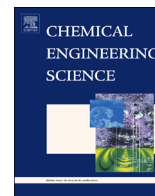




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Cellulose dissolution and regeneration in ionic liquids: A computational perspective

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HIGHLIGHTS

- Computational studies for cellulose dissolution/regeneration in ILs are reviewed.
- Hydrogen-bonding plays a paramount role in both dissolution and regeneration.
- Cosolvents facilitate hydrogen-bonding of cellulose–IL and enhance dissolution.
- Anti-solvents destruct hydrogen-bonding of cellulose–IL and cause regeneration.

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ABSTRACT

To meet the increasing global energy demand and reduce the dependency on traditional fossil fuels, renewable biomass particularly cellulose has attracted considerable interest. Prior to processing and conversion into valuable products, cellulose needs to be pretreated (dissolved and then regenerated) via an environmentally benign route. Emerging as versatile solvents, ionic liquids (ILs) have been extensively examined for cellulose dissolution/regeneration. However, the underlying mechanisms of cellulose dissolution/regeneration in ILs remain elusive and the key governing factors are not fully understood at a microscopic level. This review summarizes the recent computational studies on cellulose pretreatment, including cellulose dissolution in neat ILs and IL/solvent mixtures, as well as cellulose regeneration by anti-solvents. Atom-resolution and time-resolved insights are provided to microscopically and fundamentally elucidate cellulose dissolution/regeneration, which are indispensable in the rational screening and design of new ILs for efficient cellulose pretreatment. Furthermore, the challenges for future computational exploration in this field are discussed.

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1. Introduction

1.1. Biomass and cellulose

Biomass is an abundant resource of renewable feedstock on the Earth (Graziani and Fornasiero, 2007). Substantial attention has been received towards the development of technically feasible methods to convert biomass into valuable products such as biofuels, chemicals and biomaterials (Muhammad et al., 2012). Particularly, the conversion of biomass to biofuels is appealing, which will reduce not only the dependence on fossil fuels, but also environmental pollution (Kunkes et al., 2008). The U.S. Department of Energy has set a target to achieve by 2025, i.e., nearly 30% transportation fuel is biofuels and 25% of organic compounds are renewable biochemicals (Ragauskas et al., 2006).

Plants and plant-based (lignocellulosic) biomass contains three key components: cellulose, hemicellulose and lignin. The percentages of these components are approximately 50, 25 and 25 wt%, respectively; though they may vary depending on the source of finding and growth condition. Cellulose is a linear polymer of anhydroglucose units and exists in either crystalline or amorphous form; hemicellulose is an oligomer of glucose and xylose, composed of amorphous monosaccharide units; lignin is a cross-linked complex polymer mainly including syringyl and sinapyl units. The mechanical strength of plants is largely attributed to the lignin, which holds cell walls together and acts as a barrier preventing enzymatic attack to cellulose and hemicellulose (Petrus and Noordermeer, 2006).

As the major component of biomass, cellulose has a global quantity of 700,000 billion tons. Nevertheless, only 0.1 billion tons of cellulose is currently being used for the production of paper, textiles, pharmaceutical compounds, etc. (Olivier-Bourbigou et al., 2010). Thus, a large amount of cellulose is still untapped. Cellulose is a polysaccharide composed of linear chains, from several hundred

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to over ten thousand, linked by β (1 \rightarrow 4) D-glucose units (i.e. glucosidic linkage). The hydroxyl groups along the chains are connected via hydrogen-bonds (H-bonds) in both parallel and anti-parallel fashion, as illustrated in Fig. 1. As a consequence of the H-bond network, cellulose possesses strong mechanical strength and cannot be easily dissolved in common solvents.

For the widespread utilization of cellulose, the prime step in processing is cellulose dissolution. Traditionally, two types of solvents (derivatizing and nonderivatizing) are suggested to dissolve cellulose. The derivatizing solvents such as sodium hydroxide/carbon disulfide or sodium hydroxide/urea mixtures interact chemically with the hydroxyl groups of cellulose and form intermediates (Klemm et al., 2005; Pinkert et al., 2009). In contrast, the nonderivatizing solvents such as *N*-methylmorpholine-*N*-oxide monohydrate, *N,N*-dimethylacetamide/LiCl and dimethylsulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF) do not form intermediates (Hermanutz et al., 2008; Rosenau et al., 2001; Li and Zhao, 2007). Although these solvents are available and used by industry, they are not environmentally benign due to the lack of recyclability and the requirement of high temperature and pressure to operate (Zhu et al., 2006). Therefore, there is a critical need to develop alternative solvents to dissolve cellulose.

1.2. Ionic liquids

As a new class of solvents, ionic liquids (ILs) have attracted considerable interest. ILs are unique ionic materials with melting temperatures lower than 100 °C, substantially lower than normal salts (e.g. NaCl). If the melting temperatures are below room temperature, they are coined as room temperature ILs (RTILs). The most common cations in ILs are bulky, asymmetric and organic in nature, such as imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, piperidinium, pyrazolium, thiazolium, and sulfonium. Anions may range from simple halides, inorganic ions to large organic ions. Fig. 2 depicts the chemical structures of typical cations and anions in ILs (Plechkova and Seddon, 2008).

