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Chapter

Ionic Liquids as Environmental Benign Solvents for Cellulose Chemistry: A Review

Indra Bahadur and Ronewa Phadagi

Abstract

The application of cellulose and its derivatives is restricted because of their limited solubility in water and many organic solvents. Recently, several attempts are being made to dissolve them in inorganic and organic solvents. The solubility of these polymeric materials mainly depends upon their molecular weight, pH, and source of origin. Nowadays, there has been a new breakthrough of applying ionic liquids (ILs; designer solvents) in the field of cellulose solvent chemistry. Association of ionic liquids with several salient features such as high thermal, chemical and low vapor pressure, and so on makes them ideal environmentally green solvents to be used for cellulose. The present chapter deals with a collection of some major works in which ionic liquids have been used as solvents for cellulose dissolution. The articles also describe the works illustrating the use of ionic liquids as cosolvents (organic aprotic solvents) for the better increase of the solvent activity (solubility).

Keywords: ionic liquids, cellulose chemistry, biocompatibility, green chemistry, degree of polymerization, polysaccharides

1. Introduction

Cellulose is defined as a natural homopolymer which is obtained mainly from living organisms including fungi, bacteria, algae, and animals [1, 2]. The cellulose is constructed by repetition of D-glucose units in which two glucose units are linked together by β-(C1 → C4)-glycosidic bond [1] as shown in Figure 1. Additionally, degree of polymerization of cellulose highly depends upon the raw material; for native cellulose it can be up to 15,000 [3]. Cellulose has become one of the most widely used natural polymers because of its various fascinating physical and structural properties along with its biocompatibility and wide range of availability [4]. The several magnificent properties of cellulose arise due to the presence of multiple inter- and intrahydrogen bonding interactions as illustrated in Figure 2. The cellulose is an unbranched homopolymer because it exists in semicrystalline form containing both crystalline and amorphous phases [5].

It is clear from Figure 1 that cellulose consisted of two types of hydroxyl (─OH) substituents, one is primary hydroxyl substituent and the other is secondary hydroxyl substituent [5].

The discovery of cellulose was made in late 1830s by Anselme Paven and Hyatt. In the year 1870, manufacturing company took a positive outlook in cellulose
2. Cellulose dissolution history

Ever since cellulose has been discovered, many researches are being carried out on the most efficient ways to dissolve this natural polymer in various common solvents [8]. The first attempt toward cellulose dissolution was made by Hyatt Manufacturing Co. in which cellulose was converted into nitrocellulose with the aid of nitric acid. The nitric acid treatment of the cellulose gives cellulosic-based thermoplastic polymer that has several industrial and biological applications [4]. As time progresses a new and a better method, namely, “viscose,” was developed which became effective from the 1890s and is the most widely used method in processing cellulose to date. Approximately 3.2 million tons of cellulose are processed per year using this method [9–11]. This method makes the use of alkali (NaOH) and carbon disulfide (CS₂) and produces cellulose xanthate. The detail methodology about the
viscose process has been described elsewhere [12–14]. During the late 1960s, lyocell (amine oxides) technique was invented mainly to overcome the challenges of viscose method which is found to be more effective in processing of cellulose. Lyocell technique employs the use of N-methylmorpholine N-oxide (NMMO). NMMO dissolves cellulose directly due to its strong N-O dipole [15]. However lyocell technique was not as effective as “viscose” technique as it had significant engineering complications; hence viscose remained to be the most widely used technique [16]. Both of those cellulose dissolution techniques retain major environmental complications (some of which are listed below).

