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## An insight into the influence of hydrogen bond acceptors on cellulose/1-allyl-3-methyl imidazolium chloride solution

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Highlight (for review)

Dissolution of cellulose in AmimCl was studied for the design of novel ionic liquids.

**Abstract:** Although ionic liquids have been well established as effective solvents for the dissolution and processing of natural cellulose fibers, the detailed dissolution mechanism at the molecular level still remains unclear. Herein, the turbidimetric measurement showed that the solubility of cellulose in 1-allyl-3-methyl imidazolium chloride (AmimCl) decreased with increasing temperature. The temperature dependence of the O-H stretching vibration band of cellulose in AmimCl was investigated by infrared spectroscopy. The interaction between AmimCl and different hydrogen bond acceptors were investigated by turbidimetry and NMR spectroscopy, which indicated that the excellent compatibility of the hydrogen bond acceptors with AmimCl provides more interaction sites for the hydroxyl groups of the cellulose. In addition, ionic liquids with a similar anionic structure of hydrogen bond acceptors have been synthesized. This study provides a green and safe guide for the preparation of ionic liquids with excellent solubility of cellulose.

**Keywords:** 1-allyl-3-methyl imidazolium chloride (AmimCl); Cellulose; Hydrogen bonding acceptors; Turbidimetry; NMR

#### 1. Introduction

Cellulose is the most abundant renewable biological resource in the world, and has

been widely used in industrial domains such as fiber, paper, polymer, textile and food industries (Fukaya, Hayashi, Wada & Ohno, 2008a; Gupta & Jiang, 2015a; Hauru, Hummel, Nieminen, Michud & Sixta, 2016; Reddy et al., 2017). Nevertheless, natural cellulose is insoluble in water and common organic solvents due to the formation of three-dimensional inter- and intra-molecular hydrogen bonding caused by the hydroxyl groups in cellulose, and that seriously limit its development and utilization (El Seoud, Koschella, Fidale, Dorn & Heinze, 2007; Sasaki, Matsumura & Toshima, 2004; Zhang, Li, Li, Gibril & Yu, 2014). Solvent systems such as N,N-dimethyl acetamide (DMAc)/LiCl, dimethyl-sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF), dimethyl formamide (DMF)/N<sub>2</sub>O<sub>4</sub>, N-methyl morpholine-N-oxide monohydrate (NMMO), cuoxam, cadoxen and NaOH/urea solution have been developed to dissolve cellulose, but such processes need to be replaced for environmental issues and other reasons (Fischer, Thümmler, Pfeiffer, Liebert & Heinze, 2002; Heinze & Liebert, 2001a, b; Liebert & Heinze, 2001; Rinaldi, 2011; Xiong, Zhao, Hu, Zhang & Cheng, 2014). Therefore, it is urgent to develop green solvent systems for cellulose, in which the homogeneous derivation reactions of cellulose can be carried out (Cao, Wu, Zhang, Li, Zhang & He, 2009; Chen, Xu, Li, Wang & Zhang, 2011; Kosan, Michels & Meister, 2008; Le, Rudaz & Budtova, 2014; Pinkert, Marsh, Pang & Staiger, 2009; Suzuki, Kono, Shimomura & Minami, 2014; Vitz, Erdmenger, Haensch & Schubert, 2009; Wang, Gurau & Rogers, 2012). Room-temperature ionic liquids (or, simply called ionic liquids) are composed of organic cations and inorganic anions, which have many attractive properties, such as chemical and thermal stability, non-flammability and good dissolving capacity (Clough, Gever, Hunt, Son, Vagt & Welton, 2015; de Oliveira & Rinaldi, 2015; Gupta & Jiang, b; Laine, Asikainen, Talja, Stépán, Sixta & Harlin, 2016; Liu, Sun, Hao, Huang, Xue & Mu, 2015; Long, Zhang, Wang & Li, 2016; Minnick, Flores, DeStefano & Scurto, 2016; Xu, Cao & Wang, 2015). Therefore, ionic liquids are often called "green solvents" and have been widely used in organic synthesis, catalysis, electrochemistry and materials science and so on.

