Journal of Molecular Liquids xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Cellulose dissolution and regeneration using various imidazolium based protic ionic liquids

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ARTICLE INFO

Article history:
Received 8 March 2016
Received in revised form 27 April 2016
Accepted 4 May 2016
Available online xxxx

Keywords:
Protic ionic liquids
Cellulose
Dissolution
Regeneration

ABSTRACT

A new series of six protic ionic liquids (PILs) comprising substituted imidazolium cations paired with lactate or glycolate anions were synthesized for cellulose dissolution. All the six synthesized PILs were able to dissolve about 5 wt% of cellulose. Especially, 1-ethyl imidazolium lactate showed highest dissolution power since 5 wt% of cellulose solution was obtained within 20 min at 80 °C. The effects of dissolution temperature on cellulose dissolution time were also investigated. As the dissolution temperature increases, dissolution time reduces significantly. The regeneration of cellulose with higher yield was achieved by adding anti-solvent like deionized water to the cellulose solution. Both the initial and regenerated cellulose samples were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscope (SEM) analysis. The results showed that the crystalline structure of initial cellulose (cellulose I) gets converted to cellulose II. In addition, all regenerated cellulose possessed nanostructure and lower thermal decomposition temperature than the initial cellulose and had new vistas in the industrial applications.

1. Introduction

Recent efforts have focused on more meticulous utilization of renewable cellulosic materials for the development of alternative sources of energy and chemicals. Cellulose the most abundant crystalline polymer (biodegradable polymer) of D-glucose is linked by β-1,4-glycosidic bonds [1,2]. Cellulose an initiate material for a variety of products includes cellophane, rayon, cellulose acetate, carboxymethyl cellulose etc. These cellulose products are widely used for various industrial applications. The structure of cellulose with intra and intermolecular H-Bonds is given in Fig. 1.

Several technologies are implemented to process the cellulose. The viscose process is the oldest technology in producing regenerated cellulose in which the cellulose is transformed to cellulose xanthate using alkali and CS_2. In this method, cellulose can be regenerated using the treatment of H_2SO_4 liberating CS_2 and H_2S. This process consumes a large amount of NaOH, H_2SO_4 and CS_2 causing severe environmental problems [3]. In the NMMO (*N*-methylmorpholine-*N*-oxide) process the cellulose homogeneous solution is obtained using the process of spinning the mixture of water (10%) and NMMO (76%) at 100 °C later stabilized by gallate. The problem prevails regarding solvent stability (loss of solvent) and recovery efficiency (irreversible changes in the final product as a result of few side reactions) involved in the process. To rectify the above, NaOH/Urea process is introduced due to the advantages of lower cost, less toxicity and more economic. However, the solvent requires complex processing conditions and the wet spinning process is yet to be optimized leading to incompletion in progress.

In concord to the previous problems related to the technologies used, a new solvent has to be probed to improve recycle process, nontoxic and nonderivative. Recent research shows that certain ionic liquids (ILs) are applied as green solvents which can dissolve cellulose [4–7] and function as inert and homogeneous reaction media [8–10]. Ionic liquids are organic salts in a liquid form at or below 100 °C [11]. In addition ILs are generally stable in air and water and have low melting points [12]. ILs have properties such as high thermal stability, lack of inflammability, low volatility, chemical stability, reusability, wide liquid range, high ionic mobility and excellent solubility with many organic, inorganic, polymeric compounds which make them as a 'designer solvents' or greener solvents [13–20]. Many kinds of room temperature ionic liquids [21] with a variety of structures have shown a good ability to dissolve cellulose. The ILs with the imidazolium cation shows the best competence for the dissolution of cellulose, in which acidic proton is involved in hydrogen bonding interactions between the cations and cellulose. In addition, some imidazolium based ILs contains phosphate, formate and acetate anion showing a high ability for dissolving cellulose [22,23]. One of the most promising applications of cellulose dissolving is their use as reaction media for the homogeneous preparation of polysaccharide derivatives.

This paper examine the use of various protic ionic liquids which are subclass of ionic liquids formed by proton transfer from

