

Imidazolium-based ionic liquids for cellulose pretreatment: recent progresses and future perspectives

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Abstract As the most abundant biomass in nature, cellulose is considered to be an excellent feedstock to produce renewable fuels and fine chemicals. Due to its hydrogen-bonded supramolecular structure, cellulose is hardly soluble in water and most conventional organic solvents, limiting its further applications. The emergence of ionic liquids (ILs) provides an environmentally friendly, biodegradable solvent system to dissolve cellulose. This review summarizes recent advances concerning imidazolium-based ILs for cellulose pretreatment. The structure of cations and anions which has an influence on the solubility is emphasized. Methods to assist cellulose pretreatment with ILs are discussed. The state of art of the recovery, regeneration, and reuse aspects of ILs is also presented in this work. The current challenges and development directions of cellulose dissolution in ILs are put forward. Although further studies are still much required, commercialization of IL-based processes has made great progress in recent years.

Keywords Imidazolium-based ionic liquids · Cellulose · Dissolution · Pretreatment

Introduction

Cellulose, the most abundant carbohydrate in the biosphere, makes up about one third of all plant biomass. Cellulose has

been recognized as a potential alternative source for biofuels and bio-based chemicals instead of fossil energy. The efficient conversion of cellulosic materials into ethanol has become a research hotspot in producing affordable and renewable fuels. More and more attention is being paid to the utilization of this biopolymer (Wang et al. 2012a). The hydrolysis of cellulose is known to be the key step prior to downstream processes. However, cellulose is insoluble in water and most ordinary solvents as a result of its highly crystalline structure and the extensive network of inter- and intra-molecular hydrogen bond between its fibrils. Therefore, a pretreatment process is highly required to make cellulose more susceptible to subsequent hydrolysis. In order to solve the difficulty of processing cellulose, a variety of solvent systems have been developed, including lithium chloride/methyl acetyl amine, ammonium rhodanate/liquid ammonia, paraformaldehyde/methyl sulfoxide, and *N*-methyl morpholine (Ding et al. 2012), but there are many shortcomings in these traditional solvent systems, such as instability, toxicity, environmental pollution, difficulty to be recovered, complex dissolved process, poor product performance, and high related costs. These limitations hamper their practical applications and promote us to develop new solvent systems.

Ionic liquids (ILs) are organic salts that exist as liquids at temperatures usually lower than 100 °C. They consist of an organic cation and a smaller organic or inorganic anion. Compared with traditional solvents, ILs own many unique physicochemical properties. These properties can be summarized as follows:

- 1) ILs exhibit a very low vapor pressure and thus do not cause air pollution which avoids the environmental problems of volatile organic solvents. They can be easily separated from other products by vacuum distillation (Bier and Dietrich 2010).

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- 2) ILs possess low melting point and wide liquid range. ILs always have a stable liquid range of more than 400 °C, and some of them are liquid even at room temperature (Anouti et al. 2008).
- 3) ILs show high thermal and electrochemical stability. The decomposition temperatures of many ILs can be greater than 400 °C. ILs also have wide electrochemical windows of approximately 5–6 V or more, which are considerably larger than that of current organic electrolytes (Ong et al. 2011).
- 4) ILs exhibit excellent dissolution performance for various materials, including most organic, inorganic, and polymer compounds (Zheng et al. 2009).
- 5) The structures of ILs can be easily modified through changing the cations or anions. So far, millions of possible ILs have been designed, thousands of which have been actually synthesized. We can design ILs of different properties to meet the requirement of different application (Stolte et al. 2011).

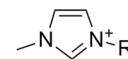
Due to the extraordinary properties discussed above, ILs have the potential to replace volatile organic compounds and been considered as new green solvents beyond supercritical fluids and aqueous two-phase systems. They have been widely used in chemical processes as catalysts for many reactions and solvents for synthesis during the last few years (Ma and Hong 2012). In 2002, Rogers and co-workers first reported that cellulose could be dissolved in high concentrations using ILs, which led to the development of a new platform for the efficient utilization of cellulose (Swatloski et al. 2002). ILs have become excellent solvents for the dissolution and the further processing of cellulose since then. Pretreatment of cellulose with ILs can improve the efficiency of hydrolysis by increasing the surface area of the substrates accessible to solvents and cellulases. Up to now, several hundred ILs have been tested for dissolving cellulose and thousands of papers are published on the applications of ILs in cellulose chemistry every year. The aim of this review is to summarize accumulated experimental experience of the use of ILs for cellulose pretreatment in recent years, with a special emphasis on imidazolium-based ones. Opinions on some fundamental factors affecting the performance of ILs are provided. Methods to assist cellulose pretreatment with ILs are also discussed. The recovery aspects and one-step hydrolysis of cellulose using cellulases/ILs systems are also analyzed, although it must be recognized that such research needs constant evaluation as new knowledge is developed.

