High-throughput screening for ionic liquids dissolving (ligno-)cellulose

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ABSTRACT

The recalcitrance of lignocellulosic biomass poses a major challenge for its sustainable and cost-effective utilization. Therefore, an efficient pretreatment is decisive for processes based on lignocellulose. A green and energy-efficient pretreatment could be the dissolution of lignocellulose in ionic liquids. Several ionic liquids were identified earlier which are capable to dissolve (ligno-)cellulose. However, due to their multitude and high costs, a high-throughput screening on small scale is essential for the determination of the most efficient ionic liquid. In this contribution two high-throughput systems are presented based on extinction or scattered light measurements. Quasi-continuous dissolution profiles allow a direct comparison of up to 96 ionic liquids per experiment in terms of their dissolution kinetics. The screening results indicate that among the ionic liquids tested EMIM Ac is the most efficient for dissolving cellulose. Moreover, it was observed that AMIM Cl is the most effective ionic liquid for dissolving wood chips.

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1. Introduction

Today's fossil fuel-based economy is facing several challenges such as decreasing reserves, increasing prices, energy security issues and the anthropogenic carbon dioxide emission (IPCC, 2007). An alternative and sustainable source for chemicals, materials, and fuels is lignocellulosic biomass (Huber et al., 2006; Lynd et al., 1999). Biofuels produced from lignocellulose minimize competition with the food chain and increase overall yields in comparison to biofuels of the first generation (Palatinus et al., 2007).

Lignocellulose consists mainly of cellulose, hemicellulose, and lignin. The typical percentages of dry weight are 35–50% cellulose, 20–35% hemicellulose, and 5–30% lignin (Lynd et al., 2002). Thus, cellulose is the most abundant biopolymer on earth (Bhat and Bhat, 1997). Cellulose is a linear polymer of β-1,4-linked D-glucopyranose monomers. Cellulose fibers are assembled by a large amount of intra- and intermolecular hydrogen bonds (Zhbankov, 1992). This makes cellulose insoluble in water and most organic solvents (Swatloski et al., 2002). While cellulose is mainly crystalline, hemicellulose, a polymer of five different sugars, is completely amorphous. Lignin is an irregular polymer of several monoaromates and forms a three-dimensional network in which cellulose and hemicellulose fibers are embedded. Especially wooden biomass exhibits high lignin contents (Huber et al., 2006). Due to this complex structure, lignocellulose has a remarkable resistance against chemicals and microbial attacks (Zhu et al., 2006) and makes it recalcitrant against its hydrolysis which is the central barrier for its widespread utilization (Lynd et al., 2002).

For the production of biofuels and chemicals the aim is to decompose this fiber structure and to utilize all components of lignocellulose (Zhang et al., 2007). One approach – besides gasification and pyrolysis – is to separate lignocellulose into its components. Subsequently, cellulose can be hydrolyzed to glucose using mineral acids or enzymes. The obtained glucose and the other components can be transformed to fuel components or valuable platform chemicals (Kamm and Kamm, 2007). In this process the pretreatment has been identified as very costly and decisive for the efficiency of a subsequent enzymatic hydrolysis (Wyman et al., 2005a).

Several pretreatments for lignocellulose were developed (Mosier et al., 2005b; Wyman et al., 2005b). After a mechanical comminution hydrothermal or chemical pretreatments are applied. Hydrothermal processes can be steam explosion (Cara et al., 2008), carbon dioxide explosion (Zheng et al., 1998), or hot water treatment (Mosier et al., 2005a). Chemical processes include dilute-acid treatment (Lloyd and Wyman, 2005), alkali treatment (Kaar and Holtzapple, 2000), organosolv process using organic solvents (Holtzapple and Humphrey, 1984), ammonia fiber explosion ("AFEX") (Teymouri et al., 2005), ammonia recycle percolation (Kim and Lee, 2005), and ozonolysis (Vidal and Molinier, 1988). However, all these pretreatment methods feature several drawbacks. They have to be tailored to the specific source of lignocellulose (Mosier et al., 2005b) and can cause significant degradation of lignocellulose components to side-products, which can inhibit subsequent hydrolysis or fermentation steps (Larsson et al., 1999; Sun and Cheng, 2002; Weil et al., 1994). Some pretreatment methods require extreme conditions such as high temperatures and pressures or strong acids or bases making special equipment necessary. Often the solvent is consumed which increases the costs. In the

