



Lignin dissolution in dialkylimidazolium-based ionic liquid–water mixtures



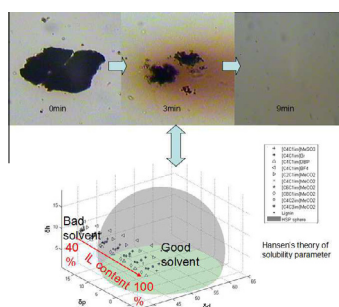
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HIGHLIGHTS

- Lignin solubility in ionic liquid (IL)–water mixtures was investigated.
- The IL type and content affect lignin dissolution in the mixed solvents.
- The maximum lignin solubility is achieved at 70 wt% IL content.
- Hansen's theory of solubility parameter aids in finding the appropriate IL content.

GRAPHICAL ABSTRACT



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ABSTRACT

Lignin dissolution in dialkylimidazolium-based ionic liquid (IL)–water mixtures (40 wt%–100 wt% IL content) at 60 °C was investigated. The IL content and type are found to considerably affect lignin solubility. For the IL–water mixtures except 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{C}_1\text{im}]\text{BF}_4$), the maximum lignin solubility can be achieved at 70 wt% IL content. Lignin solubility in IL–water mixtures with different cations follows the order 1-butyl-3-methylimidazolium ($[\text{C}_4\text{C}_1\text{im}]^+$) > 1-hexyl-3-methylimidazolium ($[\text{C}_6\text{C}_1\text{im}]^+$) > 1-ethyl-3-methylimidazolium ($[\text{C}_2\text{C}_1\text{im}]^+$) > 1-octyl-3-methylimidazolium ($[\text{C}_8\text{C}_1\text{im}]^+$) > 1-butyl-3-ethylimidazolium ($[\text{C}_4\text{C}_2\text{im}]^+$) > 1-butyl-3-propylimidazolium ($[\text{C}_4\text{C}_3\text{im}]^+$). For IL mixtures with different anions, lignin solubility decreases in the following order: methanesulfonate (MeSO_3^-) > acetate (MeCO_2^-) > bromide (Br^-) > dibutylphosphate (DBP^-). Evaluation using the theory of Hansen solubility parameter (HSP) is consistent with the experimental results, suggesting that HSP can aid in finding the appropriate range of IL content for IL–water mixtures. However, HSP cannot be used to evaluate the effect of IL type on lignin solubility.

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1. Introduction

The production of alternative chemicals and materials from sustainable biomass resources with low energy and environmental loads is receiving substantial attention (George et al., 2006). Lignocellulosic biomass is an important resource with the advantages of

carbon neutrality, storability, and abundance (Singh and Mishra, 1995) and mainly consists of the three biopolymers cellulose, hemicellulose, and lignin (Lynd et al., 2002). Cellulose and hemicellulose can be converted into fuels and fine chemicals through chemical and biotechnological process. Lignin, which consists of phenyl propanoid units, is the only aromatic native biopolymer on the earth that can also be utilized as raw materials for fuel and chemicals (Jouanin and Lapierre, 2012). Lignin forms a three-dimensional (3D) network that consists of embedded cellulose

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fibers and hemicellulose coupled with extensive intramolecular and intermolecular bonds between cellulose fibers, and can resist chemical and microbial degradation (Mosier et al., 2005). Enzyme adsorption on lignin also contributes to the inhibitory effect of lignin (Rahikainen et al., 2011). Hence, lignin removal during pretreatment can facilitate enzymatic hydrolysis and further lignin utilization.

The pretreatment of lignocellulosic biomass using an ionic liquid (IL)–water mixture is a promising technology because of its low cost, ease of IL recycling, and low viscosity (Fu and Mazza, 2011; Hou et al., 2013; Brandt et al., 2011; Zhang et al., 2012; Wei et al., 2012). Fu and Mazza (2011) reported the effective pretreatment of triticale straw using 1-ethyl-3-methylimidazolium acetate ([C₂C₁im]MeCO₂)–water mixture, as shown by the removal of lignin and reduced cellulose crystallinity. A higher fermentable sugar yield (81%) was obtained after the pretreatment using [C₂C₁im]MeCO₂–water mixture than that using only the pure [C₂C₁im]MeCO₂ (67%) under the same conditions. Brandt et al. (2011) also found that lignocellulosic biomass can be efficiently pretreated using imidazolium-based IL–water mixtures containing methyl sulfate, hydrogen sulfate, methanesulfonate, and acetate anions. The nature of the anion has a profound effect on lignin removal. With an IL content of 80 wt%, the order of delignification effectiveness follows the order: 1-butyl-3-methylimidazolium hydrogen sulfate, 1-butyl-3-methylimidazolium methanesulfonate ([C₄C₁im]MeSO₃), [C₂C₁im]MeCO₂ and 1-butyl-3-methylimidazolium chloride ([C₄C₁im]Cl). In our previous study (Wei et al., 2012), strong correlations between lignin removal and the IL content in a mixture were observed during the treatment of legume straw using a [C₄C₁im]Cl–water mixture. The total amount of the dissolved lignin accounted for 48.2% of the total lignin in the legume straw (IL content of 60 wt%, 150 °C).

