

# Synthesis and Properties of Non-Aromatic Ionic Liquids and their Role in Cellulose Dissolution

Ran Liu,<sup>b,\*</sup> Zidan Chen,<sup>a,#</sup> Hongwei Ren,<sup>a</sup> and Erhong Duan<sup>a</sup>

The dissolution of cellulose is an important pretreatment method required for some of its catalytic conversion processes. Morpholinium-based ionic liquids (ILs) are challenging solvent choices available for “greener” and “cheaper” dissolution of cellulose. In this study, morpholinium-based ILs were prepared, and their influencing factors were experimentally investigated. The unique bipolar chemical structure derived from oxygen (electron-rich center) and nitrogen (electron-poor center) considerably enhanced the Hammett acidity function ( $H_0$ ) of task-ILs. N-Methyl-N-allyl-morpholinium acetate IL showed the highest  $H_0$  (2.324) and polarizability power (1.096). The anion of ILs determined the hydrogen bond basicity ( $\beta$ ). The acetate anion contributed to  $\beta$  (0.88) values. As to fluid properties, the morpholinium-based ILs exhibited much lower viscosity. The properties of ILs improved the dissolution efficiency. The cellulose was directly dissolved in morpholinium-based ILs, and no other derivatives were formed. The cations and the anions of ILs studied reacted with oxygen and hydrogen atoms on the hydroxyl groups of cellulose, respectively.

*Keywords:* Ionic liquids; Cellulose; Dissolution; Morpholinium

*Contact information:* a: School of Environmental Science and Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei, 050018, China 102249, P. R. China; b: School of Chemistry and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang Hebei 050018, China 102249, P. R. China; \*Corresponding author: renhongweirhw@126.com

*#These authors contributed equally to this work.*

## INTRODUCTION

Cellulose, the valuable and renewable polymer, is widely used to produce high value-added biological products (Klemm *et al.* 2005; Ramamoorthy *et al.* 2015; Wang *et al.* 2016). However, the complicated hydrogen-bonded supramolecular structure hinders the full catalytic utilization of cellulose (Gümüşkaya *et al.* 2002; Huber *et al.* 2012). The efficient dissolution, as an important step for cellulose processing, would be important for its successful utilization (Roy *et al.* 2009; Işık *et al.* 2015). Sulfuric acid, lithium chloride/N, N-dimethylacetamide, and sodium hydroxide/urea have shown efficient dissolving ability for cellulose (Yang *et al.* 2014; Gu *et al.* 2015; Ru *et al.* 2015). However, potentially severe environmental pollution is of concern from such treatment (Sathitsuksanoh *et al.* 2013; Passos *et al.* 2014). The use of imidazolium-based ionic liquids (ILs) is unfavorable for its high viscosity, price, and especially toxic and recalcitrant characters caused due to its aromatic structure (Latała *et al.* 2009; Pham *et al.* 2010; Pena-Pereira and Namieśnik 2014; Jordan and Gathergood 2015). To avoid such toxicity, there is a great need for efficient, biodegradable, and inexpensive solvents.

Recently, a kind of non-aromatic morpholinium-based IL, having strong polarity has been reported (Hojniak *et al.* 2013; Domanska and Lukoshko 2014), which would potentially be favorable for the dissolution of cellulose (Badgujar and Bhanage 2015).

Raut *et al.* (2015) synthesized anion-functionalized morpholinium-based ILs and established that these ILs were benign solvents of cellulose pulps. However, none of the few articles on the study of this new class of efficient (Pernak *et al.* 2011; Raut *et al.* 2015), low-toxic, biodegradable ILs have considered the solvation properties of morpholinium-based ILs for cellulose, and the dissolution mechanism has not been investigated up to now.

This study was designed to further expand the use of the efficient morpholinium-based ILs to dissolve cellulose. Functionalized morpholinium-based ILs was synthesized, and the role of ILs in dissolution of cellulose was investigated. Additionally, an insight into the behavior of cellulose in ILs was explored.