In 2002, Robin Rogers (Swatloski, Spear, Holbrey & Rogers, 2002) et al. first found that 1-butyl-3-methyl imidazolium chloride (BmimCl) could dissolve cellulose, which opened up the development of ionic liquids as a class of solvent systems for cellulose and promoted other researchers to explore the ability of other ionic liquids to dissolve cellulose. For example, Zhang (Zhang, Wu, Zhang & He, 2005) et al. prepared a new and efficient direct solvent, 1-allyl-3-methylimidazolium chloride

(AmimCl), which was used in the dissolution and regeneration of cellulose. Many researchers are studying the dissolution mechanism of cellulose in ionic liquid, but, results are still controversial. <sup>13</sup>C and <sup>35/37</sup>Cl-NMR relaxation studies (Agarwal, Hossain, Choi, Cheong, Jang & Lee, 2013; Hesse-Ertelt, Heinze, Kosan, Schwikal & Meister, 2010; Marekha et al., 2015; Remsing, Hernandez, Swatloski, Massefski, Rogers & Moyna, 2008; Remsing, Swatloski, Rogers & Moyna, 2006; Xu & Zhang, 2015) demonstrated that the non-hydrated and strongly hydrogen-bonded chloride ions were the main reason for the cellulose dissolution by disrupting the hydrogen-bonding network present within the cellulose polymer, while the cations of ionic liquids have no interaction with cellulose. Nevertheless, the molecular simulation studies (Payal, Bejagam, Mondal & Balasubramanian, 2015) suggested that the cations of ionic liquids formed weak hydrogen bonding interaction and van der Waals interaction with cellulose. Moreover, several reports (Gao, Zhang, Wang & Li, 2010) suggested that both anion and cation of ionic liquids formed strong hydrogen bonding interaction with the hydroxyls group of cellulose, which is the major driving force for the cellulose dissolution.

In order to further investigate the interactions of cellulose with ionic liquid, the interactions of ionic liquid with different lithium salt were also investigated (Agarwal, Hossain, Choi, Cheong, Jang & Lee, 2013; Takada, Imaichi, Kagawa & Takahashi, 2008; Xu, Wang & Wang, 2010). The cellulose intermolecular hydrogen bonds were destroyed, owing to the interaction of Li<sup>+</sup> and ionic liquid with the hydroxyl oxygen O(3) of cellulose, resulting in the enhanced solubility of cellulose. The strength of hydrogen acceptors were evaluated by the Kamlet-Taft parameters ( $\beta$ : hydrogen-bonding basicity) (Taft, 1975). The cellulose dissolved in a variety of ionic liquids was investigated by the Kamlet-Taft parameter, which had large hydrogen bond basicity beta-values ( $\beta$ >0.8) (Fukaya, Asai, Kadotani, Nokami & Itoh, 2016; Fukaya, Hayashi, Wada & Ohno, 2008; Fukaya, Sugimoto & Ohno, 2006; Ohno & Fukumoto, 2007). Different molar ratio of polar solvents (DMI, DMF, sulfolane, or DMSO) were added in ionic liquids, to study the effect of ionic liquid mixture on cellulose (Rinaldi, 2011; Ohira, Yoshida, Hayase & Itoh, 2012). In this study, the solubility of cellulose in AmimCl at different temperature was characterized by the turbidimetry and infrared spectroscopy. Moreover, in order to clarify the interaction of cellulose and ionic liquids, the turbidity changes of cellulose/AmimCl solutions at different concentrations were investigated after the addition of various hydrogen acceptors such as urea, LiCl, K<sub>2</sub>HPO<sub>2</sub>, CH<sub>3</sub>COOK, K<sub>2</sub>SO<sub>4</sub>, and KPF<sub>6</sub>. Furthermore,

the influence of various hydrogen bond acceptors on AmimCl was studied by <sup>1</sup>H NMR. Finally, synthesis of ionic liquid with excellent cellulose dissolving ability was proposed.

#### 2. Materials and methods

#### 2.1 Material

N-Methylimidazole (>99%), allyl chloride (>98%), N-allylimidazolium (>99%), dimethyl phosphite (>98%) and trimethyl phosphate (>98%) were purchased from J&K Chemical Company and distilled before use. Microcrystalline cellulose, urea, LiCl, KH<sub>2</sub>PO<sub>2</sub>, CH<sub>3</sub>COOK, K<sub>2</sub>SO<sub>4</sub> and KPF<sub>6</sub> were also commercially available in analytical reagent grade and were dried in a vacuum oven at 80 °C for around 12 h before use. P<sub>2</sub>O<sub>5</sub>, acetic acid, ethyl acetate and dimethyl sulfate (>98%) were purchased from Adamas Reagent Co. Ltd.