<table>
<thead>
<tr>
<th>Viscose</th>
<th>Lyocell</th>
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<tr>
<td>• For every kilogram of cellulose produced, there is two kilograms of waste [11, 17]</td>
<td>• Poor thermal stability of NMMO [17, 18] which leads to major investment in safety measures of the industry and difficulties in recycling the solvent [16]</td>
</tr>
<tr>
<td>• Makes use of carbon disulfide and dihydrogen sulfide which are both environmental rivals and also not sustainable [10]</td>
<td>• NMMO requires high temperatures which leads to degradation of cellulose [19, 20]</td>
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Those challenges lead to further research in cellulose dissolution process in search of solvents which can be as environmental friendly as possible. Therefore the new solvents should be associated with low volatile, easily recyclable, high thermal stability, nontoxic, non-derivative, etc. [21]. The solvents which were found to be most effective were NaOH/thiourea and urea aqueous solvents as well as molten salts. The NaOH/thiourea was found to dissolve cellulose at low temperatures ranging from −8 to −5°C as described elsewhere in detail [22, 23]. However this method was found to produce cellulose fibers with high degree of crystallinity but lower degree of crystal orientation when compared to fibers obtained from viscose process [23, 24]. In order to advance this method, thiourea was replaced by urea forming a new solvent system NaOH/urea [12], and this solvent was found to have enhanced cellulose solubility by precooling the solution to −12°C. The advantage of the method is based on the fact that the by-products so formed were nontoxic. The methodologies related to the preparation of NaOH/Urea system can be elsewhere [11, 12, 24]. Another eco-friendly solvent that is still in the academia is ionic liquids (designated by ILs). Recently, the ILs have been identified as the most universal solvents for the future due to their several fascinating properties such as high polarity, negligible vapor pressure, nonflammability, low melting point, good thermal stability, tunable viscosity, broad liquid range, high thermal conductivity, good dissolution properties, etc. [25–27]. Because of the association of ILs with these fascinating properties, they (ILs) can be considered as most important, cost-effective, and environmental benign solvents for cellulose.

3. Ionic liquids

3.1 Brief summary of ionic liquids

Ionic liquids are commonly defined as molten salts; these salts are composed of inorganic or organic anions and organic cations. In ILs, the oppositely charged ions are held together by columbic forces [28–30]. Most widely studied ILs are room temperature ionic liquids (RTILs) having melting point of below 100°C [31–34]. The ILs are liquids at room temperature because they are composed of polyatomic, bulk, asymmetric organic cations and charge-diffuse ions [17, 35], and their ions are not packed well; hence, they remain liquid [36] at room temperature. The
Solvents, Ionic Liquids and Solvent Effects

RTILs are considered to be designer solvents since one can alter the physicochemical properties of an IL by simply varying anions' type or alkyl chain length of the cations [37–40]. The RTILs are composed of nitrogen or phosphorus containing dissymmetrical organic cations such as imidazolium, pyridinium, or ammonium or phosphonium cations and wide variety of simple anions such as chloride, nitrate, bromide, tetrafluoroborate, acetate, triflate, etc. [29, 41, 42] as shown in Table 1. So far, the ILs have been found to have numerous applications in various areas including solvent science for manufacturing of different materials including dissolution of biomass, electrochemistry for electrolytes in batteries, polymer chemistry for plasticizers, and separation technology for extractions and separations [26, 36, 37, 43]. Since ILs have been discovered, they are widely becoming advanced; in addition, the efficient methods of synthesis ILs are being developed. The application of ILs is vastly increasing yearly; recently, ILs have been started to be researched toward biomass processing, particularly cellulose, since cellulose is the most abundant biomaterial on earth [1, 17]; therefore, the use of ILs in cellulose chemistry can bring about economic sufficient developments archiving of the United Nation (UN) mission of moving away from depending on fossils fuels as well as using of harmful convensional solvents.

### 3.2 Cellulose dissolution using ionic liquids

The very first cellulose dissolution research was carried out by Richard P. Swatloski in the year 2002 [44]. Swatloski along with his coworkers reported that 1-butyl-3-methylimidazolium chloride ([C\textsubscript{6}MIM\textsuperscript{+}]) with Cl\textsuperscript{−}, Br\textsuperscript{−}, and SCN\textsuperscript{−} could dissolve cellulose whereas with [BF\textsubscript{4}]\textsuperscript{−} and [PF\textsubscript{6}]\textsuperscript{−} could not. They were further

