Journal of Molecular Liquids 263 (2018) 193–199

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Deep eutectic solvent as an efficient molecular liquid for lignin solubilization and wood delignification

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ARTICLE INFO

Article history:
Received 16 October 2017
Received in revised form 23 April 2018
Accepted 1 May 2018
Available online 01 May 2018

Keywords:
Lignin
Solubility
Deep eutectic solvents

ABSTRACT

Lignin is an abundant heterogeneous aromatic biopolymer in the nature with a complex and an irregular structure and very low solubility in common solvents. Such drawbacks limit lignin isolation from wood and its conversion to value-added products. Here, for the first time we report a very high solubility of lignin in the very economic and green deep eutectic solvents using ultrasound irradiation. We synthesized a series of deep eutectic solvent based on the possible favorable solute-solvent interactions. It was found that lignin can be solubilized in these solvents up to about 50% w/w. To the best of our knowledge, this is the highest amount of any lignocellulosic compound solubility which has been reported to this time. Moreover, due to the low solubility of cellulose in these deep eutectic solvents, lignin can be completely isolated from lignocellulosic biomass in one-pot procedure. We think that this exploration can open new promising window to lignin-based science and technology.

1. Introduction

Biorenewable polymers such as lignocellulosic materials have attracted a great attention of the research community due to the advantages such as eco-friendliness, low cost, biodegradability, etc. [1,2]. One of the greatest interest for using lignocellulosic compounds is their availability in a very large amount at relatively low prices. Therefore, there is a shift of world's dependence from petroleum-based to renewable biomass-based resources which is generally viewed as a key to the development of a sustainable industrial society, energy independence, and to the effective management of greenhouse gas emissions [3]. Generally, lignocellulosic materials from hardwood stems contain 40–60% cellulose, 24–40% hemicellulose, and 10–25% lignin and the softwood-stem-based materials contain 45–50% cellulose, 25–35% hemicellulose, and 25–35% lignin [4].

Lignin is a complex and recalcitrant phenolic macromolecule comprising phenylpropane type units (Fig. 1). Due to its highly irregular polymeric structure, it is resistant to microbial attack and can prevent water from destroying [5].

In last the decades, depolymerization of lignin to the high value aromatic compounds becomes the center of interest for many scientists and companies worldwide [6–9]. However, the natural complexity and high stability of lignin bonds (also as an evolutionary adaptation by plants) makes lignin depolymerization a highly challenging task [10].

Moreover, serious challenges in processing of lignocellulosic compounds makes lignin extraction a highly challenging process [11]. Lignin stability, structural complexity, and more importantly very low solubility are the most important drawbacks [8,12]. Extraction of lignin from complex structure of wood, i.e. the fractionation of lignocellulosic compound is an industrial difficulty [13]. Therefore, exploring the new methods with the potential of both fractionation of wooden materials and dissolving high amount of lignin can strongly reduce the drawbacks of lignin conversion process.

It has been shown that Ionic Liquids (ILs) are the most promising solvent for lignocellulose processing [14–16]. There many successful studies, which report the substantial solubility of the insoluble compounds such as cellulose in ILs [17–20]. However, there are still some disadvantages inherent to use ILs in industrial scales. They are generally expensive and some of them, such as imidazolium-based ILs, are toxic and non-biodegradable [21]. Moreover, ILs synthesis is not much environmentally friendly which hamper their industrial emergence [22].

Deep Eutectic Solvents (DESs), as new green and inexpensive generation of solvents, has emerged at the beginning of this century to overcome the problems of ILs [23,24]. Similar to those of ILs, DESs have interesting properties including negligible volatility, non-flammability, high conductivities, and other unusual solvent properties [25]. DESs are commonly composed of an ammonium salt and a metal halide or a hydrogen-bond donor [24]. There are also numerous natural DESs in the nature and common components of DESs are naturally occurring biocompatible compounds that are not hazardous if they are released back into nature [26]. Moreover, the synthesis methods of DESs include the simple mixing of molecular components which is economically viable and green [23]. One example is a DES which is formed between choline chloride and