Influence of the structure of the alkyl imidazolium cation of ionic liquids on the solubilization of cellulose

The properties of ILs can be tuned to meet specific applications by adjusting the structure of anions and cations. The

cations of ILs could be alkyl pyridine, alkyl imidazolium, quaternary ammonium, quaternary phosphonium, and alkyl alkoxyammonium (Moniruzzaman and Goto 2011). Several criteria should be considered whether an IL can be used for cellulose pretreatment, among which its melting point occupies a foremost place. By far, the most successful families of ILs for cellulose dissolution are those based on the alkyl imidazolium cations. The modern resurrection of IL chemistry is largely due to the unusually low melting points of many imidazolium salts. After Swatloski et al. (2002) first used 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) to dissolve cellulose, alkyl imidazolium-based ILs have become one of the research hot topics in recent years.

Figure 1 shows the model structure of the alkyl imidazolium cations. The alkyl group of the ILs can be varied by selection of different halohydrocarbons when they are synthesized and the effects of different alkyl groups have been comprehensively investigated by previous researchers. The alkyl side chains cannot determine the dissolution of cellulose, but it can assist in decreasing the viscosity of the ILs, resulting in enhanced dissolving ability (Pinkert et al. 2010). Smaller alkyl groups always facilitate the solubility of cellulose in ILs. The solubility of cellulose decreases as the length of the cation's carbon chain increases. For example, It has been reported that 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) is more powerful in dissolution of cellulose than [BMIM]Cl (Kosan et al. 2008), while 1-hexyl-3-methylimidazolium chloride ([C₆MIM]Cl) and 1-octyl-3-methylimidazolium chloride ([C₈MIM]Cl) are much weaker than [BMIM]Cl (Vitz et al. 2009). This result might be interpreted from two aspects. First, the increase of alkyl chain length will reduce the hydrophilicity of ILs, which weakens the affinity between the ILs and cellulose. Second, the increase of substituent chain length increases the size of the ILs. When the anions of ILs form hydrogen bonds with the hydroxyl group of the cellulose molecule chain, the cations also combine with the hydroxyl oxygen. Too large cation size might hamper this combination. Large side chains ($n > 7$) could also lead to an increase of the melting temperature, as the attractive van der Waals interactions between the alkyl side chains start outweighing the symmetry effect (Pinkert et al. 2009). In addition, an odd–even effect is observed for the small alkyl chains of the imidazolium



R = n-C₄H₉ ([BMIM]⁺), CH₂CH=CH₂ ([AMIM]⁺), CH₂CH₃ ([EMIM]⁺), n-C₆H₁₃ ([C₆MIM]⁺), n-C₈H₁₇ ([C₈MIM]⁺)

Fig. 1 The structure of typical alkyl imidazolium cations constituting ionic liquids for cellulose dissolving. *BMIM* 1-butyl-3-methylimidazolium, *AMIM* 1-allyl-3-methylimidazolium, *EMIM* 1-ethyl-3-methylimidazolium, *C₆MIM* 1-hexyl-3-methylimidazolium, *C₈MIM* 1-octyl-3-methylimidazolium

chlorides. Cellulose is more soluble in chloride-based ILs with even-numbered alkyl chains compared to odd-numbered alkyl chains (Vitz et al. 2009). However, this effect cannot be found in ILs with other anions, e.g., acetate (El Seoud et al. 2011).

An unsaturated ethylenic group in the alkyl chain, such as the allyl group, is known to lower the melting point of the ILs. Low temperature dissolution is a great breakthrough to the traditional cellulose dissolving method and also a strong driver force of green chemistry. Because of very low melting point of imidazolium salts after introducing the double bond, these ILs are real room temperature ILs and can be used in liquid form without heating (Ohno and Fukaya 2009). At the same time, the viscosity of the corresponding IL is lowered, as in the case of 1-allyl-3-methylimidazolium chloride ([AMIM]Cl). Moreover, these ILs have stronger dissolution capabilities for cellulose than those of the common imidazolium-based ILs with the same anions. For instance, konjac glucomannan could be dissolved in [AMIM]Cl much faster than [BMIM]Cl (Shen et al. 2011). The dissolution rate of microcrystalline cellulose in [AMIM]Cl could reach 28.8% when the cellulose was pretreated with 15% NaOH under high pressure (Guo et al. 2009). However, there are still some disadvantages of these ILs. The reactive double bond in the side chain might make them unstable (Zhao et al. 2009).

Functional groups in the cations are also crucial for the dissolution of cellulose. The presence of a hydroxyl on the cation side chain could be helpful to dissolve cellulose. It has been demonstrated that ILs containing hydroxyl group, such as 1-(2-hydroxyethyl)-3-ethyl imidazolium chloride ([HeIM]Cl) and 1-(2-hydroxyethyl)-3-ethylene imidazolium chloride ([HeVIM]Cl), exhibit better solubility to cellulose than normal ILs such as [BMIM]Cl, [AMIM]Cl, and 1-allyl-3-ethylimidazolium chloride ([AEIM]Cl) (Guo and Zhang 2010). This might be due to that the hydroxyl group on the alkyl chain could interact with the hydroxyl groups of cellulose, further weakening the hydrogen bonding among the cellulose fibers and promoting their dissolving (Muhammad et al. 2012). Recent studies showed that the dissolution efficiency of 1-(2-methoxyethyl)-3-methylimidazolium acetate ([C₃OMIM]OAc) was even greater than 1-butyl-3-methylimidazolium acetate ([BMIM]OAc), though 1-(3,6-dioxo-(1-heptyl))-3-methylimidazolium acetate ([C₅O₂MIM]OAc) displayed much lower dissolving ability. That is, the alkoxy group is more efficient in shorter side chain ILs, but not in its long-chain counterparts (El Seoud et al. 2011). On the contrary to the above discussions, Maki-Arvela et al. (2010) proposed another point of view that the hydroxyl end-group in the cations would decrease the solubility of cellulose in the corresponding ILs. The hydroxyl group could compete with cellulose in forming hydrogen bonds to the anions.