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case of acids and bases additional neutralization chemicals are required which result in large amount of salts (Lynd et al., 1999; Mosier et al., 2005a). Some pretreatments like lime pretreatment require even weeks (Kim and Holtzapple, 2005) or various steps (Fukaya et al., 2008). Moreover, most methods are not "green" since toxic and hazardous pollutants are released (Pu et al., 2007; Zhu, 2008). Therefore, more efficient pretreatment methods are needed which require low energy, modest conditions, and apply green solvents which are fully recyclable (Li et al., 2008). One promising alternative could be the use of ionic liquids (ILs).

ILs consist entirely of ions and melt below 100 °C and represent a new class of solvents with high polarities (Wasserscheid and Keim, 2000). In comparison to traditional molecular solvents ILs exhibit very interesting properties such as broad liquidus regions, high thermal stabilities and negligible vapor pressures (Brennecke and Maginn, 2001; Weingartner, 2008). Since no toxic or explosive gases are formed ILs are called "green" solvents (Anderson et al., 2002; Wasserscheid and Keim, 2000). The combination of anion and cation affects their physical and chemical properties such as melting points, viscosity, hydrophobicity, and hydrolysis stability (Huddleston et al., 2001; Wasserscheid, 2003). Therefore, optimal ILs for certain applications can be designed. However, the limited industrial experience and availability of physicochemical, thermodynamic, and toxicity data are barriers for their wide application (Joglekar et al., 2007).

In 2002 the group of Rogers discovered that several imidazolium-based ILs can dissolve large amounts of cellulose (Swatloski et al., 2002). This prompted several other groups to test a variety of other ILs on their ability to dissolve cellulose. Today more than 20 ILs are known which dissolve cellulose (Barthel and Heinze, 2006; Fukaya et al., 2006, 2008; Heinze et al., 2005; Wu et al., 2004; Xie and Shi, 2006; Zhang et al., 2005; Zhao et al., 2008). Furthermore, ILs turned out to dissolve a range of other biomaterials (Fort et al., 2006; Phillips et al., 2004; Xie et al., 2005), especially lignin and lignocellulose (Kilpelainen et al., 2007; Pu et al., 2007). This allows homogeneous chemical modifications of dissolved biomaterials (Schlufter et al., 2006; Xie et al., 2007). Dissolved cellulose can be precipitated by the addition of anti-solvents like water which enables the separation of cellulose from lignin and hemicellulose (Fort et al., 2006) and the formation of structural forms like fibers (Bagheri et al., 2008; Turner et al., 2004). The recent patents (Gurin, 2007; Myllymaki and Aksela, 2005; Swatloski et al., 2003) prove that the pretreatment using ILs obtained increased industrial interest and commercialization of such processes is underway (Zhu, 2008).

Despite these advances in the application of ILs for lignocellulose pretreatment and the increasing amount of suitable ILs, no systematic comparison of ILs has been conducted so far. Due to the high prices and the enormous number of possible ILs (Holbrey and Seddon, 1999), high-throughput screening systems on small scale are required (Joglekar et al., 2007). Moreover, until today no highly resolved temporal dissolution profiles are available. Therefore, in this work two high-throughput screening systems on small scale are presented and applied. This cost-saving screening in microtiter plates allows a direct comparison of the ILs in terms of their dissolution kinetics and will identify the most efficient IL for dissolving cellulose.