#### 2.2 Synthesis of different ionic liquids (ILs)

1-allyl-3-methyl imidazolium chloride (AmimCl) was synthesized from N-methyl imidazole and allyl chloride (Zhang, Wu, Zhang & He, 2005). 1-allyl-3-methyl imidazolium carboxylate (Amim[CH<sub>3</sub>COO]) was synthesized from 1-allyl-3-methyl imidazolium chloride and acetic acid (Yajuan Zhang, 2015). 1-allyl-3-methyl imidazolium hexafluorophosphate (AmimPF<sub>6</sub>) was synthesized from 1-Allyl-3-methylimidazolium chloride and potassium hexafluorophosphate (Majidi, Pournaghi-Azar, Fadakar Bajeh Baj & Naseri, 2015).

1-allyl-3-methyl imidazolium methyl phosphite (Amim[CH<sub>3</sub>OPO<sub>2</sub>H]) was synthesized from 1-allylimidazole and dimethyl phosphite. Briefly, after dimethyl phosphite was added dropwise into an equimolar amount of 1-allylimidazolium in an ice-water bath and nitrogen atmosphere, the reaction system heated to 90 °C for 24 h with stirring. The final product was dried in vacuum oven at 80 °C for around 12 h. 1-allyl-3-methyl imidazolium dimethyl phosphonate (Amim[(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>]) and 1-allyl-3-methyl imidazolium methyl sulfate (Amim[CH<sub>3</sub>OSO<sub>3</sub>]) were prepared according to the process for preparing Amim[CH<sub>3</sub>OPO<sub>2</sub>H] described above.

The structure and purity of all ILs was determined by <sup>1</sup>H NMR spectroscopy using a Bruker III 400 MHz spectrometer.

**AmimCl:** <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>) δ 9.76 (s, 1H, NCHN), 7.98-8.00 (d, 2H, NCHCHN), 6.09 (ddt, 1H, CH<sub>2</sub>CH<sub>1</sub>), 5.33 (m, 2H, CH<sub>2</sub>CH), 5.01 (d, 2H, CH<sub>2</sub>N), 3.97(s, 3H, NCH<sub>3</sub>)

**Amim**[CH<sub>3</sub>COO]: <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>) δ 9.99 (s,1H, NCHN), 7.98 (dt, 2H, NCHCHN), 6.11 (m, 1H, CH<sub>2</sub>CH<sub>1</sub>), 5.43 (m, 2H, CH<sub>2</sub>CH), 5.01 (d, 2H,

CH<sub>2</sub>N), 3.97(s,3H, NCH<sub>3</sub>), 1.46(s, 3H, CH<sub>3</sub>COO)

**AmimPF<sub>6</sub>:** <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>) δ 9.14 (s, 1H, NCHN), 7.69 (d, 2H, NCHCHN), 6.24 – 5.75 (m, 1H, CH<sub>2</sub>CH<sub>1</sub>), 5.54 – 5.05 (m, 2H, CH<sub>2</sub>CH), 4.83 (d, 2H, CH<sub>2</sub>N), 3.86 (s, 3H, NCH<sub>3</sub>).

**Amim**[CH<sub>3</sub>OPO<sub>2</sub>H]: <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.52 (s, 1H, NCHN), 7.81 (d, 2H, NCHCHN), 7.24, 5.81(s, 1H, PH), 6.28 – 5.90 (m, 1H, CH<sub>2</sub>CH<sub>1</sub>), 5.31 (ddd, 2H, CH<sub>2</sub>CH), 4.88 (d, 2H, CH<sub>2</sub>N), 3.89 (s, 3H, NCH<sub>3</sub>), 3.27 (d, 3H, POCH<sub>3</sub>).

**Amim**[(**CH**<sub>3</sub>**O**)<sub>2</sub>**PO**<sub>2</sub>]: 1H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.74 – 9.34 (m, 1H, NCHN), 7.94 – 7.61 (m, 2H, NCHCHN), 6.05 (ddt,, 1H, CH<sub>2</sub>CH<sub>1</sub>), 5.45 – 5.18 (m, 2H, CH<sub>2</sub>CH), 4.88 (d, 2H, CH<sub>2</sub>N), 3.89 (s, 3H, NCH<sub>3</sub>), 3.28 (d, 6H, P(OCH<sub>3</sub>)<sub>2</sub>).