Influence of the anions of imidazolium-based ionic liquids on solubilization of cellulose

Both the anions and the cations of the ILs are thought to participate in cellulose solubilization, with the former playing a more dominant role. Figure 2 shows the proposed dissolution mechanism of cellulose in ILs. ILs could interact with the cellulose hydroxyl groups to form an electron donor–electron acceptor complex, resulting in the opening of the hydrogen bonds between molecular chains of the cellulose. Anions of ILs which could efficiently dissolve cellulose are always good hydrogen bond acceptors. The degree of dissolution in an IL is positively related with the hydrogen bond accepting ability of the anion (Xu et al. 2010). The nondissolving anions, such as BF₄[−] and PF₆[−], display poor hydrogen bond acceptor characteristics. The hydrogen bond accepting ability can be roughly estimated by the anion basicity (Palgunadi et al. 2011). ILs exhibiting greater ability to dissolve cellulose always consist of anions with higher basicity. ILs containing low-basicity anions, such as dicyanamide-based ILs, are not efficient in dissolving cellulose. Anions with a relatively small size are also expected to enhance cellulose dissolution since these ILs offer a flexible arrangement of their dipoles that an energetically favored combination with cellulose can be formed. Previous studies have shown that the most promising anions are chloride, carboxylates, and alkyl phosphates.

Chloride

The chloride anion, being small-sized hydrophilic hydrogen bond acceptor, is a potent anion when aiming at cellulose dissolution. Chloride-based ILs are the most widely used ILs for cellulose pretreatment. They could be easily synthesized by a one-step quaternization reaction of alkyl imidazolium and haloalkane (Kärkkäinen et al. 2011). Other halide anions, including Br[−] and I[−], seem not to be as effective as Cl[−]. By comparing ILs with the same cation [BMIM]⁺ but with different anions of Cl[−], Br[−], and I[−], Sashina and Novoselov (2009) found that [BMIM]Cl showed much stronger dissolving capacity to cellulose. The radii of these anions increase in the following order: Cl[−] < Br[−] < I[−], which is in accordance with the decreasing cellulose dissolution properties of the following ILs: [BMIM]Cl > 1-butyl-3-methylimidazolium

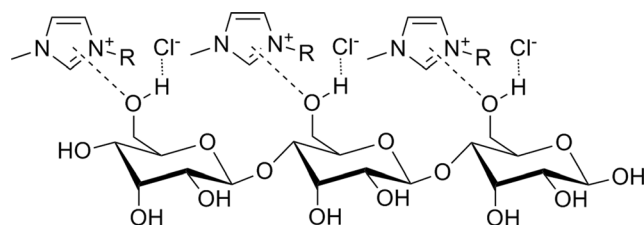


Fig. 2 Proposed dissolution mechanism of cellulose in ionic liquids. The cations and anions of ILs interact with the cellulose hydroxyl groups to break the hydrogen bonds between molecular chains of the cellulose

bromide ([BMIM]Br) > 1-butyl-3-methylimidazolium iodine ([BMIM]I) (Vitz et al. 2010). Although the applications of the halide-based ILs greatly promote the development of cellulose chemistry, they still have their disadvantages. Most chloride-based ILs are solid or a sticky paste at room temperature. The viscosity of chloride-based ILs is also higher than water and organic solvents by a factor of tens or hundreds. The high melting point and viscosity of these ILs make them difficult to handle and are generally considered as a technical drawback on the recyclability of the solvents. In addition, chloride-based ILs only provide high solubility for cellulose when the biomass is dry. The presence of trace amount water results in precipitation of cellulose and a highly viscous mixture is formed.

Carboxylate

The limitations of chloride-based ILs require us to develop new type ones to overcome these shortcomings, leading to the discovery of carboxylate-based ILs. Carboxylate-based ILs are less viscous than the chloride type and the melting points of these ILs are always below 0 °C. They are identified as one of the most promising advances towards a high dissolution property to cellulose. A series of imidazolium-based carboxylate salts have been synthesized. Their ability to dissolve cellulose and other polysaccharides under mild conditions is greater than chloride-based ILs due to their strong hydrogen bond accepting capacity. Solutions with high cellulose concentrations (up to 20%) could be obtained using 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) without any significant gel formation, which was much higher than [EMIM]Cl (Hermanutz et al. 2008). Among the common carboxylates, propionate- and acetate-based ILs show better solubility to cellulose and are more thermally stable than formate ones. Dicarboxylates always give higher solubility compared to monocarboxylates (Zhao et al. 2012a). Quantum mechanical calculations indicated that the alkyl imidazolium cation could react with the carboxylate anion to generate a carbene, a highly reactive intermediate. The carbene produced then interacted with cellulose to facilitate its dissolution in the IL solvents (Du and Qian 2011).

