



Enhancing cellulose dissolution in ionic liquid by solid acid addition



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ABSTRACT

It's challenging to dissolve natural cellulose in most solvents due to its highly ordered crystalline structure. In this paper, we developed an efficient cellulose dissolution system which incorporates solid acid (SA) with 1-butyl-3-methylimidazolium chloride (BmimCl). The results showed that addition of solid acid both Amberlyst® 15 and $C_{5x}H_{3-x}PW_{12}O_{40}$ could significantly enhance cellulose dissolution in BmimCl, which attributed to the synergistic action of free hydrogen proton from SA and chloride anion in BmimCl on hydroxyl groups of cellulose, and DMF as co-solvent also could facilitate cellulose dissolution in SA/BmimCl. In contrast to BmimCl system, the SA/BmimCl system for cellulose dissolution achieves better efficiency at mild treatment conditions and facile recovery of solvents. In addition, characterization of the regenerated celluloses showed that SA/BmimCl is a non-derivatizing solvent for cellulose, which helps achieve complete dissolution on crystalline cellulose. Attributed to its low cost and environmentally friendliness for biomass processing, SA/BmimCl systems is a promising and effective solvent system.

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1. Introduction

Cellulose is the most abundant resource biosynthesized on earth with an annual production over 7.5×10^{10} tons, featuring sustainable, renewable, biodegradable, and carbon neutral (Huber, Iborra, & Corma, 2006; Carlson, Vispute, & Huber, 2008; Ragauskas et al., 2006; Lu, Xu, & Wang, 2014). As a chemical raw material, cellulose and its derivatives have been widely utilized in many fields, such as papermaking, textile and pharmaceuticals (Fukaya, Hayashi, Wada, & Ohno, 2008; Sun, Rahman, Rogers, Qin, & Maxim, 2009; Bobleter, 1994). Generally, cellulose can be characterized as highly polymerized linear macromolecule consisting solely of 1–4- β -linked anhydro-D-glucose (Andanson et al., 2014; Brandt, Hallett, Leak, Murphy, & Welton, 2010; Brandt, Gräsvik, Hallett, & Welton, 2013). Particularly, the β configuration at the anomeric carbon of glucose unit gives rise to a stretched chain conformation. Then, these chains are linked into flat sheets via hydrogen-bonds. The linear alignment of molecular chain enables the compact packing of numerous cellulose strands into crystalline fibrils, which makes it challenging to separate individual molecular chain and thus dissolve cellulose. Moreover, many other structural aspects have been identified, including the high molecular weight, the comparatively low flexibility of polymer chain, together with the

hydrophobic surface attributed to the inferior solubility of cellulose in most solvents. Correspondingly, valorization of natural cellulose via physical and chemical conversion was severely restricted.

Dissolution of cellulose could release active groups, such as hydroxyl and glycosidic bond, consequently makes homogeneous reaction and elaborate processing possible for readily accessibility of the active groups. Exploring solvents for efficient cellulose dissolution has been conducted for nearly one decade. Many derivatizing and non-derivatizing cellulose solvents have been discovered, such as copper ethylene diamine solution, 1, 3-*N*-methyl-morpholine-*N*-oxide (NMMO) (Wendler, Grane, & Heinze, 2005; Song et al., 2016), *N*, *N*-dimethyl acetamide/lithium chloride (DMAc/LiCl) (Xu, Wang, & Wang, 2010; Mazza, Catana, Vaca-Garcia, & Cecutti, 2009; Vaca-Garcia, Thiebaud, Borredon, & Gozzelino, 1998; Liebert & Heinze, 2008), dimethyl sulfoxide/tetrabutylammonium fluoride (DMSO/TBAF),

N, *N*-dimethylformamide/dinitrogen tetroxide (DMF/ N_2O_4), lithium perchlorate trihydrate ($LiClO_4 \cdot 3H_2O$), and lithium thiocyanate hydrate ($LiSCN \cdot 2H_2O$). However, application of these solvents still was perplexed for its high environmental toxicity, inferior solvation power, difficulty in solvent recovery and harsh processing conditions (Zhu et al., 2006; Feng & Chen, 2008; Huber et al., 2012; Sun, Miao, Yu, & Zhang, 2015). In recent years, many novel green solvents with unique properties for biopolymers processing have been investigated, including supercritical fluids (SCF), deep eutectic solvents (DES), near critical fluids (NCF), high-temperature water, and ionic liquids (ILs).

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Among these novel methods application of ILs opened a new path forward for cellulose-based biofuels and biomaterials production. ILs refer to a group of molten salt with relatively low melting point (<100 °C) possessing many unique properties including nearly non-volatility, non-flammability, high stability, structural designability and unique coordination behavior (Rogers & Seddon, 2003; Welton, 1999; Sheldon, 2001). Particularly, many ILs, such as BmimCl (Kosan, Michels, & Meister, 2008), 1-allyl-3-methylimidazolium chloride (AmimCl) (Zhang, Wu, Zhang, & He, 2005), and 1-ethyl-3-methylimidazolium acetate (EmimOAc) (Sun et al., 2009) have been demonstrated to be good solvents for cellulose, lignin and other natural polymers, also it's have exhibiting excellent solubility (Kilpelaäinen et al., 2007; Pang, Dong, & Pan, 2015). In addition, the high stability and nearly non-volatility properties made ILs to be green solvent for cellulose dissolution with easiness of recovery and reuse.