**Amim[CH<sub>3</sub>OSO<sub>3</sub>]:** 1H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.05 (s, 1H, NCHN), 7.71 (s, 2H, NCHCHN), 6.28 – 5.90 (m, 1H, CH<sub>2</sub>CH<sub>1</sub>), 5.60 – 5.20 (m, 2H, CH<sub>2</sub>CH), 4.88 (s, 2H, CH<sub>2</sub>N), 3.94 (dd, 3H, NCH<sub>3</sub>), 3.51 (ddd, 3H, SOCH<sub>3</sub>).



Figure 1 Chemical structure of ionic liquids

#### 2.3 Effect of temperature on cellulose/AmimCl solutions

#### 2.3.1 Turbidimetric measurements of cellulose in AmimCl

As a typical protocol, the turbidimetric measurements of 2 wt.% cellulose/AmimCl solution was carried out as follows: 0.2 g of microcrystalline cellulose was added into 10.0g of AmimCl, and the mixture was heated to 80 °C and vigorously stirred until the cellulose sample was completely dissolved. Afterward, the cellulose/AmimCl sample was quickly transferred into a turbidimetric glass vial, which was dried in a vacuum oven at 80 °C for around 2 h. The turbidity was recorded until a stable nephelometric turbidity units (NTU) value was reached at 25 °C. Turbidimetric measurements of cellulose/AmimCl at other concentrations (4 wt.%, 6 wt.%, 8 wt.%, 10 wt.%, 12 wt.%, 14 wt.%, 16 wt.%) were carried out by the same method described above.

# 2.3.2 Effect of temperature on the turbidimetry and IR Spectra of cellulose/AmimCl solution

Different concentrations (1 wt.%, 5 wt.%, 10 wt.%, 12 wt.%, 14 wt.%) of

cellulose in AmimCl were prepared as described above. The turbidity of those solutions was measured at different temperatures by the same method described above.

Fourier transform infrared spectroscopy (FT-IR) was performed using a Bruker Tensor 27 FT-IR spectrometer for 32 scans at a resolution of 4 cm<sup>-1</sup>. The IR spectra of the 10 wt.% cellulose solution at variable temperature was measured as follows: the cellulose solution was heated at a rate of 5 °C/min over a temperature range of 30-100 °C and stabilized for 5 minutes at each temperature stage before the spectroscopic measurement.

#### 2.4 Effect of hydrogen bond acceptors on cellulose/AmimCl solutions

As a typical protocol, the turbidimetric measurements of 0.5 wt.% hydrogen bond acceptors /AmimCl solution was carried out as follows: 0.05 g of hydrogen bond acceptor was added into 10.0 g of AmimCl, and the mixture was heated to 80 °C and vigorously stirred until the hydrogen bond acceptors was completely dissolved. Afterward, the hydrogen bond acceptor/AmimCl solution was quickly transferred into a turbidimetric glass vial. The turbidity was recorded until a stable nephelometric turbidity units (NTU) value was reached at 25 °C. Additional hydrogen bond acceptor was added until the turbidity of the solution increased dramatically at 25 °C.

The molecular interaction between the 0.5wt.% hydrogen bond acceptor and AmimCl was investigated by <sup>1</sup>H NMR spectroscopy. All spectra were performed on a Bruker 600 III spectrometer at 25 °C. A mixture of hydrogen bond acceptor and AmimCl was prepared in an NMR tubes using DMSO-d<sub>6</sub> as solvent.

The Kamlet-Taft parameters of ionic liquids after adding the hydrogen bond acceptors were determined as follows. Spectroscopic grade solvatochromic dyes, 4-nitroaniline (NA), and N, N-diethyl-4-nitroaniline (EDNA) were employed. The dried ionic liquid hydrogen bond acceptor was added to the concentrated dry methanol solution of the dye in a dry oven and dried under pressure at 40 °C for 12 h. To avoid dye aggregation, a series of dye concentrations in the ionic liquid mixture were selected to give an absorbance greater than 0.15. The ionic liquid mixture containing NA or DENA were placed into capped and sealed quartz cells with 1 mm light-path length at 25 °C and were recorded on a ultraviolet-visible spectrophotometer.

