cation (usually organic) and the anion (usually inorganic) present in ILs [4] are designed so that the resulting salts cannot pack compactly. As a result, ILs do not easily crystallise and remain liquid through a wide range of temperatures [5].

**Synthetic concepts for ILs**

Principal synthetic concepts for ILs [6] involve quaternisation reactions to generate the cation followed by anion (often halide) metathesis, either by (a) addition of metal salts to precipitate the undesired anion, possibly use of silver salts, (b) addition of strong Brønsted acids to release the unwanted anion as the volatile corresponding acid, (c) use of ion exchange resins, or (d) treatment with Lewis acids to form complex anions such as chloroaluminates. Efficient synthetic procedures for imidazolium salts were described [7, 8]. Often traces of the halide ions or acids remain in the product, either giving rise to liquid eutectic mixtures of otherwise solid salts or leading to unwanted chemical reactivity. Halide-free ILs can be produced by using alkylcarbonates as alkylating reagents and removing the carbonate as gaseous CO₂ or unsoluble metal salt [9, 10].

**History**

The original family of great-grandfather ILs, N-alkylpicolinium halides, was described in 1899 [11] with melting points which classify them as RTILs. Even earlier (1876), some members of this class of salts have been prepared as sirupy liquids by the later Nobel laureate Ramsay [12]. Other great-grandfather ILs, quaternary anilinium salts, were reported at the beginning of the twentieth century [13, 14, 15, 16, 17, 18]. Generally, these early reports are overlooked or ignored. Alkylammonium nitrates were described in 1914 [19]. Several water-unstable chloroaluminates and chloroferrates were discovered in the following years. The systematic utilisation of RTILs was reported by Hurley and Wier in 1951 [20]. In their work, electrodeposition of metals from fused mixtures of ethylpyridinium bromide and metal chlorides was studied. The next decades saw the discovery of low-melting N-ethyl-2-ethoxyypyridinium tetrafluoroborate [21] and the development of guanidinium chlorides [22] and quaternary imidazolium salts [23, 24, 25, 26], which may be called "grandfather ILs" from today’s point of view. The list of ILs grows daily. Most recently, the 1st International Congress on Ionic Liquids (COIL), held in June 2005 in Salzburg (the City of Salt), Austria, attracted more than 400 participants from 33 countries (Figure 2).
New developments

In recent years, new guanidinium-based liquid salts [27], countless imidazolium salts, even imidazolium melts with carborane [28] and stannaborane anions [29], pyridinium, and pyrrolidinium salts, or eutectic mixtures [30, 31, 32] were reported. New tetraalkylphosphonium-based ILs with rather high viscosities showed nonlinear optical behaviour [33]. Fluorine-containing cations [34], such as polyfluoroalkyl-1,2,4-triazolium salts [35] possess excellent properties with respect to air-, water-, and thermal stability. Low viscosity ILs, the hydrophilic dicyanamides [36] and the hydrophobic perfluoroalkyltrifluoroborate [10, 37, 38] were investigated. Low-coordinating and non-fluorine containing anions such as bis(oxalato)boranates (BOB) were studied [39]. Properties of imidazolium salts depend on the nature of the anions [40, 41] as well as on the alkyl chain length of 1,3-dialkylimidazolium cations [42, 43]. The physico-chemical properties and reactivities of ILs were reviewed [44, 45]. For analytical applications [46, 47, 48, 49] the nature of both cation and anion is essential. Flammability and thermal stability of trialkylimidazolium salts were found to be more dependent upon the anion than the cation [50]. Recently, energetic ionic liquids such as azido derivatives of 1,2,4-triazolium salts, notably nitrate and perchlorate [51], and other energetic azolium salts with low melting points were described [27, 52, 53, 54]. However, it should be cautioned that reported melting points (Figure 3) are often unreliable due to the hygroscopicity of these materials and the existence of polymorphs [47, 55]. Finally, the vapour pressure of [BuImMe][Tf₂N] was experimentally determined by the Knudsen effusion method [56].

Polarity and solubility

The solubility of ILs in water depends on the nature of the anion, temperature and the length of the alkyl chain on the organic cation. Tetrafluoroborates, chlorides, nitrates, and trifluoroacetates display complete miscibility with water, whereas hexafluorophosphates, triflimides, and other perfluorinated anions impart very low solubilities in water. The hydrophilic/hydrophobic behaviour is important for the solvation properties of ILs as it is necessary to dissolve reactants, but it is also relevant for the recovery of products by solvent extraction.