Alkyl phosphate

The carboxylate-based ILs display much lower viscosity at room temperature, but relatively poor thermal stability due to the decarboxylation of the anions. Moreover, these ILs are prepared by a two-step reaction, in which the halide counter anion is first converted to hydroxide, and then coupled with the desired carboxylate anion (Fukaya et al. 2008). To overcome these drawbacks, we need a new class of easily preparable ILs with sufficient ability to dissolve cellulose. In recent years, alkyl

phosphate-based ILs have already resulted in cellulose solutions in commercially attractive concentrations owing to that these ILs could be synthesized by one-step quaternization of alkyl imidazolium with corresponding phosphoric acid esters. Compared to the carboxylate anions, alkyl phosphates show weaker ability to delocalize the charge between oxygen atoms in cellulose. This is possibly due to that the larger anion size hinders efficient interaction with the hydrogen bond network of cellulose. However, alkyl phosphate-based ILs possess even lower melting point and viscosity than the other types. They can dissolve cellulose at 45–65 °C, a temperature at which chloride-based ILs are solid (Fukaya et al. 2008). Recent studies showed that both of 1-ethyl-3-methylimidazolium dimethyl phosphate ([EMIM]DMP) and 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM]DEP) had the ability to dissolve untreated cellulose under mild conditions, while the latter exhibited a faster dissolving rate (Zhao et al. 2012b). In addition, phosphate-based ILs display the best biocompatibility among currently synthesized ILs, which promote their applications in the following enzymatic hydrolysis of cellulose (Jones and Vasudevan 2010).

Methods assisting cellulose pretreatment in ionic liquids

Cellulose dissolving in ILs is a slow process and always requires stirring and thermal heating. Previous researchers have developed different techniques to accelerate the course of dissolution, among which organic co-solvents, microwave, and ultrasound are the most promising ones.

Organic co-solvents

Despite their efficiency, the high viscosity of the obtained cellulose/ILs solution is the main drawback for pretreatment. Co-solvents might facilitate the dissolution of cellulose by reducing the viscosity of the solution. Acetic acid is a suitable acidic catalyst for the hydrolysis of cellulose. It also works as a co-solvent, increasing the solubility of cellulose in ILs (van Spronsen et al. 2011). Highly effective cellulose solvents for the dissolution of cellulose have been designed by adding dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), or *N,N*-dimethylacetamide (DMA) to ILs (Xu et al. 2013). DMSO was found to increase the conductivity of the cellulose/ILs mixture, facilitating mass transport without significantly affecting the interactions between ILs and cellulose. Therefore, DMSO could improve the solvation capability and allow much faster dissolution of cellulose (Andanson et al. 2014). The co-solvents DMSO, DMF, and DMA were further tested their capability on cellulose dissolution by adjusting

their ratio to ILs. The enhancement of cellulose dissolution by these co-solvents was observed in both [EMIM]OAc and [EMIM]DMP other than [EMIM]Cl (Mai et al. 2014b). This might be explained by the reducing in the hydrogen bond basicity of ILs/co-solvents at high ratio of co-solvents. Another co-solvent, ethanolamine was found to render greater enhancement of both corncob and rice straw pretreatment than [EMIM]OAc or [BMIM]Cl (Weerachanchai and Lee 2013). 1,3-Dimethyl-2-imidazolidinone could also enhance cellulose dissolution in [EMIM]DEP by 20–60% compared to pure [EMIM]DEP at mass ratios up to 1:1 (Minnick et al. 2016). Most of the co-solvents used for the enhancement of cellulose dissolution are aprotic polar compounds. These aprotic polar solvents serve to mainly solvate cation and less likely anion of the ILs. The hydrogen bond accepting ability of the anions is improved, thus resulting enhanced cellulose dissolution (Velioglu et al. 2014).

Microwave irradiation

Microwave irradiation can significantly improve the solubility of cellulose in ILs. Microwave heating is characterized as an internal heating process due to the direct absorption of energy by polar molecules which may be responsible for the effective breakdown of the hydrogen bond between the cellulose fibrils. It is an environmentally friendly heating method which is usually applied to the dissolution of cellulose (Li et al. 2011b). The accelerating effect of microwave irradiation on alkali- or acid-catalyzed hydrolysis of cellulose has long been recognized. Impressive results have been obtained when microwave irradiation was used to dissolve cellulose instead of regular heating. Because ILs consist of anions and cations, they have excellent microwave conductivity and thus the substances in ILs may be heated up much more rapidly by microwave than conventional heating. When Swatloski et al. (2002) first applied ILs for cellulose pretreatment, solutions containing up to 25% cellulose could be prepared in [BMIM]Cl under microwave heating compared to 3–10% of cellulose solution by conventional heating. Microwave irradiation not only enhances the solubility of cellulose in ILs but also significantly decreases the degree of polymerization of regenerated cellulose after IL pretreatment, resulting in significant improvement of subsequent cellulose hydrolysis (Ha et al. 2011). Microwave also leads to much shorter dissolving times. Compared with conventional oil bath heating mode, microwave irradiation at an appropriate power significantly reduced the reaction time and increased the yields of reducing sugars for cellulose hydrolysis in [BMIM]Cl (Zhang and Zhao 2009). The degradation of cellulose could be controlled by the intensity of microwave. Microwave-assisted cellulose dissolution in [BMIM]Cl without changing the degree of

polymerization was obtained by use of low-energy microwave heating (Possidonio et al. 2010).