The wavelength of the maximum absorption ( $\lambda_{max}$ ) was determined and the  $\beta$  values were calculated by the following equations:

$$V_{(NA)} = 1/(\lambda_{max(NA)} \times 10^{-4})$$

 $v_{(DENA)} = 1/_{(\lambda max(NA))} \times 10^{-4}$ 

 $\beta = (1.035 v_{(NA)} + 2.64 - v_{(EDNA)})/2.80$ 

In order to investigate the effect of the hydrogen bond acceptor on the turbidity of cellulose/AmimCl solution, the determined amounts (2 wt.%, 4 wt.%, 6 wt.% and 8 wt.%) of cellulose were dissolved in AmimCl containing 0.5 wt.% of those hydrogen bond acceptors by stirring at 80 °C, even dried and measured by turbidimetry after complete dissolution at 25 °C.

#### 2.5 Turbidimetric measurements of cellulose in different ILs

0.05g of microcrystalline cellulose was added into 10.0 g of dried different ILs, and the mixture was heated to 80 °C and vigorously stirred until the cellulose was completely dissolved. Afterwards, the turbidity of the cellulose/ILs was measured according to the section of 2.3.1. Additional microcrystalline cellulose was added until the turbidity of the solution increased dramatically. Cellulose was thought to be saturated, when the cellulose could not be further dissolved within 1 h by turbidimetry.

#### 3. Results and discussion

#### 3.1 Effect of temperature on cellulose/AmimCl solution

When a beam of parallel light pass through the transparent liquid, the turbidity value is zero due to the absence of suspended particles. Once the solid particles are existed, scattering light could be received and recorded as turbidity value. As the solid particles increased, the turbidity value increased. The maximum solubility of solute was determined by an abrupt change of turbidity, and the value is not affected by the color of the liquid. Mazza et al (Mazza, Catana, Vaca-Garcia & Cecutti, 2009) got the maximum solubility of cellulose solution in BmimCl by turbidimetry, and further studied the effect of water on the cellulose solution in ionic liquids. Using the same method, Luo et al (Luo, Lu, Kong, Fu, Li & Luo, 2013) obtained the maximum solubility of five different types of starch in AmimCl.



Figure 2 (A) Maximum solubility of cellulose in ionic liquid (AmimCl) at 25 °C; (B) Influence of temperature on the turbidity of cellulose/AmimCl solutions

The maximum solubility of cellulose in AmimCl was determined by an abrupt increase point in turbidity. As shown in Figure 2 (A), the turbidity increased slightly with the cellulose concentration in AmimCl in the range 0-14wt.%, indicating that the cellulose could be molecularly dispersed in AmimCl. When the cellulose concentration was increased from 14 wt.% to 18 wt.%, the turbidity of the cellulose/AmimCl sharply increased. The bigger turbidity values indicated the presence of solid particles. Therefore, the maximum solubility of cellulose in AmimCl is 14-16 wt.% at 25 °C, which correlates with the onset of cellulose precipitation.

The turbidity of the cellulose/AmimCl solution was monitored as a function of temperature. As shown in Figure 2 (B), the turbidity of pure AmimCl kept constant at different temperatures. The turbidity value of 1 wt.% cellulose/AmimCl solution was similar to that of the pure AmimCl, which fell slightly from 0.78 NTU to 1.25 NTU as the temperature raised from 30 °C to 70 °C. The similar tendency of turbidity change was also observed for 5 wt.%, 10 wt.%, 12 wt.% cellulose/AmimCl solutions, with the decrease of temperature, their turbidity decreased from 4.74, 16.73 and 24.14 NTU to 6.18, 21.12 and 26.69 NTU, respectively. This phenomenon may be attributed to the gradual breakdown of the hydrogen bond network between cellulose and AmimCl due to the increase of temperature, resulting in the slight precipitation and agglomeration of cellulose.