Empirical solvent polarity scales give insight into solvent-solute interactions. Recently, the solvent parameters α, β, and π* of several ILs were determined using three solvatochromic dyes [57].

Task-specific ILs

The concept of task-specific ILs (TSILs), which incorporate functional groups designed to impart to them particular properties, stimulated applications extending far beyond those likely for more conventional ILs [58]. One important feature of these liquids is the possibility of tuning their physical and chemical properties by varying the nature of the anion and cation. It is evident that the number of possible combinations is extremely high, and it should be possible to tailor the best IL for any application [44].

The acidity of the C(2)-H in imidazolium cations is well known, and they can be deprotonated to form carbenes [59]. In order to improve the stability against basic ligands, the 2-methylimidazolium cation was introduced. ILs containing thiol-functionalised imidazolium cations [60] for the modulation of gold surface properties were synthesised. ILs with nitrile-functionalised alkyltrifluoroborate anions [61, 62, 63], zwitterionic liquids [64, 65], and dual-functionalised ILs [61, 66] were reported.

The dicobalthexacarbonyl adduct of 1-allyl-3-propargylimidazolium tetrafluoroborate was the first ionic liquid bearing an organometallic moiety covalently attached to the cation [67]. 1,3-dialkyne-functionalised imidazolium salts were described [68]. The chromium tricarbonyl...
fragment was introduced onto the imidazolium cation [69]. Imidazolium cations with ferrocenyl appendages were prepared [70]. Metal-containing imidazolium-based ILs were reviewed [71].

ILs containing reducing (cyanoboranate, trichlorogermanate(II)) or oxidising anions (perchlorate, chlorate) open new areas in synthetic chemistry [72].

Different methods to prepare chiral ILs either from chiral starting materials or by asymmetric synthesis and their applications were reviewed [73].

In addition, 1-methyl-3-octylimidazolium tetrafluoroborate was used for enbalming and tissue preservation, and as a fixative for histological purposes [74, 75]. At least, ILs are odorless.

Miscibility

Many ILs are immiscible with either water or organic solvents, so their use in creating biphasic systems has attracted interest, especially for separation purposes. Therefore, novel liquid-liquid partitioning systems (water-ionic liquids) have been considered [76, 77].

Potential and Drawbacks as Solvents and Reaction Media for Industrial Processes

Industrial aspects of ILs have been reviewed recently [78, 79, 80, 81]. Some of the most intriguing highlights are discussed in the following paragraphs.

Extraction of metal ions

A series of hydrophobic TSILs, designed to extract Hg²⁺ and Cd²⁺ from water, were prepared by appending urea-, thiourea-, and thioether-substituted alkyl groups to imidazoles and combining the resulting cationic species with PF₆⁻ [82]. ILs were examined as novel media for the extraction of rare earth metal cations such as Eu³⁺, Ce³⁺ and Y³⁺ [83].

BASIL process

This commercial application (biphasic acid scavenging utilizing ionic liquids) uses N-methylimidazole on a multiton scale to scavenge acid that is formed in the process. The reaction results in the formation of the ionic liquid N-methylimidazolium chloride, which has a melting point of 75°C. Conventional acid scavengers such as triethylamine produce solids, whereas the ionic liquid separates as a clear liquid phase from the pure product and is recycled.

Desulphurisation

CuCl based ILs exhibit remarkable desulphurisation ability for gasoline [84]. Very promising ILs for deep desulphurisation (down to values of 10 ppm S or even lower) are [BuImMe][OctSO₄] and [EtImMe][EtSO₄], as they are halogen-free and available from relatively cheap starting materials [85, 86]. [EtImMe][BF₄], [BuImMe] [PF₆], [BuImMe] [BF₄] showed high selectivity for extractive desulphurisation and denitrogenation [87], optionally in the presence of an oxidising agent which oxidises the sulfur compounds to sulfoxides or sulfones during the extraction step. Fuels that can be desulphurised by this method are gasoline, crude petroleum, liquefied petroleum gases, diesel fuel, jet fuel, and distillate fuel oils [88].