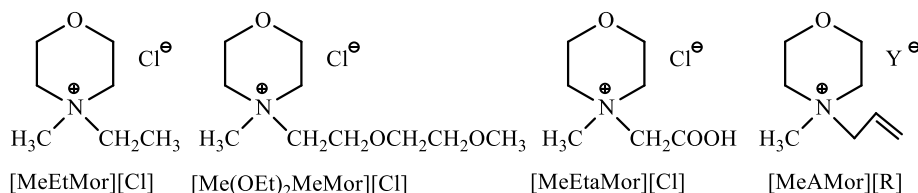
## EXPERIMENTAL

### Materials

The cellulose used for the study was a kind of cotton linter pulp, and the degree of polymerization was 575 (Helon, China). The cellulose was first dried at 100 °C for 12 h. The chemical reagents, including N-methyl-morpholinium chloride, chloroethane, thionyl chloride, sulfuric acid, formic acid, acetic acid, and lactic acid were of analytical grade and obtained from Beijing Chemical Reagents Co., China. The indicators of 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio) phenolate (Reichardt's dye 30, RD), 4-nitroaniline (NA), and N,N-diethyl-4-nitroaniline (DNA) were acquired from Fluorochem Ltd, UK.

### Synthesis of morpholinium-based ILs

Morpholinium-based ILs was synthesized and characterized according to previous studies (Raut *et al.* 2015; Liu, *et al.* 2012) (Scheme 1) (S1). FTIR spectra of the ILs were obtained from a FTS-135 Fourier transform infrared (FTIR) (Bio-Rad, USA). <sup>1</sup>H NMR spectra of the ILs were operated on an AVANCE III nuclear magnetic resonance (NMR) (Bruker, Germany) spectrometer at 500 MHz. The viscosity of ILs was measured with a VS4450 rotational viscometer (Marimex, Germany). The thermogravimetric property of ILs was measured with a TG209 TG/DSC thermal analysis instrument (Netzsch, Germany). The water content was determined by a Karl Fischer analyzer. The purity of ILs was obtained by Liquid Chromatography (LC) (Agilent, USA) (S2).



Y: Cl, HCOO<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, or HL<sup>-</sup>

**Scheme 1.** Structure and abbreviations of ILs

### Dissolution of Cellulose

Cellulose was gradually put into the morpholinium-based ILs in a three-necked flask under the protection of nitrogen. The solubility was investigated with increasing temperature from 30 °C to 120 °C at intervals of 10 °C. When the solution became optically transparent under a polarization microscope, it meant the end of the dissolution

process. The solubility was calculated in terms of the mass of cellulose dissolved per gram of ILs ( $\text{g} \cdot \text{g}^{-1}$ ) (Chatel *et al.* 2014). To regenerate cellulose, it was operated as follows: The cellulosic solution was first washed with an anti-solvent (ethyl alcohol) to remove cellulose from ILs, and then filtered by Buchner funnel and washed for several times. At last, the regenerated cellulose was produced. The regenerated cellulose was then dried at 50 °C for 24 h under vacuum drying.

### Measurements of Cellulose

FTIR, S-4800 scanning electron microscope (SEM) (Hitachi, Japan), and XRD-6000 X-ray powder diffraction (XRD) (Shimadzu, Japan) were used to analyze the structure of cellulose. The dissolution process was monitored with a XP-203 polarization microscope (Changfang, China). The degree of polymerization (DP) of cellulose was measured according to Hubbell and Ragauskas (2010).

The Hammett acidity function ( $H_0$ ) was calculated according to Eq. (1) (Thomazeau *et al.* 2003):

$$H_0 = \text{p}K(I)_{\text{aq}} + \log([I]_{\text{s}}/[IH^+]_{\text{s}}) \quad (1)$$

Here,  $I$  represents 4-nitroaniline indicator;  $\text{p}K(I)_{\text{aq}}$  is a constant value (0.99); the ratio  $[I]_{\text{s}}/[IH^+]_{\text{s}}$  is calculated according to Beer-Lambert Law;  $[IH^+]_{\text{s}}$  and  $[I]_{\text{s}}$  represent the molar concentration of protonated and unprotonated forms of  $I$ , respectively.

Hydrogen-bond donating acidity ( $\alpha$ ), hydrogen bond basicity ( $\beta$ ), and Dipolarity/polarizability effects ( $\pi^*$ ) were calculated by Eqs. (2) to (7) as the Kamlet-Taft empirical polarity scales (Mortimer and Taft 1976; Taft *et al.* 1976; Ab Rani *et al.* 2011):

$$\alpha = 0.1885\nu_{\text{(RD)}} - 2.03 - (0.72\pi^*) \quad (2)$$

$$\beta = (1.035 \nu_{\text{(DENA)}} + 2.64 - \nu_{\text{(NA)}}) / 2.80 \quad (3)$$

$$\pi^* = 0.649 - 0.314\nu_{\text{(NA)}} \quad (4)$$

$$\nu_{\text{(RD)}} = 1/(\lambda_{\text{max(RD)}} * 10^{-4}) \quad (5)$$

$$\nu_{\text{(NA)}} = 1/(\lambda_{\text{max(NA)}} * 10^{-4}) \quad (6)$$

$$\nu_{\text{(DENA)}} = 1/(\lambda_{\text{max(DENA)}} * 10^{-4}) \quad (7)$$

where  $\nu_{\text{(RD)}}$ ,  $\nu_{\text{(NA)}}$ , and  $\nu_{\text{(DENA)}}$  represent the wavelengths of maximum absorptions of Reichardt's dye, 4-nitroaniline and N,N-diethyl-4-nitroaniline, respectively.