Ultrasonication

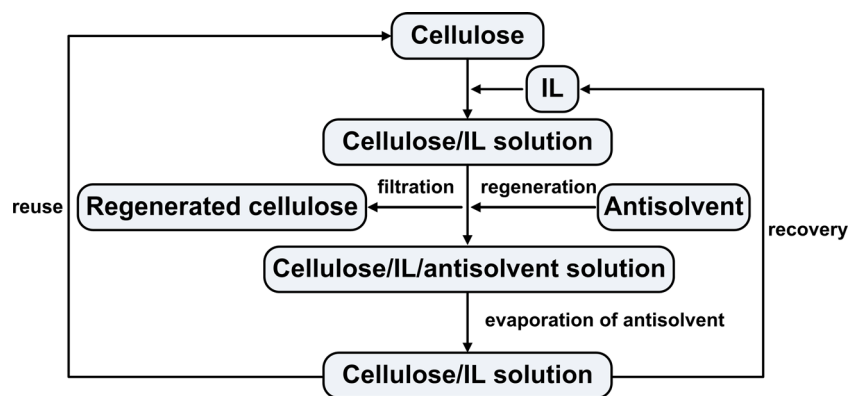
Ultrasonic irradiation has damaging impact on cellulose fibers, which is a novel method to assist and improve the efficiency of cellulose pretreatment. The mechanical effects of ultrasound are related to cavitation, heating, dynamic agitation, shear stress, and turbulence. Mikkola et al. (2007) first demonstrated the possibility to apply ultrasonication in cellulose processing with ILs such as [BMIM][Cl] and [AMIM][Cl]. The dissolution process of cellulose was profoundly enhanced by means of high-intensity ultrasound. Ultrasonic irradiation could effectively reduce the dissolving time of cellulose in [BMIM]Cl. The thermal stability of cellulose decreased and the pyrolysis residues increased after dissolution and regeneration in this IL (Lan et al. 2011). The results of Ma et al. (2012) showed that ultrasound irradiation was helpful to modification of sugarcane bagasse cellulose in [BMIM]Cl. The enzymatic hydrolysis of cellulose was also drastically enhanced following ultrasonic pretreatment of kenaf powder in five different types of ILs compared to conventional thermal pretreatment (Ninomiya et al. 2012).

Regeneration and recovery of sugars and ionic liquids

Due to their current high cost, the effective regeneration, recovery, and recycle of ILs are required for commercial use in biomass pretreatment, as well as to emphasize the environmental benefits of ILs. High-performance recovery of IL and cellulose is essential for an IL-based pretreatment technology to be economically feasible. A strategic approach for the reuse, regeneration, and recovery of ILs has been conceived and represented in Fig. 3. After being pretreated with ILs, most of the dissolved cellulosic content can be easily precipitated by the addition of an anti-solvent such as water, ethanol, or acetone, with anti-solvents and ILs forming a single phase (Tan et al. 2011). Cellulose can be recovered by filtration or centrifugation and washed to remove excess ILs. The resulting monomeric sugars in the ILs could also be extracted using boronates, such as phenylboronic acid and naphthalene-2-boronic acid, which showed high chemical affinity to sugars (Brennan et al. 2010).

The recovery operations of ILs from aqueous solutions can be accomplished by several different strategies: liquid extraction, chromatography, and membrane filtration (Mai et al. 2014a). ILs have a very good solubility with organic materials and inorganic salts. However, an aqueous biphasic system can be formed when electrolytes are added to the mixture of ILs and water. The phase rich in ILs could be easily separated and then recovered using other methods (Fernández et al. 2011b). The combination of distillation, liquid extraction, and

Fig. 3 Simplified diagram of strategic approach for the reuse, regeneration, and recovery of ionic liquids



precipitation was successfully employed to recover [EMIM]OAc from the lignocellulosic hydrolysates with a recovery rate of 89% (Dibble et al. 2011). Ion exclusion chromatography enabled separation of the sugars and ILs from the corn stover hydrolysis reaction mixture. A mixture containing electrolyte and nonelectrolyte solutes was separated by passing it through a charged resin (Binder and Raines 2010). Alumina column chromatography method was developed for the separation of hydrophilic IL 1-methyl-3-methylimidazolium dimethyl phosphate ([MMIM]DMP) and glucose, which was the main ingredient of the monosaccharide hydrolysate. Regenerated ILs had no apparent difference to fresh ones (Feng et al. 2011). Simulated moving bed chromatography equipped with ion exclusion column was also investigated to recover [EMIM]OAc and sugars from the hydrolyzed biomass (Mai et al. 2012). As ILs are composed of cations and anions, electrodialysis can be also used for the recycle of ILs. The highest recovery ratio of ILs could reach 85.2% using this method (Wang et al. 2012b). [BMIM]Cl and [BMIM]OAc could be recovered from the aqueous solution by nanofiltration after the dissolution of cellulose and further regeneration by water addition, which was also almost free of undesired by-products (Fernández et al. 2011a).