Absorption of gases

One of the most exciting and impressive potential industrial applications of ionic liquids is their use for the storage and delivery of gases
that are highly toxic, flammable, and/or reactive. The electronics industry uses toxic gases such as phosphine (PH₃), boron trifluoride (BF₃), and arsine (AsH₃) to dope silicon with phosphorus, boron, and arsenic ions. It was realised that chemical complexation could be a superior alternative to physical adsorption and that ionic liquids have properties that are ideally suited for this application [89, 90]. The solubility of carbon dioxide in [BuImMe][PF₆] and [BuImMe][BF₄] was studied [91, 92], and enhanced CO₂ absorption in poly(ionic liquid)s was observed [93]. It was also found that the nature of the anion had the most significant influence on the gas solubilities [94, 95].

Catalytic reactions in ILs

The key to waste minimisation in chemicals manufacture is the widespread substitution of classical "stoichiometric" syntheses by atom-efficient, catalytic alternatives. In the context of homogeneous catalysis, efficient recycling of the catalyst is a conditio sine qua non for economically and environmentally attractive processes. Motivated by one or both of the above issues, much attention has been devoted to homogeneous catalysis in biphasic systems. Similarly, the use of ILs as novel reaction media may offer a convenient solution to both the solvent emission and catalyst recycling problem [4, 98, 99]. Some unidentified mechanism is operating in olefin dimerisation [100].

Nonaqueous biocatalysis [101] and biochemical transformations in ILs [102] were reviewed.

Hydroformylation

Hydroformylation of alkenes has excellent potential as a reaction for use with IL systems allowing continuous-flow reactors to be used [103]. Supercritical fluid-ionic liquid biphasic systems were described for the separation of the products from the catalyst [104, 105].

Hydrogenation

Increased rates and effective recycling of the catalyst were observed for the rhodium-catalysed hydrogenation of alkenes in ILs [106, 107]. There has been some speculation that hydrogenation in ILs is due to colloidal rhodium particles [108]. Again, temperature-dependent miscibility and phase-separation add to the opportunities of these processes.

Oxidation

ILs were used for asymmetric epoxidations, oxidation of alcohols to carbonyl compounds, and PdCl₂-catalysed oxidation of styrene to acetophenone (Wacker process) [109]. The coordinating ability of the anion was found to affect the kinetics of these oxidation reactions [110]. A mixture of [BuImMe][BF₄] and water was recycled up to eight times in the PdCl₂/CuCl-catalysed oxidation of terminal alkenes (with an increase of selectivity in the case of 4-methylstyrene) [111].

Oligomerisation and polymerisation

The high polarity of ILs should make them attractive solvents for ionic polymerisation processes [112]. The methodology is still in its infancy but has great potential for the future [99].

Magnetic ILs

Recently, the IL [BuImMe][FeCl₄] was discovered to exhibit an unexpectedly strong magnetic behaviour [113]. This property may lead to novel and unusual applications.

Brönstedt-acidic systems

A new series of Brönsted acid-base ionic liquids were derived from the controlled combination of a monoprotonic acid with an organic base under solvent-free conditions. Bis(trifluoromethanesulfonyl)amine (Tf₂NH) and imidazole were mixed. The resulting Brönsted acid-base ionic liquid system was investigated as a candidate for a new proton conductor such as a fuel cell electrolyte to operate under anhydrous conditions and at elevated temperature [114].

Zwitterionic ILs containing a sulfonic acid group in a pyridinium cation were successfully employed for catalytic esterification reactions [64].

Electrochemistry

Electrochemical aspects and applications were recently reviewed [115]. ILs have clearly potential as conducting media with large electrochemical windows. For example, reversible electrochemical deposition of
magnesium on a silver surface was realised in the IL [BuImMe][BF_4] [116]. The hydrophobic ILs [BuImMe][PF_6] and [Tf_2N] were used in developing a highly efficient anode system for lithium/seawater batteries [117].

**Materials science**

The unique adaptability and flexibility of ILs provides an attractive alternative for synthetic protocols which are otherwise inaccessible. Thus, exciting new materials such as TiO_2 microspheres, Bi_2S_3 nanorods, or CuCl nanoplatelets with unique and tunable properties have been obtained [118].

**Carbohydrates and other biomacromolecules, wood, pulp, and paper**

ILs offer promise as solvents for the dissolution of highly polar compounds such as carbohydrates. Over the past few years, carbohydrate chemists have witnessed the use of ILs in a variety of important reactions [5].

There is an increasing willingness to develop new cellulose-based materials due to the fact that cellulose is the earth's most abundant biorenewable macromolecular resource.