The crystallinity index (CrI) of cellulose was calculated from the diffracted intensity, using the empirical method suggested by Segal *et al.* (1959),

$$\text{CrI} (\%) = (I_{002} - I_{\text{am}}) \times 100 / I_{002} \quad (8)$$

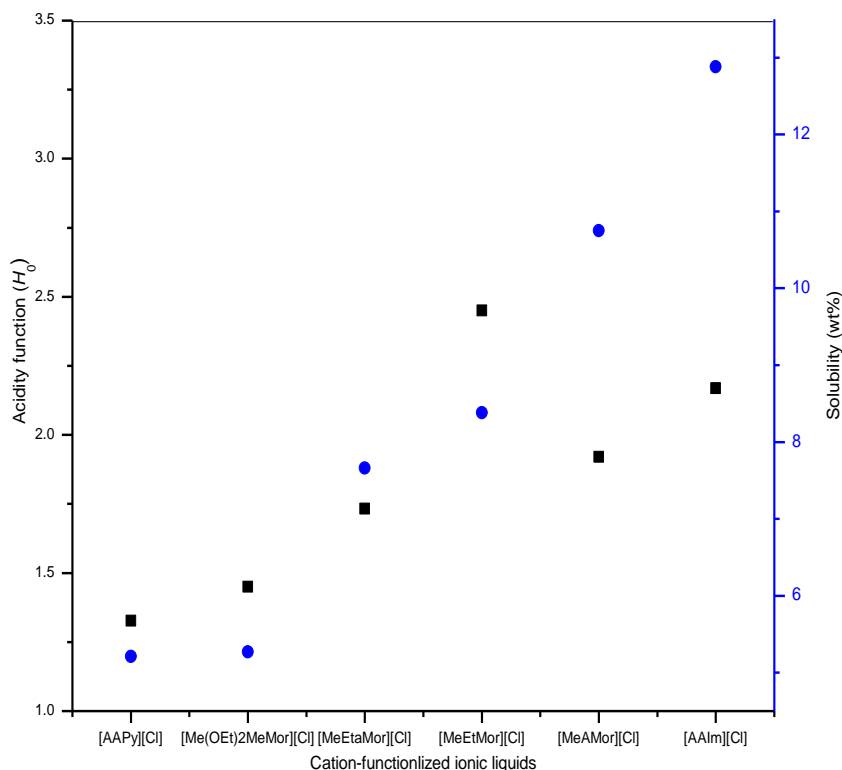
where CrI is the degree of crystallinity. The  $I_{002}$  means the maximum intensity of the principal peak (002) lattice diffraction.  $I_{\text{am}}$  means the diffraction intensity of amorphous cellulose between the planes (200) and (110).

## RESULTS AND DISCUSSION

### Effects of Morpholine-based ILs on Dissolution of Cellulose

#### *Effect of acidity*

According to the previous work (Hou *et al.* 2013), the acidity of ILs played an important role in enhancing the dissolution process, and Hammett acidity function ( $H_0$ ) could effectively represent the acidity strength of an acid in organic solvents. In this research, the  $H_0$  values (Fig. 1) of morpholine-based ILs were calculated according to Eq (1) and the Beer-Lambert Law. In addition, the values were compared with those of conventional imidazolium-based or pyridine-based cations.



■:  $H_0$ ; ●: solubility (wt%)

**Fig. 1.**  $H_0$  values of ILs and the solubility of cellulose

For a series of cation-functionalized ILs, the order of  $H_0$  value was [MeEtMor][Cl] (2.450) > [AAIm][Cl] (2.169) > [MeAMor][Cl] (1.920) > [MeEtaMor][Cl] (1.733) > [Me(OEt)<sub>2</sub>MeMor][Cl] (1.450) > [AAPy][Cl] (1.327). The solubility of cellulose followed the same sequence. It was obvious that the stronger the acidity of ILs the better the dissolution power. This is consistent with the “hydrogen bond donor and acceptor theory” (Xu *et al.* 2012). The cations in ILs, acts as the hydrogen bond donor, with oxygen on the hydroxyl (–OH) groups of cellulose as the acceptor, promoting the dissolution by disrupting inter- and intra- molecular hydrogen bonds. The  $H_0$  reflects the ability of cations to donate hydrogen ions or its acidity. As a result, the strong acidity greatly promoted the formation of C-H···O bonds between cations and cellulose, thus resulting in better dissolving ability.