<table>
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<th>S. no.</th>
<th>Cations</th>
<th>Anions</th>
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<tr>
<td>1</td>
<td>Imidazolium</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pyridinium</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ammonium</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Phosphonium</td>
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Table 1. Structures and abbreviations of some common cations and anions of ionic liquids employed as solvents.
observed that as increase in the alkyl chain length of the ILs decreases the solubility of the investigated ionic liquids as \([\text{C}_4\text{MIM}]\text{[Cl]}\), \([\text{C}_6\text{MIM}]\text{[Cl]}\), and \([\text{C}_8\text{MIM}]\text{[Cl]}\) since \([\text{C}_4\text{MIM}]\text{[Cl]}\) dissolved 10 wt%, \([\text{C}_6\text{MIM}]\text{[Cl]}\) dissolved 5 wt% and \([\text{C}_8\text{MIM}]\text{[Cl]}\) were slightly soluble. In addition the dissolution could be significantly enhanced by heating the solution using oil bath, microwave, or ultrasonic technique. This research indicated that “ionic liquids” can be used as solvents for cellulose and opened a new horizon in green chemistry [45]. Ever since Swatloski et al. [44] breakthrough in cellulose chemistry, many researchers proceed with his outcomes to further understand the dynamics and factors associated with the dissolution of cellulose using ionic liquids. To determine dynamics and factors that play a role in cellulose dissolution using ILs, properties such as different structures of the ionic liquids, degree of polymerization of cellulose, dissolution time, temperature, water content, and cosolvent were investigated starting from Zhang et al. [46] to Meenatchi et al. [47] including Kosan et al. [48], Heinze et al. [49], Lee et al. [50], Kilpeläinen et al. [51], Erdmenger et al. [52], Zavrel et al. [53], Sun et al. [54], Vits et al. [55], Fukaya et al. [21, 56], Sashina et al. [43], Xu et al. [57], Sescousse et al. [58], Zhen et al. [59], and Freire et al. [60], and the detailed summary of the factors affecting cellulose solubility is given in Table 2. It can be concluded that most of the studied ionic liquids are imidazolium-based ionic liquids; this is due to a fact that imidazolium ILs have the finest properties among other ILs; they have the lowest melting points; many of them are liquid at room temperature; they have high conductivity and a wide electrical window stability that makes them suitable for a variety of applications including solvents for the dissolution of cellulose [61]. Among the most widely studied imidazolium-based ILs \([\text{BMIM}]\text{[Cl]}\), \([\text{BMIM}]\text{[Ac]}\), \([\text{BMIM}]\text{[Fmt]}\), and \([\text{BMIM}]\text{[OAc]}\) together with \([\text{AMIM}]\text{[Cl]}\) and \([\text{AMIM}]\text{[Fmt]}\)

<table>
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<tr>
<th>Factor</th>
<th>Explanation</th>
<th>Reference</th>
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<tr>
<td>Presence of water</td>
<td>Water content should be very low in both IL and cellulose, typically less than 1%</td>
<td>Swatloski et al. [44], Muhammad et al. [62]</td>
</tr>
<tr>
<td>Anions type</td>
<td>ILs containing anions that have strong electronegativity such as halides, e.g., (\text{Cl}^-), have better dissolution properties unlike noncoordinating anions such as ([\text{BF}_4^-]) and ([\text{PF}_6^-])</td>
<td>Holm et al. [63], Dadi et al. [64], Swatloski et al. [44]</td>
</tr>
<tr>
<td>Alkyl chain length</td>
<td>Methyylimidazolium cations with even number of carbons were found to have high solubilizing power than the one with odd number and pyridinium-based ionic liquids showed that as alkyl chain length of the cation increases, the solubility decreases</td>
<td>Erdmenger et al. [52], Sashina et al. [43], Olivier-Bourdigou et al. [65]</td>
</tr>
<tr>
<td>Degree of polymerization</td>
<td>Solubility rate of cellulose decreases as degree of polymerization increases</td>
<td>Kosan et al. [48], Zhang et al. [46]</td>
</tr>
<tr>
<td>Dissolution time</td>
<td>Dissolution time should be short typically around 12 h at low heating temperature</td>
<td>Kilpeläinen et al. [51]</td>
</tr>
<tr>
<td>IL viscosity</td>
<td>Low viscosity promotes higher dissolution since it promotes greater ions mobility</td>
<td>Tywabi [24], Fort et al. [66], Kilpeläinen et al. [51]</td>
</tr>
<tr>
<td>Cosolvent</td>
<td>Polar aprotic cosolvents promote higher and quicker dissolution at low temperature Polar protic is non-solvent which causes precipitation of the cellulose from the IL solution</td>
<td>Rinaldi et al. [67], Zhao et al. [68], Xu et al. [69, 70], Xu and Zhang [71], Bengtsson [72], Andanson et al. [73], Holding et al. [74], Swatloski et al. [44]</td>
</tr>
</tbody>
</table>