The efficient dissolution of cellulose is a long-standing goal in cellulose research and development and is still of great importance. There are various solvents known [119], however, among quaternised nitrogen bases only N-methylmorpholine-N-oxide monohydrate is applied commercially. The cellulose is processed via direct dissolution to produce fibers (Lyocell process) [120]. Side reactions and byproduct formation in the system NMMO/cellulose have been reviewed [120].

Many solvents have been studied with regard to their application as medium for homogeneous phase chemistry under lab scale conditions. The application of N,N-dimethylacetamide/LiCl and dimethylsulfoxide in combination with tetrabutylammonium fluoride trihydrate has broadened the diversity of synthetic paths. In addition, the degree of substitution and the distribution of functional groups may be controlled.

In his pioneering work, Graenacher [121] first suggested in 1934 that molten N-ethylpyridinium chloride, in the presence of nitrogen-containing bases, could be used to dissolve cellulose. However, this seems to have been treated as a novelty of little practical value since the molten salt system was, at the time, somewhat exotic and had a relatively high melting point (118°C).

The unconventional dissolution of cellulose in molten lithium perchlorate trihydrate was demonstrated to be efficient for acetylation and carboxymethylation reactions [122].

Cellulose can be dissolved in a number of ILs (so-called green solvents) and easily regenerated by contacting with water or alcohols. 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 [123].

The dissolution of cellulose in [BuImMe]Cl [124] and the production of cellulose films reconstituted from [BuImMe]Cl [125] looked promising. The ILs used have the ability to dissolve cellulose with a degree of polymerisation (DP) in the range from 290 to 1200 in high concentrations. Using [BuImMe]Cl, no degradation of the polymer was observed. By ^13^C NMR measurement, it was concluded that this IL is a so-called non-derivatising solvent [126]. However, our results are to the contrary. It is evident, that ^13^C NMR in not a suitable method to determine molar mass distributions.

"New" and powerful non-derivatising solvents (1-allyl-3-methylimidazolium and 1,3-diallylimidazolium chlorides) for cellulose were described [119, 127], and conductivity and viscosity data were given [128]. Homogeneous acetylation of cellulose in the "new" IL [AllImMe]Cl was reported [129]. However, this IL is not new at all [23, 24].

ILs that dissolve carbohydrates in high concentrations include alkyloxyalkyl-substituted imidazolium dicyanamides [130]. Other imidazolium-based RTILs containing ether and alcohol groups in the side chain [131, 132, 133, 134], even poly(ethylene glycol)imidazolium salts (grafted system) [135], were described. The oligo-ether units are expected to act as Lewis-basic/hydrogen-accepting functionalities [136].

The suitability of ILs for dissolving and regenerating silk was studied. Thus, [BuImMe] Cl, [Bu(2-Me)ImMe]Cl, and [EtImMe]Cl were found to be able to disrupt the hydrogen bonding.
network in silk fibroin [137, 138]. Starch was selectively depolymerised by mixing with 1-butyl-3-methylimidazolium chloride. Stirring native barley starch at 100°C gave a product mixture containing monomeric products of depolymerised amylose, but amyllopectin remained intact. However, all the starch was converted into monomeric products at 150°C [139]. This is an interesting example of selective degradation of biopolymers. [BuImMe]Cl was also used for the dissolution and regeneration of wool keratin fibers, which can be used to prepare wool/cellulose blended materials directly [140].

Solubilisation and derivatisation of the amino polysaccharide chitin [141] in RTILs clearly has potential for exciting new products [142, 143]. Certain ILs were proposed for wood preservation [144, 145, 146]. Impregnation of paper using ILs as curing agents reportedly decreased strength, improved wettability, and provided resistance to moulds and fungi [147].

Let us take a look at the patent situation: there are of course numerous patents for ILs, e.g. [148, 149], but only a very limited number concerning ILs and cellulose [150, 151, 152, 153, 154, 155]. It is surprising which patents are granted today, taking into account that they involve long-known facts.

**Drawbacks**

Lack of exhaustive physical parameters such as conductivity, viscosity etc. are a serious drawback for the industrial use of ILs at the moment. The establishment of a comprehensive database was proposed [156], and in 2003, an international effort was launched through the IUPAC to meet this important need.