#### Effect of solvent parameters

The solvent parameters were investigated in terms of Kamlet-Taft parameters (H-bond acidity ( $\alpha$ ), dipolarity/polarizability effects ( $\pi^*$ ), and H-bond basicity ( $\beta$ )) (Bhanage *et al.* 2015). The DP of cellulose after dissolution was also measured.

**Table 1.** Comparison of Cellulose Dissolution Power for Various ILs

ILs	Temp (°C)	Time (h)	$\alpha$	$\beta$	$\pi^*$	DP	Solubility (wt%)
[MeAMor][Cl]	120	1.0	0.51	0.91	1.131	525	10.75
[MeEtaMor][Cl]	110	1.5	0.63	0.87	1.047	515	8.38
[MeEtMor][Cl]	120	1.5	0.37	0.79	0.986	560	7.66
[Me(OEt) <sub>2</sub> MeMor][Cl]	105	1.0	0.43	0.81	1.022	531	5.27
[MeAMor][HSO <sub>4</sub> ]	95	0.5	0.49	0.91	1.124	437	11.37
[MeAMor][OAc]	120	0.5	0.50	1.10	1.096	507	11.05
[MeAMor][HCOO]	100	0.5	0.54	1.04	0.993	488	9.20
[MeAMor][HL]	120	4.0	0.36	0.70	0.871	548	2.11
[AAIm][Cl]	120	1.5	0.46	0.83	1.098	510	12.88
[AAPy][Cl]	110	2.0	0.33	0.75	1.013	460	5.21

To investigate the effect of head groups of ILs,  $\alpha$  and  $\pi^*$  values were measured. The results were [MeAMor][Cl] (0.51, 1.131) > [AAIm][Cl] (0.46, 1.098) > [AAPy][Cl] (0.33, 1.013). Therefore, the morpholinium, a non-aromatic heterocyclic compound, showed stronger ability to accept hydrogen ions and possesses polarity comparable to aromatic heterocyclic imidazole and pyridine. The results might be attributed to the interaction between electron-rich center of oxygen with electron-poor center of nitrogen in the morpholinium ring. The morpholinium cation was loosely bound with anion, promoting enhanced activation of anions, and thus facilitating the formation of O-H...O bonds between anions and cellulose.

For functional groups on cations such as alkyl-, allyl-, acid-, and ether-, the order of  $\alpha$  value was [MeEtaMor][Cl] (0.63) > [AMMor][Cl] (0.51) > [Me(OEt)<sub>2</sub>MeMor][Cl] (0.43) > [MeEtMor][Cl] (0.37). The introduction of allyl functionality to morpholine-based ILs exhibited higher polarizability. This could be due to the more conjugated structure of allyl functionality in IL.

The polarizability was related with the nature, steric hindrance, and interaction of the cation and anion of ionic liquids. With different cations, the order of  $\pi^*$  value was [MeAMor][Cl] (0.91) > [MeEtMor][Cl] (0.87) > [Me(OEt)<sub>2</sub>MeMor][Cl] (0.81) > [MeEtaMor][Cl] (0.79). With different anions, [MeAMor][Cl] and [MeAMor][HSO<sub>4</sub>] showed higher  $\pi^*$  value, 1.131 and 1.124, respectively, and [MeAMor][HL] showed a much lower  $\pi^*$  value of 0.871.

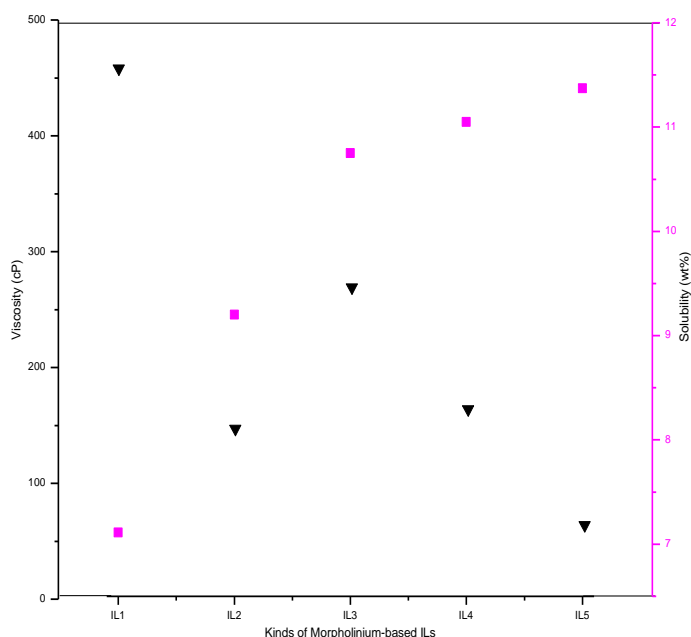
The dense electron cloud of HSO<sub>4</sub><sup>-</sup>, OAc<sup>-</sup>, and Cl<sup>-</sup> had stronger electron-donating ability, and were easier to break the hydrogen bonds in cellulose to achieve higher solubility, which was consistent with the previous studies (Fukaya *et al.* 2008; Glasser *et al.* 2012).