Figure 3 FT-IR spectra of the 10 wt.% cellulose solution in the temperature range of 30-100 °C

As shown in Figure 3, the change of FI-IR spectra of the 10wt.% cellulose solution mainly occurred in the range of  $3600-3200 \text{ cm}^{-1}$  and  $3100-2900 \text{ cm}^{-1}$  by varying the temperature from 30 °C to 100 °C, which were assigned to the O-H stretching vibration of cellulose and C<sub>2</sub>–H stretching vibration of imidazolium ion, respectively. The O-H stretching vibrations with more useful information were studied in detail. The peak intensity of O-H stretching vibration of the cellulose was weakened and the peak position shifted to a higher wavenumber with the increase of temperature, indicating that the hydrogen bond was weakened and partially destroyed. Moreover, as the temperature increased, the peak position of the C<sub>2</sub>–H stretching vibration of the imidazolium ions shifted toward a lower wavenumber (red shift). This phenomenon indicated that the hydrogen bonds were formed between the C<sub>2</sub>–H bond of imidazolium ion and the O-H bond of cellulose.

3.2 Effect of hydrogen bond acceptors on the cellulose/AmimCl solution

Hydrogen bond Urea LiCL KH2PO2 CH2COOK K2SC	)4 KPF6						
acceptor							
<b>Solubility</b> 40wt.% 15wt.% 9wt.% 6.5wt.% 1wt.	% 0.5wt.%						

Table 1 Solubility of hydrogen bond acceptors in AmimCl by turbidity

The maximum solubility of different hydrogen bond acceptors in AmimCl were listed in Table 1, which arranged in descending order: Urea > LiCl >  $KH_2PO_2$  >  $CH_3COOK$  >  $K_2SO_4$  >  $KPF_6$ . In addition, since the turbidity changes of pure AmimCl

and cellulose/AmimCl solutions at different concentrations (2 wt.%, 4 wt.%, 6 wt.%, 8 wt.%) were almost negligible after the addition of 0.5 wt.% of different hydrogen bond acceptors (data not shown), thus, a 0.5 wt.% of hydrogen bond acceptor ( $\chi$ HBs(Urea, LiCl, KH<sub>2</sub>PO<sub>2</sub>, CH<sub>3</sub>COOK, K<sub>2</sub>SO<sub>4</sub>, KPF<sub>6</sub>): 0.013, 0.019, 0.0092, 0.0081, 0.0046, 0.0043) was set for further research.



Figure 4<sup>1</sup>H NMR chemical shift of AmimCl

<sup>1</sup>H NMR (600MHz, DMSO-d<sub>6</sub>) δ 9.35 (1H, NC**H**N), 7.54 (2H, NC**H**C**H**N), 5.25

(1H, CH<sub>2</sub>=CHCH<sub>2</sub>), 4.43 (4H, CH<sub>2</sub>=CHCH<sub>2</sub>), 3.38(3H, NCH<sub>3</sub>)

Table 2 <sup>1</sup>H NMR chemical shift of the C<sub>2</sub>-H protons in AmimCl with hydrogen

bond acceptors							
hydrogen bond acceptor	Pure	Urea	LiCl	KH <sub>2</sub> PO <sub>2</sub>	CH₃COOK	$K_2SO_4$	KPF <sub>6</sub>
Chemical shift	9.35	9.21	9.24	9.28	9.30	9.48	9.50
Δδ	0	-0.14	-0.11	-0.07	-0.05	+0.13	+0.15

The interaction between imidazolium cation and hydrogen bond acceptors could be accessed by the differences of chemical shift of AmimCl in the presence of hydrogen bond acceptors based on that of pure AmimCl.<sup>1</sup>H NMR chemical shift of the C<sub>2</sub>-H protons in AmimCl was list in Table 2. In the presence of co-hydrogen bond acceptors (The co-hydrogen bond acceptor is defined as a hydrogen bond acceptor that increases the solubility of the cellulose in the ionic liquid, such as urea, LiCl, KH<sub>2</sub>PO<sub>2</sub>, CH<sub>3</sub>COOK.) such as urea, LiCl, KH<sub>2</sub>PO<sub>2</sub>, CH<sub>3</sub>COOK, the chemical shifts of the C<sub>2</sub>-H protons in AmimCl were smaller approximately 0.1 ppm than that of pure AmimCl,