Among the different generations of ILs, hydrolytically stable yet hydrophobic ILs would allow easiest recovery from biphasic processes (such as spinning cellulose fibers into an aqueous precipitation bath). However, these systems can obviously be never designed to dissolve carbohydrate-based macromolecules, since their solubilisation relies on the competitive replacement of intermolecular hydrogen bridges which is only feasible with hydrophilic solvent systems. Another potential problem with ILs is the possible pathway into the environment through waste water. However, this situation is common with every solvent.

**Experimental**

**Synthesis of 1-allyl-3-butylimidazolium chloride**

To 99.5 g of freshly destilled 1-allylimidazole (0.92 mol, 1 equiv.) in a round-bottomed flask equipped with reflux condenser was added an excess of 1-chlorobutane (93.7 g, 1.01 mol, 1.1 equiv.). The reaction mixture was refluxed for 24 h. Excess 1-chlorobutane was removed by means of an oil pump (80°C) yielding 182.7 g of a slightly yellow, viscous liquid (98% of theory).

\(^1\)H NMR (CDCl\(_3\)): δ 1.12 (3H, t, J 7.3 Hz), 1.54 (2H, m), 2.10 (2H, m), 4.50 (2H, t, J 7.3 Hz), 5.13 (2H, d, J 6.3 Hz), 5.65 (2H, m), 6.30 ppm (1H, m), 7.91 (1H, m), 8.00 (1H, m), 9.38 (1H, s). \(^13\)C NMR (CDCl\(_3\)): δ 13.3, 19.3, 32.9, 49.5, 51.7, 122.0 (2C), 122.6, 130.1, 137.0 ppm. IR (neat, ATR): 3047, 2957, 2934, 2871, 1644, 1561, 1458, 1424, 1163, 994, 942 cm\(^{-1}\). Mp.: not crystalline down to –50°C, turns into a glass.

**Synthesis of 1-allyl-3-butylimidazolium dicyanamide**

To a solution of 18.5 g 1-allyl-3-butylimidazolium chloride (0.092 mol, 1 equiv.) in 80 ml acetone were added 8.17 g of sodium dicyanamide (0.092 mol, 1 equiv.). The suspension was stirred for 24 h at room temperature, then sodium sulfate was added. The mixture was stirred for additional 20 minutes and then filtered with suction through a G4 frit. The solvent was removed by means of a rotary evaporator and the product finally dried on a vacuum line (oil pump, 70°C, 8 h) yielding 20.7 g of a slightly yellow liquid (97% of theory).

\(^1\)H NMR (neat, C\(_6\)D\(_6\) external locking capillary): δ 1.06 (3H, t, J 7.3 Hz), 1.48 (2H, m), 2.04 (2H, m), 4.44 (2H, t, J 7.3 Hz), 5.07 (2H, d, J 6.3 Hz), 5.59 (2H, m), 6.25 ppm (1H, m), 7.85 (1H, m), 7.94 (1H, m), 9.32 (1H, s). \(^13\)C NMR (neat, C\(_6\)D\(_6\) external locking capillary): δ 13.7, 19.7, 32.2, 49.9, 52.0, 119.9, 121.7, 122.9, 123.2, 131.5, 136.6 ppm. IR (neat, ATR): 3136, 3093, 2934, 2871, 1644, 1561, 1458, 1424, 1163, 994, 942 cm\(^{-1}\).

**Synthesis of 1-allyl-3-methylimidazolium dicyanamide**

To a solution of 27.9 g 1-allyl-3-methylimidazolium chloride (0.175 mol, 1 equiv.) in 80 ml acetone were added 15.6 g of sodium dicyanamide (0.175 mol, 1 equiv.). The mixture...
was stirred for 24 h at room temperature and then dried with sodium sulfate (2 spatulas). After stirring for additional 20 minutes the mixture was filtered with suction through a G4 frit and the solvent removed by means of a rotary evaporator. After drying the product on a vacuum line (oil pump, 70°C, 8 h), 29.2 g of a reddish liquid were obtained (88% of theory).  

1H NMR (neat, C6D6 external locking capillary): δ 4.21 (3H, s), 5.13 (2H, d, J 6.3 Hz), 5.61 (2H, m), 6.31 (1H, m), 7.88 (2H, m), 9.24 (1H, s) ppm. 13C NMR (neat, C6D6 external locking capillary): δ 36.6, 51.9, 119.9, 121.4, 122.9, 124.4, 131.7, 137.2 ppm. IR (neat, ATR): 3136, 3093, 2961, 2874, 2225, 2191, 2124, 1561, 1461, 1304, 1160, 993, 944 cm–1.