Toxicity of ionic liquids

Although the low vapor pressure of ILs avoids their diffusion to the atmosphere, their solubility in water is far from negligible. Therefore, ILs cannot completely eliminate the environmental hazards. Considering the possible large-scale utilization of ILs for cellulose pretreatment, they will be present in the wastewater and their toxicity must be evaluated. ILs possess excellent chemical and thermal stability, which gives a negative aspect for their treatment prior to disposal. Recent studies in this field have shown that ILs could be degraded by physical, chemical, and biological methods. The common oxidation process by UV/H₂O₂ was investigated for their applicability in the degradation of imidazolium-based ILs in aqueous solution. ILs with longer alkyl chains were found to be

more difficultly degraded (Stepnowski and Zaleska 2005). Biodegradation of imidazolium-based ILs was first conducted by Gathergood and Scammells (2002) when they introduced functional groups into the cation's side chain. The introduction of an ester group into the alkyl chains would reduce the toxicity and improve the biodegradability of ILs (Coleman and Gathergood 2010).

Cellulose pretreated with ILs could be enzymatically hydrolyzed into carbohydrates. However, the inhibition effects of ILs have been observed to many different enzymes (Thuy Pham et al. 2010). Therefore, the residual ILs would be harmful to subsequential enzymatic hydrolysis. The enzyme inhibition assays suggested that the alkyl imidazolium cation was the dominating factor affecting the toxicity of ILs, which might guide the design of enzyme-compatible ILs. The alkyl chain length of the imidazolium cations would also affect the structural changes and enzyme activity (Kim et al. 2016). The sugars obtained by ILs pretreatment and hydrolysis are generally fermented by microorganisms to produce biofuels and value-added chemicals (Cao et al. 2016). Therefore, the toxicity of ILs to microorganisms is critical to further biotransformation. Toxicity tests showed that imidazolium-based ILs have anti-microbial activities towards a variety of bacteria (Cho et al. 2016a), yeasts (Ouellet et al. 2011), fungi (Cho et al. 2016b), and microalgae (Pham et al. 2008), hampering the growth rate of microbes and the products' yield. Reducing the toxicity of ILs to enzymes and microorganisms is an important direction for future studies.

Design of cellulase-compatible ionic liquids

Cellulose pretreated with ILs cannot be directly utilized for biofuel and bio-based chemical production. They must be hydrolyzed to monosaccharides for further applications. Enzymatic hydrolysis of cellulose by cellulase is one research hotspot among all the hydrolysis methods. However, native cellulases are severely inhibited by ILs, even when present at very low concentrations. Thus, a cumbersome recovery process as described above is necessary to retrieve the

regenerated cellulose prior to enzymatic hydrolysis. It is a painstaking and time-consuming task. A potential approach to overcome this drawback is to in situ hydrolyze dissolved cellulose in ILs, which requires developing ILs compatible with both cellulose solubility and cellulase activity. Kamiya et al. (2008) reported that the enzymatic saccharification of cellulose in aqueous-IL media was made possible by adjusting the ratio of [EMIM]DEP to water. Over 50% of the cellulose could be converted to glucose in 24 h, indicating that [EMIM]DEP showed good compatibility with cellulase. But the efficiency of cellulose hydrolysis into glucose is still not high enough in aqueous-[EMIM]DEP system. In-depth studies concerning biocompatibility of ILs and process intensification of in situ enzymatic saccharification would be necessary to make the hydrolysis more applicable. Li et al. (2010) compared nine ILs and chose [MMIM]DMP as an environmentally friendly solvent to pretreat corn cob. The in situ saccharification process in 20% [MMIM]DMP aqueous solution was efficiently performed, and more than 70% saccharification rates were obtained. After further optimization of reaction parameters concerning cellulase concentration, temperature, and IL concentration, even higher conversion (95.48%) of cellulose was obtained in the media of aqueous-[MMIM]DMP by conducting the pretreatment with ultrasonic heating (Yang et al. 2010). [EMIM]OAc was also found to be efficient for in situ enzymatic hydrolysis of microcrystalline cellulose among several representative ILs. Microwave treatment could give rise to a significant improvement in the conversion of cellulose to glucose (Li et al. 2011a). Wahlstrom et al. (2012) compared the activity and action of two endoglucanases in the ILs [EMIM]OAc and [MMIM]DMP. Both of the employed ILs severely inactivated the endoglucanases, while the in situ saccharification rate of microcrystalline cellulose in [EMIM]OAc was much lower as compared to [MMIM]DMP. Recently, microcrystalline cellulose was pretreated by a commercial cellulases/[EMIM]OAc system and further used for high-value α -ketoglutaric acid production by the yeast *Yarrowia lipolytica* (Ryu et al. 2015).