From the results for the DP of cellulose, it could be observed that all the ILs would not cause serve degradation at higher temperature (100 to 120 °C) except [MeAMor][HSO<sub>4</sub>] and [AAPy][Cl] (from 575 to 437 and 476, respectively).

#### *Effect of viscosity*

Fluid properties of ILs greatly affected the equilibrium of the dissolution (Badgajar and Bhanage 2015). From the results of Fig. 2, it could be seen that lower viscosity favored cellulose dissolution, which was consistent with previous studies

(Badgujar and Bhanage 2015). The order of viscosity values was [MeAMor][HL] (458 cP) > [MeAMor][Cl] (269 cP) > [MeAMor][HCOO] (147 cP) > [MeAMor][OAc] (164 cP) > [MeAMor][HSO<sub>4</sub>] (64 cP), lower than the conventional solvent [AAIm][Cl] (380 cP). The low viscosity can be regarded as a superior property of morpholinium-based ILs, which enlarged the contact between anions in ILs and hydrogen atoms on –OH groups of cellulose. [MeAMor][OAc] was shown to be an environmentally friendly IL to dissolve cellulose considering the potential contamination risk of sulfuric acid treatment.

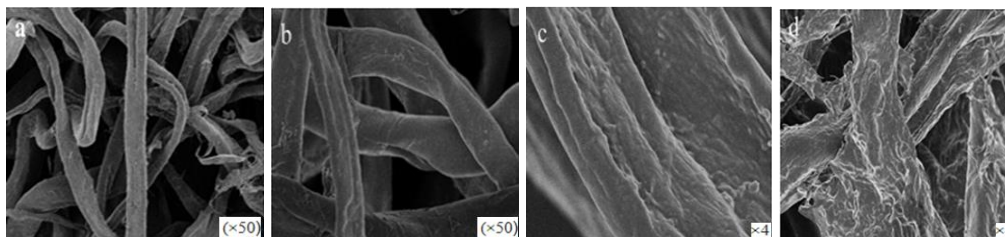


▼: Viscosity; ■: solubility of cellulose; IL1: [MeAMor][HL]; IL2: [MeAMor][HCOO]; IL3: [MeAMor][Cl]; IL4: [MeAMor][OAc]; IL5: [MeAMor][HSO<sub>4</sub>]

**Fig. 2.** Viscosity of morpholinium-based ILs and the solubility of cellulose in those ILs (110 °C)

### Dissolving Behavior of Cellulose in Ionic Liquids

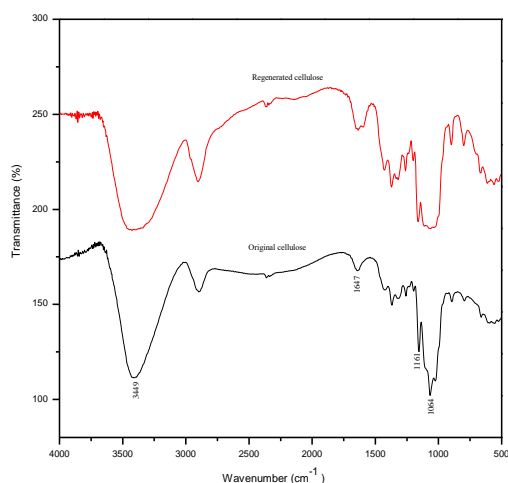
The dissolving behavior of cellulose in [MeAMor][OAc] was further studied. At low magnification ( $\times 50$ ) the SEM image of cellulose (Figs. 3a and 3b) indicated that the cellulose was swelled, and its volume became larger. A higher magnification ( $\times 4$ ) view (Figs. 3c and 3d), shows that the surface of original cellulose was ordered and condensed, and the rough and disordered surface of regenerated cellulose was observed. The loosed-accessible structure would greatly facilitate the further process of regenerated cellulose.