Synthesis of 1-allyloxy-3-methylimidazolium dicyanamide

To a solution of 4.3 g 1-allyloxy-3-methylimidazolium iodide (0.016 mol, 1 equiv., prepared from 1-allyloxyimidazole [157]) in 30 ml of distilled water were added 2.8 g of silver dicyanamide (0.016 mol, 1 equiv.). The suspension was stirred at room temperature. A yellow precipitate of silver iodide was formed, and 10 ml of acetone were added. Stirring was continued for 1 h, then the suspension was filtered with suction through a S4 frit. The solvents were removed by means of a rotary evaporator and the product dried on a vacuum line (oil pump, 70°C, 12 h) yielding 2.6 g of a light brown liquid (79% of theory).  

1H NMR (DMSO-d6): δ 3.84 (3H, s), 4.91 (2H, d, J 6.6 Hz), 5.30 (2H, m), 6.02 (1H, m), 7.72 (1H, t, J 2.0 Hz), 8.13 (1H, t, J 2.0 Hz), 9.58 (1H, t, J 2.0 Hz) ppm. 13C NMR (DMSO-d6): δ 36.6, 81.9, 119.1, 119.3, 121.6, 124.5, 129.8, 133.5 ppm. IR (neat, ATR): 3129, 3062, 2119, 1557, 1422, 1343, 1154, 994, 945 cm–1.

Dissolution experiments

The IL was melted at 100-105°C, stabilising agent (0.1 % propyl gallate) was added if desired, then cellulose (FEZ 1167, 3%; KZO3 or Solucell 1175, 10% and more) was added and stirred until a clear solution was obtained (30 mbar) as indicated in Tables 1 and 2.

NMR experiments

13C NMR spectroscopy of carbohydrates such as cyclodextrin in ILs is an emerging field of research [158]. A Bruker AC 200 spectrometer was used.

Spinning experiments

Spinning experiments were performed by a dry jet–wet spinning process according to the Lyocell process (use of an air gap; water as spinning bath; 100 µm nozzle).

Gel permeation chromatography (GPC)

Molecular mass distribution of reconstituted cellulose samples was determined by gel permeation chromatography (size exclusion chromatography) using DMA/LiCl as eluent. The method was described in detail earlier [159].

Results and Discussion

Solubility experiments

Solutions of 3% cellulose could be obtained only in chloride-containing ILs (Table 1). The presence of water in the IL was found to decrease the solubility of cellulose [124]. The acidity of the C(2)-H in imidazolium cation-based ILs is presumed to be beneficial for
Although oxygen-containing side chains were expected to facilitate solvation, cellulose was insoluble in [AllOImMe]Cl. It was also insoluble in dicyanamides and other ILs (Table 2). Solutions of 10% cellulose in [BuImMe]Cl and in [AllImBu]Cl are shown in Figure 4. The solution in [AllImBu]Cl turned irreversibly into a jelly on cooling.

**Table 1.** Solubility of 3 % cellulose (FEZ 1167) in ILs

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Solubility</th>
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<tbody>
<tr>
<td>1-Butyl-3-methylimidazolium chloride</td>
<td>+</td>
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<tr>
<td>1-Allyl-3-methylimidazolium chloride</td>
<td>+</td>
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<tr>
<td>1-Allyl-3-butylimidazolium chloride</td>
<td>+</td>
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<tr>
<td>1,3-Diallylimidazolium chloride</td>
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<td>1-Butyl-2,3-dimethylimidazolium chloride</td>
<td>slow</td>
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<tr>
<td>1-Allyl-3-propargylimidazolium chloride</td>
<td>reacts</td>
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<tr>
<td>1-Butyl-2,3-dimethylimidazolium thiocyanate</td>
<td>–</td>
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<tr>
<td>1-Butyl-3-methylimidazolium saccharinate</td>
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<td>1-Butyl-3-methylimidazolium dicyanamide</td>
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</tr>
<tr>
<td>Choline chloride : urea = 1 : 2</td>
<td>–</td>
</tr>
</tbody>
</table>