In the previous studies, ILs used for one-pot hydrolysis of cellulose are based on alkyl phosphate and acetate anions. Basic anions such as Cl^- , Br^- , and NO_3^- seem to strongly inactivate cellulase activity as they interfere with the hydrogen bond network keeping the enzyme together (Bose et al. 2010). Moreover, cellulase activity was highly dependent on the IL content in aqueous-IL media, and it was found that 20% ILs in the media gave the best results while very little enzymatic activity was observed in IL contents over 40% (Moniruzzaman et al. 2010). Recently, a new approach to improve the cellulase stability against ILs by coating of immobilized enzyme particles with hydrophobic ILs was proposed. The stability of cellulase immobilized onto a polymeric support in [BMIM]Cl mixtures was greatly improved with respect to [BMIM]Cl alone. A stabilized cellulase derivative

obtained by coating immobilized enzyme particles with butyltrimethyl-ammonium bis(trifluoromethylsulfonyl)imide ($[\text{N}_{1114}][\text{NTf}_2]$) was then successfully used for the saccharification of dissolved cellulose in [BMIM]Cl at a low water content (Lozano et al. 2011). Immobilized cellulose also preserved partial activity after being incubated in ILs containing Br^- , Ac^- , or OTs^- anions (Ungurean et al. 2014).

Utilization of ionic liquids for the pretreatment of lignocellulosic biomass

In nature, cellulose always co-exists with hemicellulose and lignin to form lignocellulosic biomass, the most abundant plant material on the earth. The utilization of ILs for the deconstruction of real lignocellulosic materials was more important for practical applications (Brandt et al. 2013). Imidazolium-based ILs have already been used in attempts to dissolve the whole lignocellulosic biomass. Table 1 summarizes the representative research achievements on the pretreatment of cellulose or lignocellulosic biomass using different imidazolium-based ILs and their main findings. As early as 2007, Rogers and co-workers first described the dissolution of wood powder in [BMIM]Cl, while cellulose could be reconstituted from the ILs-based wood liquors by the addition of anti-solvents (Fort et al. 2007). The dissolution of both hardwoods and softwoods in different ILs was investigated afterwards and [AMIM]Cl was found to be more effective than its dialkyl analogs under the same conditions (Kilpeläinen et al. 2007). The solubility of an easily available lignocellulosic feedstock, *Miscanthus*, was also tested in various ILs. The anions of the ILs were demonstrated to have a significant effect on solubility and rate of dissolution (Padmanabhan et al. 2011). The cellulose fraction recovered could be subjected to enzymatic hydrolysis, and most of the carbohydrates in the original biomass were released by the combined ILs pretreatment and enzymatic hydrolysis (Brandt et al. 2011). The amino acid IL 1-ethyl-3-methylimidazolium glycine ([EMIM]Gly) was used for the pretreatment of bamboo and the cellulose proportion was regenerated from the total biomass (Muhammad et al. 2015). In a recent study, [BMIM]Cl and [BMIM]OAc were used for the pretreatment of rubber wood. Kinetics and thermodynamic parameters were determined during these processes, which indicated that ILs pretreatment decreased the thermal stability of the rubber wood. The separation of lignin and hemicellulose during pretreatment provided a potential way to improve the hydrolysis of rubber wood (Khan et al. 2016). The efficient separation of cellulose from the mixture is more important for the utilization of lignocellulose. Although researchers have explored the possibility for the separation of cellulosic components with ILs (Muhammad et al. 2012), it is still difficult to completely achieve this goal. To design and prepare new task-specific ILs which are ought to have high separation

Table 1 Advances of cellulose and lignocellulosic biomass pretreatment using imidazolium-based ionic liquids