Table 2. Detailed summary of factors affecting cellulose solubility.
as well as [EMIM][Cl], [EMIM][OAc], and [EMIM][MP] have been documented to be one of the most effective ILs for cellulose dissolution, with [BMIM][Cl] able to dissolve up to 25% wt of cellulose having a DP = 1000 using a microwave heating method. During dissolution process, it has been shown by aid of various analytical techniques that the strong inter- and intramolecular hydrogen bonding of cellulose is broken up by formation of intense hydrogen bonding between ionic liquid anions and cellulose hydroxyls making cellulose to be soluble; hence, ILs with noncoordinating anions are nonsolvents [44].

3.3 Cellulose dissolution using ionic liquids and cosolvents (organic solvents)

The use of organic solvents in the cellulose chemistry has been vain for many decades, which lead to the use of solvents like oxide amines (NMMO), NaOH/urea, LiCl/DMI, ILs ([BMIM][Cl], [AMIM][Cl]), etc. However every solvent has its own rewards and drawbacks; so far the greenest solvents proposed are the ILs. However, the use of ILs is still not yet practical and faces a lot of industrial challenges since ILs are available in small amount, are relatively costly, and have very high viscosity compared to other common aqueous thermochemical pretreatment reagents, and it deactivates regular cellulolytic enzymes [75–77]. To overcome these challenges faced by ILs, Renaldi [67] created a solvent system, which is a bicomponent containing both ionic liquid and cosolvent (polar aprotic solvents such as DMSO, DMF, DMI, etc.) that significantly lowers the IL viscosity, which increases ionic mobility, thereby promoting higher cellulose dissolving rate than net ILs [57, 67] at ambient temperature [78]. Furthermore, Renaldi [60] in his studies conducted an experiment which revealed that the use of solvent system [BMIM][Cl]/DMI dissolves more cellulose (10 wt% in few minutes) than convectional solvent LiCl/DMI (2 wt% at 150°C for 30 min). Many researches today have further carried experiments to understand the cellulose chemistry using bicomponent IL with aprotic solvent [68–71, 73–75]. The results of studied cosolvents (DMSO, DMF, DMA, and DMI) with certain ILs showed that during the dissolution of cellulose, the aprotic cosolvent does not slightly interact with the hydroxyl of the cellulose; however, it decreases the association of the IL cation with the anion making more free ions to be available for the interaction of the cellulose hydroxyls; hence, more cellulose becomes readily soluble at ambient temperatures; furthermore, as more amount of the cosolvent is added to the solution, more cellulose continues to dissolve since more IL anions become available [67–71, 73–75, 78, 79]; in addition, Xu et al. [70] further indicated that the best aprotic cosolvent are the ones which have the highest dipole moment; hence, as the dipole moment decreases, the effectiveness of the aprotic cosolvent weakens.

4. Conclusion

In this review we summarized the major solvents that are applied in the cellulose chemistry. The ILs are implemented as new solvents for the dissolution of cellulose and its derivatives having several biological and industrial applications. The cellulose can be modified such as ether, ester, sulfate, amine, hemiacetal, carbamate, etc., and the resulting material can be used for other applications. The cellulose derivatives can be used for various purposes such as textile, medicine, agriculture, biofuels, etc. In order for ionic liquids to be applied industrially, there are major problems still to be addressed such as:

- Development of the efficient ways to synthesis ionic liquids so that ILs can be available in high quantity.
The need to do further research in solvent recovery for both ILs and for ILs with a cosolvent.

To do research on IL chemical and toxicological data with cellulose.

The dissolution mechanism of cellulose with ILs in details.

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