**Table 2.** Solubility of cellulose in [AllImMe]Cl and [BuImMe]Cl

<table>
<thead>
<tr>
<th>Solution no.</th>
<th>Ionic liquid</th>
<th>Pulp</th>
<th>Conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>[AllImMe]Cl</td>
<td>KZO3 (1085)</td>
<td>12.5</td>
</tr>
<tr>
<td>(2)</td>
<td>[AllImMe]Cl</td>
<td>KZO3 (1085)</td>
<td>12 *</td>
</tr>
<tr>
<td>(3)</td>
<td>[AllImMe]Cl</td>
<td>Solucell 1175</td>
<td>10</td>
</tr>
<tr>
<td>(4a)</td>
<td>[BuImMe]Cl</td>
<td>Solucell 1175</td>
<td>11</td>
</tr>
<tr>
<td>(4b)</td>
<td>[BuImMe]Cl</td>
<td>Solucell 1175</td>
<td>16 *</td>
</tr>
<tr>
<td>(4c)</td>
<td>[BuImMe]Cl</td>
<td>Solucell 1175</td>
<td>25 *</td>
</tr>
</tbody>
</table>

* The pulp was suspended in 50 ml of water, which evaporated during the dissolution process
* 5 % pulp added to 11% solution
* 9 % pulp added to 16% solution, many undissolved fibers

**NMR results**

Although cellulose could not be dissolved in all of the tested dicyanamides, solutions of other carbohydrates were obtained by stirring for 20 minutes at 60°C. The 13C NMR of the disaccharide palatinose (14%) was recorded at 20°C in [AllImBu][NCN] (Figure 5) and found to be identical with published data [160].

**Figure 5.** 13C NMR of palatinose in [AllImBu][NCN]

**GPC results**

In [BuImMe]Cl, excessive degradation of the cellulose was observed in 25% solution at 100°C, but could be prevented by the presence of propyl gallate as stabiliser. In contrast, little degradation occurred when [AllImMe]Cl was used with or without stabiliser. The results are summarised in Table 3. Molecular mass distribution of reconstituted cellulose samples is shown in Figure 6. The second maximum in the curve for [BuImMe]Cl arises from the stepwise addition of the cellulose (cf. Table 2, entry 4b). It is evident that [AllImMe]Cl is a truly non-degradative solvent, whereas pure [BuImMe]Cl cannot be considered a "non-derivatising" solvent [124, 126].

**Table 3.** GPC results of reconstituted cellulose from IL solutions w/o stabiliser

<table>
<thead>
<tr>
<th>Mn (10^3 g/mol)</th>
<th>Mw (10^3 g/mol)</th>
<th>w(DP &lt;50)</th>
<th>w(DP &lt;100)</th>
<th>w(DP &gt;2000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting material (Solucell 1175)</td>
<td>67</td>
<td>170</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>[AllImMe]Cl, KZO3 (1085) unstabilised</td>
<td>40</td>
<td>191</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>[AllImMe]Cl, Solucell 1175 stabilised</td>
<td>58</td>
<td>149</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>unstabilised</td>
<td>51</td>
<td>132</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>[BuImMe]Cl, Solucell 1175 stabilised</td>
<td>43</td>
<td>94</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>unstabilised</td>
<td>10</td>
<td>27</td>
<td>34</td>
<td>57</td>
</tr>
</tbody>
</table>
**Figure 6.** Molecular mass distribution of cellulose (Solucell 1175) recovered from unstabilised solutions in [AllImMe]Cl and [BuImMe]Cl

**Figure 7.** Cellulose fibers obtained from [AllImMe]Cl

**Fiber data**

The fibers obtained from IL solutions exhibit somewhat lower tenacity and elongation values compared with conventional Lyocell fibers. However, we expect to improve these values by optimising the spinning parameters. Weight, tenacity and maximum elongation data of the dry fibers are summarised in Table 4. A typical fiber as prepared from [AllImMe]Cl solution is displayed in Figure 7.