The salient characteristics distinguishing ILs from conventional solvents are the wide range of melting temperature (−40 to 400 °C), high thermal stability (up to 400 °C), low vapor pressure, weakly coordinating properties, low flammability, high conductivity (both ionic and thermal), and broad electrochemical potential window (−4 to 4 V). Their physical and chemical properties can be tuned by the permutation of cations and anions, which is barely possible in conventional solvents (Freudenmann et al., 2011). Therefore, ILs have been considered as a good substitute for

traditional volatile solvents and hence classified as “green” solvents for a broad spectrum of potential applications in both industrial-scale (Plechkova and Seddon, 2008) and laboratory scale (Olivier-Bourbigou et al., 2010).

Among various applications schematically demonstrated in Fig. 3, ILs have been recommended for cellulose dissolution and regeneration. The first attempt using IL for cellulose dissolution was dated back to 1934 by Graenacher, who used *N*-ethylpyridinium chloride in the presence of *N*-containing bases (Graenacher, 1934). At that time, however, the practical importance of ILs was not realized. Only in 2002, Swatloski et al. found that 1-*n*-butyl-3-methylimidazolium chloride [C₄mim][Cl] could dissolve cellulose up to 25 wt% by microwave heating. They further reported that the dissolved cellulose could be readily regenerated by adding anti-solvents such as water, ethanol, and acetone (Swatloski et al., 2002). Thereafter, 1-*n*-allyl-3-methylimidazolium chloride [Amim]Cl was tested for cellulose dissolution as well as regeneration (Zhang et al., 2005). Cellulose dissolution in six Cl[−] and [Ac][−]-based ILs and its regeneration using water were investigated

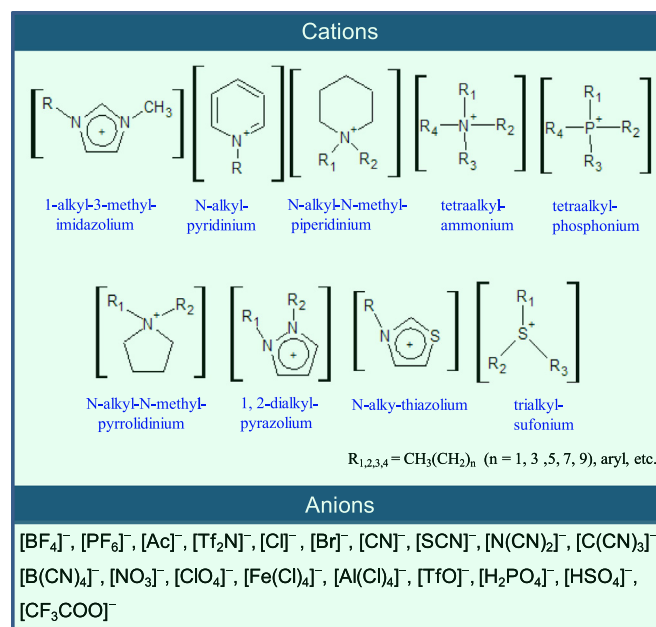


Fig. 2. Typical cations and anions in ILs.

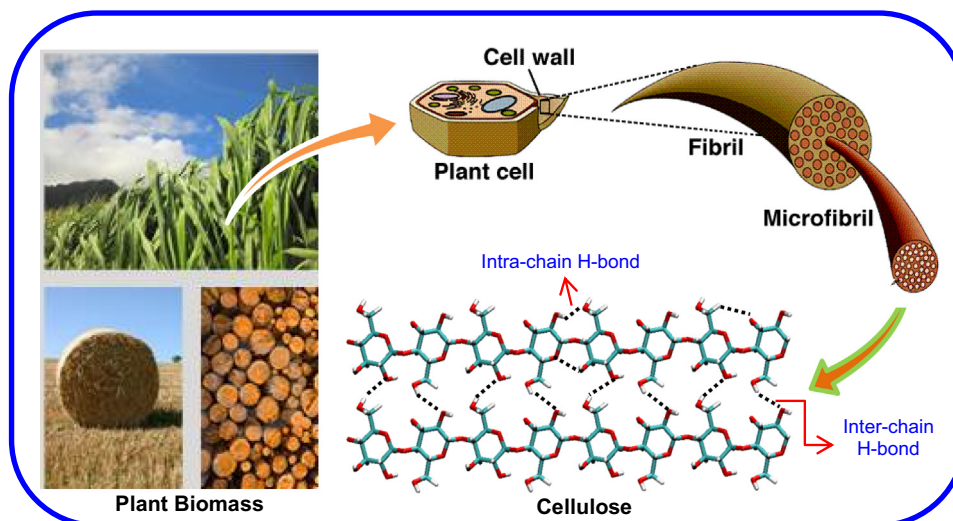


Fig. 1. Cellulose network in plant biomass.

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