| Cations | Anions | Substrates | Main findings | References |
|---|--|---|---|------------------------------|
| [BMIM] ⁺ | Cl ⁻ , Br ⁻ , SCN ⁻ | Pulp cellulose, fibrous cellulose, Whatman cellulose filter paper | ILs can be used for cellulose dissolving. | Swatloski et al. (2002) |
| [EMIM] ⁺ , [BMIM] ⁺ | Cl ⁻ , OAc ⁻ | Eucalyptus prehydrolysis sulfate pulp, cotton linters pulp | [EMIM] ⁺ is better than [BMIM] ⁺ and OAc ⁻ is better than in Cl ⁻ . | Kosan et al. (2008) |
| [MMIM] ⁺ to [C ₁₀ MIM] ⁺ | Cl ⁻ , Br ⁻ , OAc ⁻ , DMP ⁻ , DEP ⁻ | Avicel PH-101 cellulose | Increasing alkyl chain length of ILs will reduce dissolubility of cellulose. | Vitz et al. (2009) |
| [AMIM] ⁺ , [BMIM] ⁺ | Cl ⁻ | Konjac glucomannan | [AMIM]Cl dissolves cellulose much faster than [BMIM]Cl. | Shen et al. (2011) |
| [C ₃ OMIM] ⁺ , [C ₅ O ₂ MIM] ⁺ | Cl ⁻ , OAc ⁻ | Eucalyptus sheets | The alkoxy group in side chain will facilitate cellulose dissolution. | El Seoud et al. (2011) |
| [BMIM] ⁺ | Cl ⁻ , Br ⁻ , SCN ⁻ , OAc ⁻ | Cellulose | The order of decrease in the solubility is as follows: OAc ⁻ > Cl ⁻ >> Br ⁻ = SCN ⁻ | Sashina and Novoselov (2009) |
| [MMIM] ⁺ , [EMIM] ⁺ | OAc ⁻ , propionate, butyrate, Maleate, succinate | α-Cellulose | Dicarboxylates always give higher solubility compared to monocarboxylates. | Zhao et al. (2012a) |
| [EMIM] ⁺ , [BMIM] ⁺ | Cl ⁻ , OAc ⁻ | Sigmacell type 101-F, Avicel PH-101, Whatman filter paper 1, Advantec filter paper 4A | Microwave irradiation enhances the solubility of cellulose and subsequent cellulose hydrolysis. | Ha et al. (2011) |
| [MMIM] ⁺ | DMP ⁻ | Microcrystalline cellulose | Ultrasonic heating could significantly increase cellulose solubility. | Yang et al. (2010) |
| [BMIM] ⁺ | Cl ⁻ | Pine, poplar, eucalyptus, oak wood shavings | [BMIM]Cl could dissolve wood biomass and cellulose can be separated from the IL-based wood liquors. | Fort et al. (2007) |
| [EMIM] ⁺ | DEP ⁻ | Wheat straw | [EMIM]DEP could dissolve wheat straw and accelerate further enzymatic hydrolysis. | Li et al. (2009) |
| [MMIM] ⁺ , [EMIM] ⁺ , [BMIM] ⁺ | Cl ⁻ , OAc ⁻ , DMP ⁻ | <i>Miscanthus</i> | Chloride, acetate, and phosphate-based ILs favor solubility of <i>Miscanthus</i> . | Padmanabhan et al. (2011) |
| [MMIM] ⁺ , [EMIM] ⁺ | DMP ⁻ , DEP ⁻ | Cotton-ramie pulp | [EMIM]DEP was better to dissolve cellulose. | Zhao et al. (2012b) |
| [MMIM] ⁺ , [EMIM] ⁺ , [BMIM] ⁺ | Cl ⁻ , OAc ⁻ , DMP ⁻ , DEP ⁻ | Barely straw | [EMIM]OAc was found most effective in pretreating barely straw. | Mood et al. (2013) |
| [EMIM] ⁺ | Glycine | Bamboo | [Emim]Gly could be used for the pretreatment of bamboo and regeneration of cellulose. | Muhammad et al. (2015) |
| [BMIM] ⁺ | Cl ⁻ , OAc ⁻ | Rubber wood | ILs pretreatment could improve the thermal conversion of rubber wood. | Khan et al. (2016) |

capability for lignocellulose is an important aspect of future studies.

Conclusions and future perspectives

Because of the worldwide energy shortage and environmental pollution, we have to make full use of cellulosic biomass in the future. ILs have played an important role in the production of clean energy and bio-based products owing to their excellent physicochemical properties and outstanding performance in the dissolution and separation of lignocellulose. The pretreatment of cellulose using ILs has been providing a new platform for “green” utilization of cellulose. This might bring the breakthrough in production of chemicals such as ethanol and lactic acid from lignocellulosic materials and reduce the dependence on nonrenewable petroleum-based feedstocks (Cao et al. 2015). However, the research on this area is still at its infant stage. Although cellulose pretreatment with ILs is a viable method, it faces many challenges. In the future work, the following issues are suggested.

1) Up to now, no noteworthy published reports have been made on the costs of commercial-scale production of ILs and ILs are obviously more expensive than traditional solvents (Andreani and Rocha 2012). Thus, the application of ILs is currently facing economic challenges. In order to make the process of cellulose pretreatment economically feasible, we should develop new synthetic process to lower the production cost of ILs. Meanwhile, inexpensive methods should be developed for the recovery and recycle of ILs.

2) The dissolving process of cellulose in ILs always requires thermal heating. The high viscosity of ILs and the slow rate of dissolution also cause agglomeration of cellulose and result in high energy consumption for stirring (Tian et al. 2011). This requires us to develop real room temperature ILs and ILs with much lower viscosity.

In any case, our knowledge of ILs has advanced significantly during the past few years, and the steadily growing interest in ILs as solvents is not expected to cease in the near future. Further research is required to address the current facing challenges in order to meet the demand of large-scale application, probably the only viable perspective for these promising systems. It can be stated that a thorough understanding of the influence of the ion type and structure on the behavior of the ILs would be achieved. The mechanism of cellulose dissolution in ILs will be clarified, and the use of environmentally benign solvents for cellulose will open broad prospects for the development of new high-quality cellulose materials. It is quite clear that the commercialization of ILs-based processes will take place in the foreseeable future, and we will benefit a lot from these technologies.

Compliance with ethical standards

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