Zhang et al. (2013) reported that the effectiveness of a mixture of water and [C₄C₁im]MeSO₃ (pH 0.9) to deconstruct the biomass and delignification is higher than that of a mixture of water and [C₄C₁im]Cl (pH 5.9) or [C₂C₁im]Cl (pH 6.0). Pretreatment effectiveness of IL–water mixtures can simply be estimated from solution pH. However, the significant abilities of IL–water mixtures to delignification compared with HCl solution at the same pH 0.4 are also found, suggesting that IL–water mixtures may play an important role during pretreatment and delignification.

The treatment of lignocellulosic biomass using the IL–water mixture was defined as “the Ionosolv Process” by Brandt et al. (2012), which is characterized by the selective delignifying biomass through the dissolution of lignin. Therefore, the characterization of lignin solubility in IL–water mixtures is essential for the Ionosolv Process. This study can provide a general understanding and optimized Ionosolv Process. However, lignin solubility in IL–water mixtures as a function of IL content, as well as its interpretation using Hansen’s theory of solubility parameter, has not yet been studied to the best of our knowledge.

The objectives of this study were to determine the lignin solubility in IL–water mixtures and to explain the effects of the IL content and type on lignin solubility. In this study, we first investigated the process of lignin dissolution in IL–water mixtures using the optical microscopy technologies. Lignin solubility in IL–water mixtures was then further analyzed based on Hansen’s theory of the solubility parameter.

2. Experimental

2.1. Materials

Lignin (cat. No. 371017, organosolv) was purchased from Sigma–Aldrich Co. and was referred to as Alcell lignin from mixed

hardwoods (50% maple, 35% birch, 15% poplar). All ionic liquids (98% purity) were supplied by Lanzhou Institute of Chemical and Physics. The water content of the newly purchased ionic liquid was 0.5 wt%. All chemical agents (purchased from Aladdin Co.) were analytical grade and used without further purification.

The IL and deionized (DI) water were mixed to form a treatment solvent with different weight percentages. To simplify the discussion, we devised a notation to indicate the IL content in the mixture, with the remainder being water. An example is ([C₄C₁im]MeCO₂)_{80%}, which means a mixture of 80 wt% [C₄C₁im]MeCO₂ and 20 wt% DI water.

2.2. Experimental procedure

2.2.1. Lignin dissolution screening by optical microscopy technologies

The IL–water mixture (0.5 g) and lignin (0.003 g) were mixed in a container made of two glass plates, as schematically shown in Fig. A.1 in Appendix in the electronic supplementary information (ESI). The space between the glass plates was sealed with paraffin oil to prevent solvent leakage. The system was not agitated, and the lignin could move freely in the solvent. The lignin dissolution was evaluated at 60 °C using an optical microscope equipped with a CK-300 temperature controlled hot stage (purchased from Shanghai Caikon Optical Instrument Factory). Images of the lignin dissolution were taken at 1000 × magnification.

2.2.2. Lignin solubility in IL–water mixtures

Lignin was gradually added to 3 g of the IL–water mixture (40, 50, 60, 70, 80, and 100 wt% IL) in small screw-capped flasks, each equipped with a magnetic stir bar. The suspensions were stirred in an oil bath at 60 °C. The lignin dissolution (homogeneous solution, no undissolved particles) was evaluated using an optical microscope. Each test was repeated three times to measure the error limit.

2.2.3. Hansen solubility parameters (HSPs) of ILs and lignin

HSP theory suggests that the cohesion energy of solvents and polymers can be expressed as a sum of three terms:

$$\delta_T = \left(\frac{E}{V}\right)^{0.5} = \left(\frac{E_d + E_p + E_h}{V}\right)^{0.5} = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{0.5} \quad (1)$$

where δ_T is the total solubility parameter (Hildebrand solubility parameter); E is the cohesion energy; E_d , E_p , and E_h are the energies from the nonpolar/dispersion forces, permanent dipole–permanent dipole forces, and hydrogen bonding forces, respectively; V is volume; δ_d , δ_p , and δ_h are the solubility parameters for dispersion, polar, and hydrogen bonds, respectively. Each solubility parameter was generally measured in MPa^{0.5}.

The HSPs of ILs and lignin were analyzed using inverse gas chromatography (IGC) method. A TECHCOMP 7890II gas chromatograph equipped with a thermal conductivity detector and a N2000 Workstation software were used in this study.

The empty column was shaped into a coil to adjust to the injector, and the column was packed with the stationary phase through suction method. The stationary phase used in this study was prepared by dissolving a certain amount of the ILs and lignin with a precision of ±0.0001 mg in 1, 2-dichloromethane and depositing the solution on a certain amount of support (Chromosorb PAW). The mixture was dried using a rotary evaporator through slow evaporation while being stirred to insure a homogeneous mixture. The stationary phase consisted of 10 wt% IL or lignin. The oven temperature was maintained at 60 °C.

The flow rate of carrier gas H₂ was about 20 mL/min, as measured using a calibrated soap bubble flow meter, which was placed at the outlet after the detector. The injector and detector

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