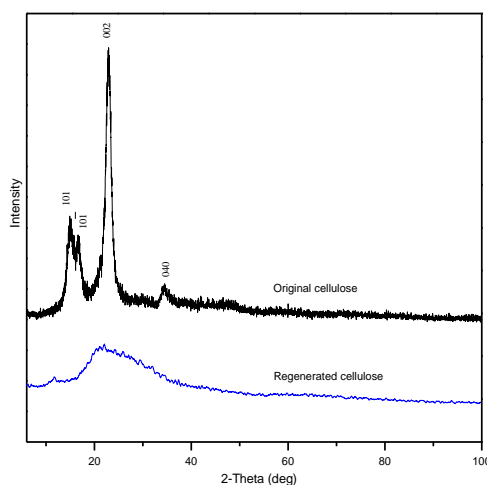
a, c: Original cellulose; b, d: Regenerated cellulose

**Fig. 3.** SEM images of cellulose in [MeAMor][OAc]

The FTIR spectra of original and regenerated cellulose are shown in Fig. 4. The peak at wavelength  $3450\text{ cm}^{-1}$  to  $3412\text{ cm}^{-1}$  denotes the O-H stretching vibration of the hydroxyl group of cellulose. The peaks at approximately  $2960\text{ cm}^{-1}$  and  $2900\text{ cm}^{-1}$  represent the C-H stretching vibration of the alkyl groups ( $-\text{CH}_2$ ) in cellulose. The absorbance at  $1647\text{ cm}^{-1}$  was attributed to the O-H bending vibrations of water absorbed by cellulose. For the C-O-C stretching vibration of the glycosidic bond in cellulose, the absorbance peak was found at  $1161\text{ cm}^{-1}$ . The peak at  $1064\text{ cm}^{-1}$  was related to the C-O pyranose ring skeleton. Upon comparison of the FTIR spectra of original and regenerated celluloses, only slight blue shift occurred and the peak width increased after dissolution, indicating the intramolecular interactions of cellulose was broken down which improved the destabilization of crystals. The negligible change of characteristic peak positions meant that no new functional groups and derivatives were generated during the dissolution process.



**Fig. 4.** FT-IR spectra of original and regenerated cellulose



**Fig. 5.** XRD patterns of original and regenerated cellulose

The crystallinity of original and regenerated celluloses was evaluated by XRD (Fig. 5). In the original cellulose, the type I cellulose were observed at  $14.93^\circ$ ,  $16.57^\circ$ , and  $22.84^\circ$ , respectively. However, the changed shift and intensity of peaks in XRD all suggested the change of crystal form of cellulose after dissolution. The new broader ( $21.79^\circ$ ) and disappeared diffraction peaks indicated that the form of regenerated cellulose was type II. The degree of crystallinity decreased from 85.4% to 47.7%, and it was attributed to the breakage of hydrogen bonds in cellulose.

## CONCLUSIONS

1. This study demonstrated that the morpholinium-based ILs has a high capacity for the dissolution of cellulose. Different functionalized morpholinium-based ILs were studied.
2. The high  $H_0$ , solvent parameters, and well-behaved fluid properties all improved the dissolution of cellulose in morpholinium-based ILs. The hydrogen bonds in cellulose were destructed by both cations and anions of ILs.

- This study showed the potential of morpholinium-based ILs to dissolve cellulose and this was identified as a series of low-cost, non-aromatic, and biodegradable solvents.

## ACKNOWLEDGMENTS

This work was supported by the Science and Technology Research Projects in Hebei Universities (NO.2017067) and Hebei Natural Science Foundation (E2017208083).