**Table 4.** Data of fibers spun from [AllImMe]Cl and [BuImMe]Cl solutions

<table>
<thead>
<tr>
<th>Yarn count (dtex)</th>
<th>Tenacity (cN/tex)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>[AllImMe]Cl, 75°C, unstabilised, KZO3 (1085)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>1.3</td>
<td>32.2</td>
</tr>
<tr>
<td>Minimum</td>
<td>1.0</td>
<td>23.3</td>
</tr>
<tr>
<td>Maximum</td>
<td>1.6</td>
<td>37.3</td>
</tr>
<tr>
<td>VarCoeff</td>
<td>10.6</td>
<td>11.2</td>
</tr>
<tr>
<td><strong>[AllImMe]Cl, 100°C, unstabilised, Solucell 1175</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>1.6</td>
<td>26.8</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.7</td>
<td>21.7</td>
</tr>
<tr>
<td>Maximum</td>
<td>2.0</td>
<td>31.1</td>
</tr>
<tr>
<td>VarCoeff</td>
<td>22.8</td>
<td>9.7</td>
</tr>
<tr>
<td><strong>[AllImMe]Cl, 80°C, stabilised, Solucell 1175</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>1.3</td>
<td>36.8</td>
</tr>
<tr>
<td>Minimum</td>
<td>1.1</td>
<td>27.6</td>
</tr>
<tr>
<td>Maximum</td>
<td>1.6</td>
<td>43.6</td>
</tr>
<tr>
<td>VarCoeff</td>
<td>9.6</td>
<td>10.9</td>
</tr>
<tr>
<td><strong>[BuImMe]Cl, 100°C, stabilised, Solucell 1175</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>1.3</td>
<td>33.1</td>
</tr>
<tr>
<td>Minimum</td>
<td>1.1</td>
<td>20.9</td>
</tr>
<tr>
<td>Maximum</td>
<td>1.6</td>
<td>39.6</td>
</tr>
<tr>
<td>VarCoeff</td>
<td>10.6</td>
<td>12.4</td>
</tr>
<tr>
<td><strong>[BuImMe]Cl, 105°C, stabilised, Solucell 1175</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>1.0</td>
<td>37.9</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.8</td>
<td>33.1</td>
</tr>
<tr>
<td>Maximum</td>
<td>1.3</td>
<td>42.9</td>
</tr>
<tr>
<td>VarCoeff</td>
<td>12.3</td>
<td>8.4</td>
</tr>
</tbody>
</table>

\[ g/10000 \text{m fiber} \]

**X-ray diffraction single-crystal structure**

An X-ray crystal structure determination of the grandfather IL 1-allyl-3-methylimidazolium chloride [65039-10-3] (mp.: 17°C [129]; in contrast, 55°C was reported by Sigma-Aldrich-Fluka [161] and confirmed by us by DSC; maybe there are polymorphs, but this compound definitely is very hygroscopic) from commercially available [162] single crystals, was carried out, using Mo Kα radiation and refined on \( F^2 \): space group \( P2_1/c \), monoclinic, \( a=7.931, b=12.836, c=16.452 \text{ Å}, \beta=96.22°, V=1665.0 \text{ Å}^3, Z=4, D_{\text{calc}}=1.266 \text{ g cm}^{-3}, \mu=0.387 \text{ mm}^{-1}, T=173 \text{ K}, 12319 \text{ reflections collected, 3535 independent} (R_{\text{int}}=0.034), 2857 \text{ } (I>2\sigma(I)), \theta \text{ range 2.0-26.9°, R}_{1}(I>2\sigma(I))=0.0364, wR_{2}(I>2\sigma(I))=0.0735, R_{1}(\text{all }=0.0523, wR_{2}(\text{all})= 0.0789, \text{ GOF}=1.053. A crystal packing diagram is shown in Figure 8, short C(2)-H...Cl distances of 2.58 Å are indicated. In the two independent molecules in the asymmetric unit, the allyl group was found to be tilted out of the ring plane by 59.3 and 89.6°, respectively (Figure 9).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-286726. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
Figure 8. Crystal packing of 1-allyl-3-methylimidazolium chloride showing short C(2)-H...Cl contacts of 2.58 Å

Figure 9. ORTEP plot of 1-allyl-3-methylimidazolium chloride (50% probability ellipsoids) showing the two independent molecules

Conclusions

The opportunity to use ILs as solvents for processing of cellulose was investigated. Over the last ten years, interest and publications involving ILs have expanded exponentially. At this moment, it is really too early to pick favorites in this area. Exciting developments are to be expected, e.g. fibers from molecular composites such as silk/cellulose or wool/cellulose hybrid fibers. The use of chiral ILs for biomacromolecules may also hold promise for interesting developments in the future.

Acknowledgement

Financial support was provided by the Austrian government, the provinces of Lower Austria, Upper Austria and Carinthia as well as by Lenzing AG. We also express our gratitude to the Leopold Franzens University, Innsbruck, the Johannes Kepler University, Linz, the University of Natural Resources and Applied Life Sciences, Vienna, and to Lenzing AG for their contributions in kind.

References


