CELLULOSE DISSOLUTION IN IONIC LIQUIDS: COMPUTATIONAL AND EXPERIMENTAL STUDIES

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Nomenclature

[Amim][CL]	1-Alyl-3-Methylimidazoium Chloride
[BF4]	Tetrafluoroborate
[Bmim][CL]	1-Butyl-3-Methylimidazoium Chloride
13C NMR	Carbon-13 Nuclear Magnetic Resonance
COSMO-RS	Conductor-like Screening Model for Real Solvents
DFT	Density Functional Theory
DMSO	Dimethyl Sulfoxide
[Emim][Gly]	1-Ethyl-3-Methylimidazoium Glycine
[Emim][OAc]	1-Ethyl-3-Methylimidazoium Acetate
[3MBpy][CL]	N-butyl-3-methylpyridinium Chloride
MD	Molecular Dynamic
[P4444][Gly]	Tetrabutylphosphonium Glycine
[PF6]	Hexafluorophosphate
SAXRS	Small Angle X-ray Scattering
SEM	Scanning Electron Microscopy
TBAF	Tetrabutylammonium Fluoride
WAXRS	Wide-Angle X-Ray Scattering

INTRODUCTION

Lignocellulose is the most abundant biomaterial on earth, with an annual production of 170x 10^{12} tons [1]. Lignocellulosic biomass consists of three major biopolymers, namely cellulose (40-50 wt%), hemicellulose (20-35 wt%), and lignin (20-25 wt%) [2]-[3]. A recent study showed a large untapped value in cellulose, and only 0.1 billion tons out of 40x 10^{12} tons of cellulose are utilised in the industry as raw materials [1]. Cellulose consists of thousands of β(1-4) glycosidic bonds whereby the C1 of one glucose ring is linked through oxygen covalently linked together with C4 of the adjoining glucose ring [4]-[5]. Cellulose presents in lignocellulosic biomass in the form of a microfibrillar structure where sheets of parallelly aligned chains linked together to construct a structure having a three-dimension with a wide range of lengths (0.1-100 μm) and diameters(2-20 nm) [6]. This highly ordered structure with intra and inter-hydrogen bonding makes cellulose dissolution and subsequent disintegration a challenging process.

The dissolution of cellulose is a basic pre-requisite to convert the biopolymer into value-added chemicals and bioenergy [7]. Traditionally, there are several aqueous and nonaqueous solvents such as sodium hydroxide/disulfide mixture, *N*, *N*-dimethyl acetamide/lithium chloride, and dimethyl sulfoxide (DMSO)/ tetrabutylammonium fluoride (TBAF) have been used to dissolve cellulose. However, some limitations of these solvents, such as high flammability, high cost, toxicity, poor solvent recovery, and difficulty in the downstream process, hindered their wide use [8]. Hence, developing green and cleaner alternative solvents is crucial to address these drawbacks.

Ionic liquids are salts that consist of anions (organic or inorganic) as well as cations (generally organic), and they are liquids at or close to room temperature [9]-[10]. The exceptional physicochemical properties of ILs, such as high solvation ability to dissolve various biopolymers, high thermal stability, and extremely low vapour pressure, among others, introduce ILs as ideal and promising candidates to potentially replace the conventional cellulose solvents [11]-[13]. Additionally, ionic liquids structure (anions/ cations) can easily be altered to impart the desired properties hence called "Designer Solvents" [14]-[15]. As such, ILs have been employed in enormous applications, including organic synthesis, electrospinning, and extraction.