## REFERENCES CITED

- Ab Rani, M. A., Brant, A., Crowhurst, L., Dolan, A., Lui, M., Hassan, N. H., Hallett, J. P., Hunt, P. A., Niedermeyer, H., Perez-Arlandis, J. M., *et al.* (2011). "Understanding the polarity of ionic liquids," *Phys. Chem. Chem. Phys.* 13(37), 16831-16840. DOI: 10.1039/C1CP21262A
- Badgujar, K. C., and Bhanage, B. M. (2015). "Factors governing dissolution process of lignocellulosic biomass in ionic liquid: Current status overview and challenges," *Bioresour. Technol.* 178, 2-18. DOI: 10.1016/j.biortech.2014.09.138
- Chatel, G., Pereira, J. F. B., Debbeti, V., Wang, H., and Rogers, R. D. (2014). "Mixing ionic liquids—'simple mixtures' or 'double salt'?" *Green Chem.* 16(4), 2051-2083. DOI: 10.1039/c3gc41389f
- Domanska, U., and Lukoshko, E. V. (2014). "Thermodynamics and activity coefficients at infinite dilution for organic solutes and water in the ionic liquid 1-butyl-1-methylmorpholinium tricyanomethanide," *J. Chem. Thermodynamics* 68, 53-59. DOI: 10.1016/j.jct.2013.08.030
- Fukaya, Y., Hayashi, K., Wada, M., and Ohno, H. (2008). "Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions," *Green Chem.* 10(1), 44-46. DOI: 10.1039/B713289A
- Glasser, W. G., Atalla, R. H., Blackwell, J., Brown, Jr., R. M., Burchard, W., French, A. D., Klemm, D. O., and Nishiyama, Y. (2012). "About the structure of cellulose: Debating the Lindman hypothesis," *Cellulose* 19(3), 589-598. DOI: 10.1007/s10570-012-9691-7
- Gu, F., Wu, W., Wang, Z., Yokoyama, T., Jin, Y., and Matsumoto Y. (2015). "Effect of complete dissolution in LiCl/DMSO on the isolation and characteristics of lignin from wheat straw internode," *Ind. Crops Prod.* 74, 703-711. DOI: 10.1016/j.indcrop.2015.06.002
- Gümüşkaya, E., Usta, M., and Kirci, H. (2002). "The effects of various pulping conditions on crystalline structure of cellulose in cotton linters," *Polym. Degrad. Stabil.* 81(3), 559-564. DOI: 10.1016/S0141-3910(03)00157-5
- Latała, A., Nedzi, M., Stepnowski, P. (2009). "Toxicity of imidazolium and pyridinium based ionic liquids towards algae *Bacillaria paxillifer* (a microphytobenthic diatom) and *Geitlerinema amphibium* (a microphytobenthic blue green alga)," *Green Chem.*, 11, 1371-1376. DOI: 10.1039/B901887E
- Hojniak, S. D., Khan, A. L., Hollóczki, O., Kirchner, B., Vankelecom II, I. F. J., and Dehaen, W. (2013). "Separation of carbon dioxide from nitrogen or methane by



- supported ionic liquid membranes (SILMs): Influence of the cation charge of the ionic liquid,” *J. Phys. Chem. B* 117(48), 15131-15140. DOI: 10.1021/jp409414t
- Hou, X., Li, N., and Zong, M. (2013). “Significantly enhancing enzymatic hydrolysis of rice straw after pretreatment using renewable ionic liquid–water mixtures,” *Bioresour. Technol.* 136(12), 469-474. DOI: 10.1016/j.biortech.2013.02.118
- Huber, T., Müssig, J., Curnow, O., Pang, S., Bickerton, S., and Staiger, M. P. (2012). “A critical review of all-cellulose composites,” *Asian J. Mater. Sci.* 47(3), 1171-1186. DOI: 10.1007/s10853-011-5774-3
- Hubbell, C. A., and Ragauskas, A. J. (2010). “Effect of acid-chlorite delignification on cellulose degree of polymerization,” *Bioresour. Technol.* 101 (19), 7410-7415. DOI: 10.1016/j.biortech.2010.04.029
- Işık, M., Sardon, H., and Mecerreyes, D. (2015). “Ionic liquid and cellulose technologies: dissolution, modification and composite preparation,” in: *Applications of Ionic Liquids in Polymer Science and Technology*, D. Mecerreyes (ed.), Springer, Berlin, Germany, pp. 135-152. DOI: 10.1007/978-3-662-44903-5\_6
- Jordan, A., and Gathergood, N. (2015). “Biodegradation of ionic liquids—A critical review,” *Chem. Soc. Rev.* 44(22), 8200-8237. DOI: 10.1039/c5cs00444f
- Klemm, D., Heublein, B., Fink, H., and Bohn, A. (2005). “Cellulose: Fascinating biopolymer and sustainable raw material,” *Angew. Chem. Int. Ed.* 44(22), 3358-3393. DOI: 10.1002/chin.200536238
- Liu, D., Xia, K., Cai, W., Yang, R., Wang, L., and Wang, B. (2012). “Investigations about dissolution of cellulose in the 1-allyl-3-alkylimidazolium chloride ionic liquids,” *Carbohydr. Polym.* 87(2), 1058-1064. DOI: 10.1016/j.carbpol.2011.08.026
- Mortimer, J. K., and Taft, R. W. (1976). “The solvatochromic comparison method. I. The  $\beta$ -scale of solvent hydrogen-bond acceptor (HBA) basicities,” *J. Am. Chem. Soc.* 98(2), 377-383. DOI: 10.1021/ja00418a009
- Passos, H., Freire, M. G., and Coutinho, J. A. P. (2014). “Ionic liquid solutions as extractive solvents for value-added compounds from biomass,” *Green Chem.* 16, 4786-4815. DOI: 10.1039/C4GC00236A
- Pena-Pereira, F., and Namieśnik, J. (2014). “Ionic liquids and deep eutectic mixtures: Sustainable solvents for extraction processes,” *ChemSusChem* 7(7), 1784-1800. DOI: 10.1002/cssc.201301192
- Pernak, J., Borucka, N., Walkiewicz, F., Markiewicz, B., Fochtman, P., and Stolte, S. (2011). “Synthesis, toxicity, biodegradability and physicochemical properties of 4-benzyl-4-methylmorpholinium-based ionic liquids,” *Green Chem.* 13(10), 2901-2910. DOI: 10.1039/C1GC15468K
- Pham, T. P. T., Cho, C. W., and Yun, Y. S. (2010). “Environmental fate and toxicity of ionic liquids: A review,” *Water Res.* 44(2), 352-372. DOI: 10.1016/j.watres.2009.09.030
- Ramamoorthy, S. K., Skrifvars, M., and Persson, A. (2015). “A review of natural fibers used in biocomposites: Plant, animal and regenerated cellulose fibers,” *Polym. Rev.* 55(1), 107-162. DOI: 10.1080/15583724.2014.971124
- Raut, D. G., Sundman, O., Su, W., Virtanen, P., and Sugano, Y. (2015). “A morpholinium ionic liquid for cellulose dissolution,” *Carbohydr. Polym.* 130, 18-25. DOI:10.1016/j.biortech.2014.09.138
- Roy, D., Semsarilar, M., Guthrie, J. T., and Perrier, S. (2009). “Cellulose modification by polymer grafting: a review,” *Chem. Soc. Rev.* 38, 2046-2064. DOI: 10.1039/B808639G