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http://dx.doi.org/10.1016/j.molliq.2016.05.008
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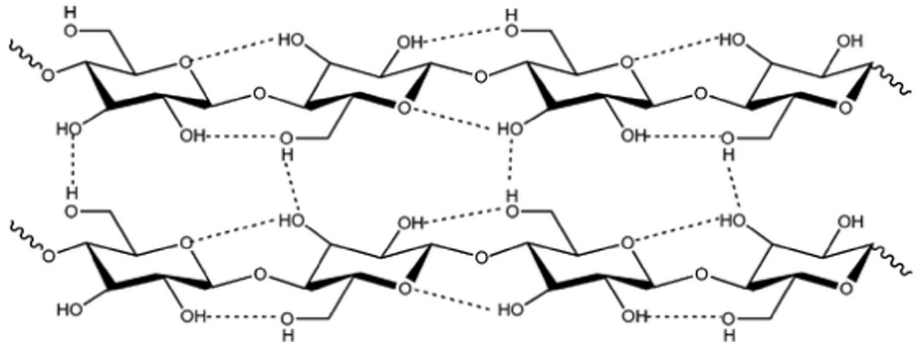
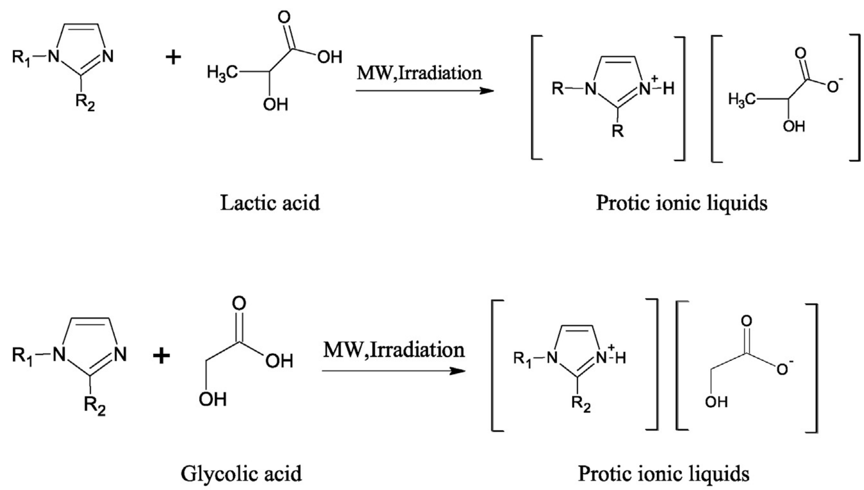


Fig. 1. Structure of cellulose with intra and intermolecular H-Bond.



where R_1-H,C_2H_5- or C_4H_9-. R_2-H, CH_3

MW-Microwave

Scheme 1. Synthesis of protic ionic liquids.

Bronsted acids to Bronsted bases [24] with imidazolium cation such as 2-methylimidazolium lactate,1-ethylimidazolium lactate,1-butylimidazolium lactate, 2-methylimidazolium glycolate,1-ethylimidazolium glycolate,1-butylimidazolium glycolate for the dissolution of cellulose with higher efficiency. It is found that cellulose can be dissolved in all the ionic liquids up to 5 wt% and can be regenerated easily by the addition of antisolvent like deioinized water.

2. Materials and methods

2.1. Synthesis of protic ionic liquids

The imidazolium protic ionic liquids such as 2-methylimidazolium lactate ([Hmim]$CH_3CH(OH)COO^-$), 1-ethylimidazolium lactate([Heim] $CH_3CH(OH)COO^-$), 1-butylimidazoliumlactate ([Hbim]$CH_3CH(OH)COO^-$), 2-methylimidazolium glycolate ([Hmim]$CH_2(OH)COO^-$), 1-ethylimidazolium glycolate ([Heim]$CH_2(OH)COO^-$), 1-butylimidazolium glycolate ([Hbim]$CH_2(OH)COO^-$) were synthesized according to the method outlined in the literature [25] and the synthesis was presented in the Scheme 1.

Table 1
Dissolution condition for cellulose in various PILs.

S.·no.	PILs	Dissolution time (minutes)		
		40 °C	60 °C	80 °C
1.	2-Methylimidazolium lactate	145	117	79
2.	1-Ethylimidazolium lactate	40	32	20
3.	1-Butylimidazolium lactate	75	61	45
4.	2-Methylimidazolium glycolate	155	128	92
5.	1-Ethylimidazolium glycolate	51	41	30
6.	1-Butylimidazolium glycolate	95	73	55

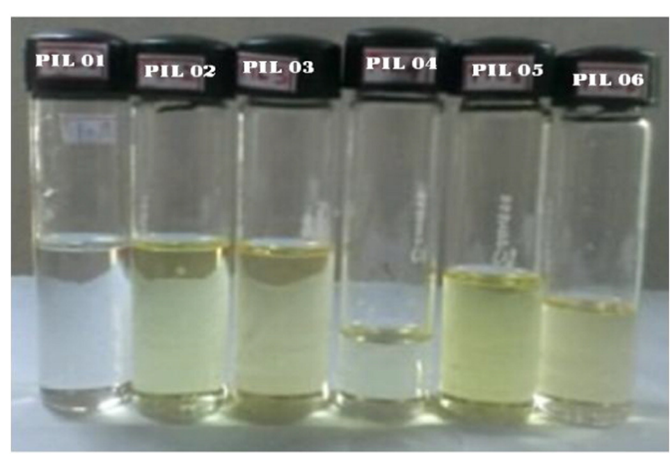


Fig. 2. Pure PILs without cellulose where PIL 01, PIL 02, PIL 03, PIL 04, PIL 05, PIL 06 are [Hmim]$CH_3CH(OH)COO^-$, [Heim]$CH_3CH(OH)COO^-$, [Hbim]$CH_3CH(OH)COO^-$, [Hmim] $CH_2(OH)COO^-$, [Heim] $CH_2(OH)COO^-$, [Hbim] $CH_2(OH)COO^-$ respectively.

Please cite this article as: B. Meenatchi, et al., Cellulose dissolution and regeneration using various imidazolium based protic ionic liquids, J. Mol. Liq. (2016), http://dx.doi.org/10.1016/j.molliq.2016.05.008