These ILs solvates on cellulose efficiently primarily attributed to the effective breakage of inter- and intra-molecular hydrogen-bonds which extensively existed in cellulose, wherein hydroxyl protons and oxygen of cellulose interact with anions and cations of ILs, respectively (Swatloski, Spear, Holbrey, & Rogers, 2002; Tan, Li, Chen, & Xie, 2016; Liu, Hou, Wu, Ren, & Wang, 2012; Raja et al., 2016). Generally, cellulose dissolution in ILs in reported literatures was conducted at harsh conditions, such as high temperature and long residence time. However, understanding on the thermal stability of ILs recently has been revised because degradation of ILs occurs even at lower temperature for a longer residence time. Unfortunately, degradation of ILs could decrease its recovery performance and exert an additional burden on effluent treatment for formation of side-products. Therefore, economical and environment-friendly application of ILs necessitated developing efficient cellulose dissolution at mild conditions to reduce its detrimental degradation.

Many attempts have been conducted to improve the efficiency of cellulose dissolution in ILs, such as design of novel ILs by combination of various cations and anions, microwave heating, ultrasonic pretreatment, addition of co-solvent and additive. By applying these techniques, dissolution of cellulose could proceed smoothly with advantages of efficient energy transfer, reduced energy consumption and rapid dissolution. Therefore, exploring enhanced cellulose dissolution in ILs could facilitate the comprehensive applications of ILs on biopolymer processing at industrial scale. Typically, breakage of the extensive hydrogen-bonds in cellulose are required for cellulose dissolution, and the reported excellent solvents for cellulose dissolution possess moieties, such as hydrogen cation, lithium cation, hydroxide ion, chloride, which could effectively coordinate with hydroxyls in cellulose. Hydrogen cation was the smallest cations with strong coordination power and high motility, which could exert a positive role on cellulose dissolution. However, hydrogen ion simultaneous would induce acid-catalyzed conversions in cellulose treatment with many side-products formed and treatment of cellulose by acids was only used as a pretreatment step. Emergence of solid acid (SA) offers a new method to release hydrogen ion into solvent without water molecule. In this paper, a novel method using SA as additive for enhancement on cellulose dissolution in ILs was presented, and cellulose dissolution with lowered treatment severity could be achieved. Furthermore, SA could be easily recovered by the traditional filtration operation.

2. Experimental

2.1. Materials

All reagents used in this experiments were of analytical grade and used without any further purification. Microcrystalline cel-

lulose (MCC) with degree of polymerization (DP) of 150 was purchased from Anhui Shanhe Pharmaceutical Co., Ltd. 1-Butyl-3-methylimidazolium chloride (BmimCl) with purity of 99.0% was obtained from Shanghai Chengjie Chemical, China. DMF (purity $\geq 99.8\%$) was purchased from Tianjin Bodie Chemical Corporation. SA Amberlyst® 15 ion-exchange resin was supplied by Aladdin Industrial Corporation. Cs₂CO₃ (purity $\geq 99.5\%$) and H₃PW₁₂O₄₀·xH₂O were purchased from Tianjin Kermel Chemical Corporation.

2.2. The dissolution and regeneration of cellulose in ionic liquids

Dissolution of cellulose was conducted in a 40-mL vial, which was placed into a heating oil bath with magnetic stirring (stirring speed) under nitrogen gas atmosphere. Prior to dissolution experiments, MCC, SA, DMF and BmimCl were vacuum-dried at 50 °C for 48 h to thoroughly eliminate moisture. Then BmimCl (4.6 g), SA, DMF and water with specified dosage if needed were successively added into the vial. During the dissolution process, a drop of suspension was withdrawn at intervals and observed using a PM6000 polarization microscope (Jiangnan, China) to monitor cellulose dissolution, in the obtained images correspond to the undissolved crystalline domain of cellulose. In addition, the complete cellulose dissolution was defined as disappearance of crystalline spots observed by polarized-light microscopy.

After treatment for specified time, the solution was cooled down to room temperature for regeneration. The solution was diluted with ultra-pure water to cellulose consistency about 1.0 wt%, and then vigorously stirred (1500 rpm) for 30 min. Subsequently, the solution was filtered through ash-free filter paper (Whatman No. 1442 070) on a Buchner funnel. The regenerated cellulose on filter paper were washed several times with distilled water for thoroughly removal of IL, which was monitored by addition of AgNO₃ solution in filtrate until no white precipitate could be observed. Finally, the washed samples were vacuum-dried at 50 °C for 48 h.

2.3. FT-IR analysis of the original and regenerated MCC

An alpha Fourier transform infrared spectroscopy (FT-IR, Bruker, Germany) was used to analyze the functional groups in the samples obtained by KBr pellet technique. Samples were ground and mixed with KBr and pressed in an evacuated die under suitable pressure. The spectra were collected for 16 scans within wavenumber from 400 to 4000 cm⁻¹ at 2-cm⁻¹ resolution.

2.4. Determination of crystallinity of cellulose

The crystalline structure and crystallinity index (CrI) of the original and regenerated celluloses were analyzed by X-ray diffraction (XRD). The samples were scanned on a D8 Advance X-ray diffractometer (Bruker, Germany), with a Co radiation source at 40 kW and 35 mA, over a 2θ range from 5° to 50° at a scan speed of 0.18° min⁻¹, and a step size of 0.018°. CrI of the samples was determined using Eq. (1) on normalized spectra.

$$CrI(\%) = (I_{200} - I_{am})/I_{200} \times 100 \quad (1)$$

where I_{200} is the maximum intensity of the main crystalline plane (200) diffraction at 22.8°, and I_{am} is the maximum intensity of the amorphous domain of cellulose at 18.0°.

2.5. Determination of DP of the original and regenerated MCC

The average DP of the original and regenerated cellulose was measured using capillary viscometer method according to the

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