- Ru, G., Luo, H., Liang, X., Wang, L., Liu, C., and Feng, J. (2015). "Quantitative NMR investigation on the low-temperature dissolution mechanism of chitin in NaOH/urea aqueous solution," *Cellulose* 22(4), 2221-2229. DOI: 10.1007/s10570-015-0667-2
- Sathitsuksanoh, N., Georgeb, A., and Zhang, Y. H. P. (2013). "New lignocellulose pretreatments using cellulose solvents: A review," *J. Chem. Technol. Biotechnol.* 88(2), 169-180. DOI: 10.1002/jctb.3959
- Segal, L., Creely, J. J., Martin, A. E., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," *Text. Res. J.* 29(10), 786-794. DOI: 10.1177/004051755902901003
- Taft, R. W. (1976). "The solvatochromic comparison method. 2. The  $\alpha$ -scale of solvent hydrogen-bond donor (HBD) acidities," *J. Am. Chem. Soc.* 98(10), 2886-2894. DOI: 10.1021/ja00426a036
- Thomazeau, C., Hélène, O. B., Magna, L., Luts, S., and Gilbert, B. (2003). "Determination of an acidic scale in room temperature ionic liquids," *J. Am. Chem. Soc.* 125(18), 5264-5265. DOI: 10.1021/ja0297382
- Wang, S., Lu, A., and Zhang, L. (2016). "Recent advances in regenerated cellulose materials," *Prog. Polym. Sci.* 53, 169-206. DOI: 10.1016/j.progpolymsci.2015.07.003
- Xu, H., Pan, W., Wang, R., Zhang, D., and Liu, C. (2012). "Understanding the mechanism of cellulose dissolution in 1-butyl-3-methylimidazolium chloride ionic liquid via quantum chemistry calculations and molecular dynamics simulations," *J. Comput.-Aided Mol. Des.* 26(3), 329-337. DOI: 10.1007/s10822-012-9559-9
- Yang, Y. J., Shin, J. M., Kang, T. H., Kimura, S., Wada, M., and Kim, U. J. (2014). "Cellulose dissolution in aqueous lithium bromide solutions," *Cellulose* 21(3), 1175-1181. DOI: 10.1007/s10570-014-0183-9

Article submitted: January 12, 2017; Peer review completed: March 4, 2017; Revisions accepted: June 7, 2017; Published: June 12, 2017.

DOI: 10.15376/biores.12.3.5407-5416