which manifested that the C<sub>2</sub>-H protons in AmimCl have more electron density, owing to stronger interactions between the cation of imidazolium cation and the anion of hydrogen bond acceptor. When cellulose was added, the mixture of hydrogen bond acceptor and AmimCl were potentially capable of forming more and stronger interactions with the hydroxyl groups of the cellulose. Conversely, in the presence of anti-hydrogen bond acceptor that decreases the solubility of cellulose in the ionic liquid, such as K<sub>2</sub>SO<sub>4</sub> and KPF<sub>6</sub>.) such as K<sub>2</sub>SO<sub>4</sub> and KPF<sub>6</sub>, the chemical shifts of the C<sub>2</sub>-H protons in AmimCl were bigger than that of pure AmimCl, which manifested that the C<sub>2</sub>-H protons in AmimCl experience reduced shielding, which AmimCl and anti-hydrogen bond acceptors generate strong hydrogen bonds. When cellulose was added, the hydrogen bonds between hydrogen bond acceptor and AmimCl were not destroyed.

Hydrogen bond acceptor	Pure	Urea	LiCl	KH <sub>2</sub> PO <sub>2</sub>	CH₃COOK	K <sub>2</sub> SO <sub>4</sub>	KPF <sub>6</sub>
The $\beta$ parameter	0.84	0.92	0.88	0.87	0.85	0.82	0.81

Table 3 The  $\beta$  parameter values of the investigated ionic liquid mixture

The  $\beta$  parameter values of the investigated ionic liquid mixture were listed in Table 3. In the presence of co-hydrogen bond acceptors, the  $\beta$  parameter ( $\beta$ >0.84) in AmimCl was higher than that of pure AmimCl, indicating that the interaction between imidazolium and the anion of hydrogen bond acceptor and co-hydrogen bond acceptors was stable in AmimCl by the formation of complex structure, which further improved the solubility of cellulose in ionic liquids. Conversely, in the presence of anti-hydrogen bond acceptors, the  $\beta$  parameter in AmimCl was lower than that of pure AmimCl, indicating that hydrogen bonds were generated between AmimCl and anti-hydrogen bond acceptors. The sulfate ions or hexafluorophosphate ions formed hydrogen bonds with the hydroxyl groups of the cellulose and competed with AmimCl, which ultimately reduced the maximum solubility of the cellulose in AmimCl.



Figure 5 Effect of different hydrogen bonding acceptors on the turbidity of cellulose/AmimCl solutions containing different amounts of cellulose

As shown in Figure 5, the turbidity of cellulose/AmimCl solutions became more sensitive to different hydrogen bond acceptors as the cellulose concentration increased. Like the controlled cellulose/AmimCl solution, the turbidity of cellulose/AmimCl solutions containing co-hydrogen bond acceptors (urea, LiCl, KH<sub>2</sub>PO<sub>2</sub> or CH<sub>3</sub>COOK) slightly increased with the increase of the cellulose concentration, indicating that the mutual dissolution occurred between AmimCl and co-hydrogen bond acceptors. These results correlated well with the analytical data on the limited solubility of different hydrogen bond acceptors in AmimCl (Table 1), confirming that co-hydrogen bond acceptors could exist stably in AmimCl by the formation of complex structure, which further improved the cellulose dissolution in ionic liquids. In contrast, the turbidity of cellulose/AmimCl solution with 2 wt.% cellulose was similar to that of pure AmimCl in the presence of  $K_2SO_4$  or KPF<sub>6</sub>, while the turbidity of the above solution sharply increased when the cellulose concentration reached 8 wt.%. This may be due to the fact that the sulfate ions or hexafluorophosphate ions formed hydrogen bonds with the hydroxyl groups of cellulose, which competed with the chloride ions of AmimCl, and ultimately decreased the maximum solubility of cellulose in AmimCl. As mentioned above, the transparent cellulose/AmimCl solution with 0.5wt.% hydrogen bond acceptor could be obtained at a relatively low cellulose concentration, which possibly due to the fact that the excess chloride ions may be associated with the hydroxyl proton of cellulose. However, when the cellulose concentration was high (up to 8 wt.%), the competition of the phosphate or sulfate ions with the chloride ions of AmimCl could not be avoided during the turbidity measurement, which is harmful for

the cellulose dissolution in AmimCl. A comparison between co-hydrogen bond acceptor and anti-hydrogen bond acceptor on the cellulose dissolution in ionic liquid was schematically shown in Figure 6.



Figure 6 (A) Mechanism of cellulose dissolution in the mixture of co-hydrogen bond acceptors and AmimCl; (B) Mechanism of cellulose dissolution in the mixture of anti-hydrogen bond acceptors and AmimCl dissolve cellulose.