2. Methods

2.1. Ionic Liquids

In total 21 ILs were screened for their ability to dissolve cellulose and lignocellulose. Table 1 lists these ILs with their abbreviations. Moreover, it is indicated if these are liquid at room

temperature. ECOENG, BMIM Cl, EMIM Ac and EMIM BTI were obtained by Solvent Innovation (Cologne, Germany) and BMPY Cl from Merck (Darmstadt, Germany). All other ILs were purchased from IoLiTec (Denzlingen, Germany). Since some ILs are hygroscopic or unstable in water, the ILs were dried thoroughly in a drying oven at 80 °C for at least 10 h. Thereby, the water content, which was checked by Karl-Fischer-Titration, was in average reduced to approximately 0.7% and the water activity to 0.04.

2.2. (Ligno-)cellulose

As substrates cellulose and wood chips were used. Two kinds of cellulose were chosen, microcrystalline cellulose "Avicel" and α-cellulose, which features the typical fiber structure. Both substrates originate from hardwood pulp and were obtained by Sigma–Aldrich (Deisenhofen, Germany). They were used without further purification. As wood source both softwood and hardwood were chosen. As softwood spruce (*Picea abies*) and silver fir (*Abies alba*) were used, as hardwood common beech (*Fagus sylvatica*) and chestnut (*Castanea sativa*). All wood was obtained from local sawmills. The wood chips were produced by sawing and were in the range of 1–2 mm in length, which was determined by sieving.

2.3. In situ microscopy

The preliminary *in situ* microscopic experiments were conducted at ca. 30 °C using an Eclipse E 600 microscope (Nikon, Amstelveen, The Netherlands) with a magnification of 40. 1% (w/w) Avicel or α-cellulose were dissolved in EMIM Ac on a microscope slide.

2.4. High-throughput screening

Two high-throughput systems were applied. For both devices microtiter plates with non-transparent walls and transparent well

Table 1
List of ILs used for screening.

Systematic name	Abbreviation	Aggregate state at 25 °C
1-(2-Hydroxyethyl)-3-methylimidazolium-tetrafluoroborate	HEMIM BF$_4$	Liquid
1,3-Dimethylimidazolium-dimethylphosphate (ECOENG 1111P)	ECOENG	Liquid
1-Allyl-3-methylimidazolium-chloride	AMIM Cl	Liquid
1-Butyl-3-methylimidazolium-bromide	BMIM Br	Solid
1-Butyl-3-methylimidazolium-chloride	BMIM Cl	Solid
1-Butyl-3-methylimidazolium-hexafluorophosphate	BMIM PF$_6$	Liquid
1-Butyl-3-methylimidazolium-iodide	BMIM I	Liquid
1-Butyl-3-methylimidazolium-methanesulfonate	BMIM CH$_3$SO$_3$	Solid
1-Butyl-3-methylimidazolium-tetrafluoroborate	BMIM BF$_4$	Liquid
1-Butyl-3-methylpyridinium-chloride	BMPY Cl	Solid
1-Butyl-3-methylpyrrolidinium-chloride	BMPL Cl	Solid
1-Butyl-3-methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide	BMPL BTI	Liquid
1-Ethyl-3-methylimidazolium-acetate	EMIM Ac	Liquid
1-Ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide	EMIM BTI	Liquid
1-Ethyl-3-methylimidazolium-chloride	EMIM Cl	Solid
1-Ethyl-3-methylimidazolium-ethylsulfate	EMIM C$_2$H$_5$OSO$_3$	Liquid
1-Ethyl-3-methylimidazolium-tetrafluoroborate	EMIM BF$_4$	Liquid
1-Hexyl-3-methylimidazolium-chloride	HMIM Cl	Liquid
1-Hexyl-3-methylimidazolium-tetrafluoroborate	HMIM BF$_4$	Liquid
1-Methyl-3-octylimidazolium-chloride	OMIM Cl	Liquid
Tetrabutylphosphonium-chloride	TBPM Cl	Solid