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https://doi.org/10.1016/j.molliq.2018.05.001
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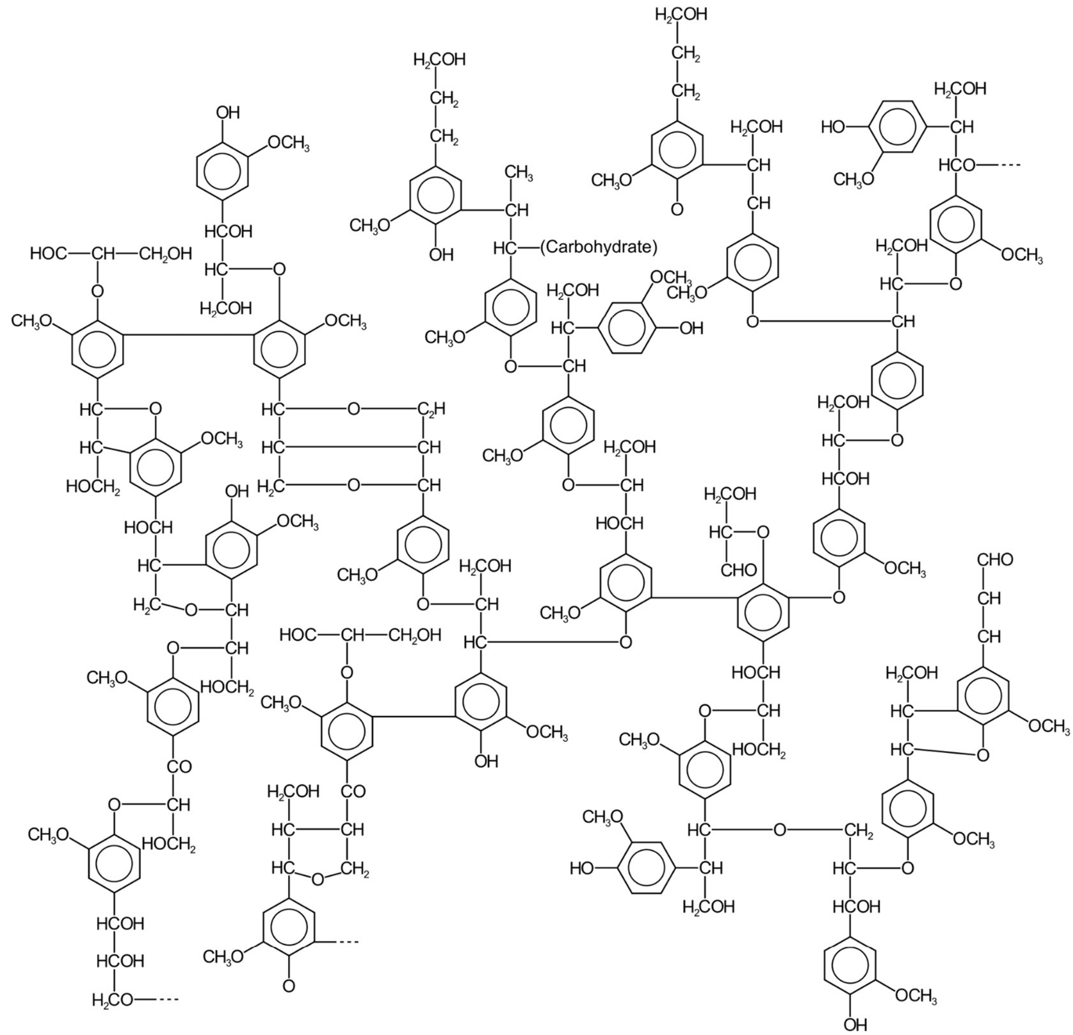

Fig. 1. Chemical structure of lignin.

urea (trade name: Reline). When choline chloride and urea are mixed at the molar ratio of 1:2, a eutectic occurs at a freezing point of 12 °C which is significantly lower than that of its original precursors [23].

All of these properties make DESs as so excellent solvents which are named “Solvents for the 21st Century” by some researchers [27]. Since DESs are young solvents, many of the corresponding papers are about their physical properties [28–31].

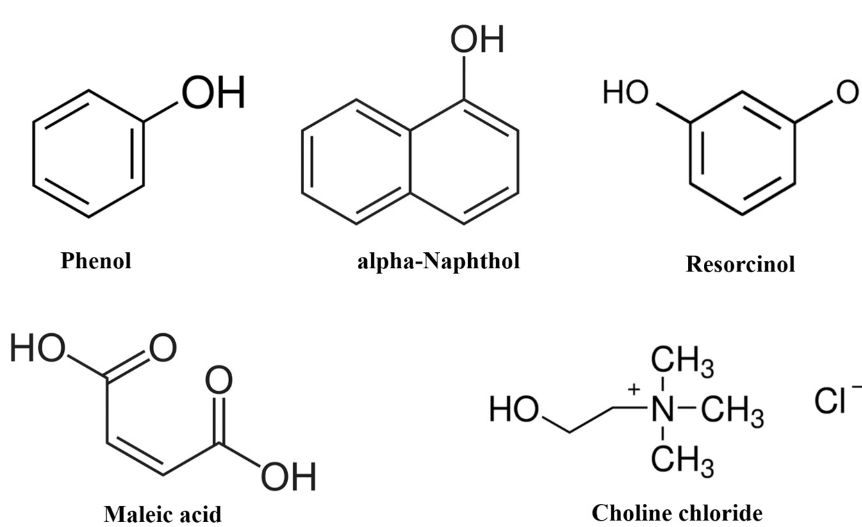

Fig. 2. Chemical structure of components of DESs for dissolving lignin. Phenol, alphanaphtol, resorcinol, and maleic acid serve as hydrogen bond donors while choline chloride is hydrogen bond acceptor molecule.