3.3 Measurements of cellulose solubility in different ionic liquids

Figure 7 Maximum solubility of cellulose in different ionic liquids

As shown in Figure 7, the maximum solubility of cellulose in the AmimCl/urea mixture was 16-18 wt.%, exceeding that of AmimCl, which were mainly related to the good compatibility of imidazole cation with hydrogen bond acceptors anion. Furthermore, AmimCl, Amim[CH<sub>3</sub>OPO<sub>2</sub>H], Amim[(CH<sub>3</sub>O)<sub>2</sub>PO<sub>2</sub>] and Amim[CH<sub>3</sub>COO] and were synthesized in order to correspond to the anion structure of LiCl, KH<sub>2</sub>PO<sub>2</sub>, CH<sub>3</sub>COOK, and the solubility of cellulose was 15 wt.%, 10 wt.%, 6

wt.% and 8 wt.%, respectively. In contrast, the cellulose was almost insoluble in Amim [CH<sub>3</sub>OSO<sub>3</sub>] and AmimPF<sub>6</sub>, which was consistent with the previously discussed results that K<sub>2</sub>SO<sub>4</sub> and KPF<sub>6</sub> was hardly soluble in AmimCl. The above results showed that the turbidity of the cellulose/AmimCl solution could be affected by different types of hydrogen bond acceptors, which was directly associated with the compatibility of AmimCl and hydrogen bond acceptors. Our research not only proves quantitative agreement with known experimental data, but also develops a basic understanding of the properties of ionic liquids, which provides a guide to the synthesis of new ionic liquids with excellent cellulose solubility.

#### Conclusion

In conclusion, the maximum solubility of cellulose in ionic liquid AmimCl is 14-16 wt.%, which is consistent with the literature results (Zhang, Wu, Zhang & He, 2005). It's demonstrated that the hydrogen bond interaction causes the change of the turbidity of the cellulose/AmimCl solution at different temperature. The temperature rise will destroy the hydrogen bond interaction between cellulose and ionic liquid, similar to the aqueous solution of the hydroxyl polymer. Furthermore, different hydrogen bond acceptors have different compatibility with ionic liquids due to their different structures and electron-donating strengths. The solubility of cellulose was increased by the addition of co-hydrogen bond acceptors, but decreased by the addition of anti-hydrogen bond acceptors. And, the ionic liquids with a similar chemical structure to that of the hydrogen bond acceptor were synthesized, which have outstanding solubility of cellulose. This study provides a green and simple guide for the preparation of ionic liquids with excellent solubility of cellulose.

### **References:**

Agarwal, S., Hossain, A. M., Choi, Y., Cheong, M., Jang, H. G., & Lee, J. S. (2013). Imidazolium Chloride-LiCl Melts as Efficient Solvents for Cellulose. *Bulletin of the Korean Chemical Society*, *34*(12), 3771-3776.

Cao, Y., Wu, J., Zhang, J., Li, H., Zhang, Y., & He, J. (2009). Room temperature ionic liquids (RTILs): A new and versatile platform for cellulose processing and derivatization. *Chemical Engineering Journal*, *147*(1), 13-21.

Chen, Q., Xu, A., Li, Z., Wang, J., & Zhang, S. (2011). Influence of anionic structure on the dissolution of chitosan in 1-butyl-3-methylimidazolium-based ionic liquids. *Green Chemistry*, *13*(12), 3446-3452.

Clough, M. T., Geyer, K., Hunt, P. A., Son, S., Vagt, U., & Welton, T. (2015). Ionic liquids: not always innocent solvents for cellulose. *Green Chemistry*, *17*(1), 231-243.

de Oliveira, H. F. N., & Rinaldi, R. (2015). Understanding Cellulose Dissolution: Energetics of Interactions of Ionic Liquids and Cellobiose Revealed by Solution Microcalorimetry. *ChemSusChem*,

8(9), 1577-1584.

El Seoud, O. A., Koschella, A., Fidale, L. C., Dorn, S., & Heinze, T. (2007). Applications of Ionic Liquids in Carbohydrate Chemistry: A Window of Opportunities. *Biomacromolecules*, *8*(9), 2629-2647.

Fischer, S., Thümmler, K., Pfeiffer, K., Liebert, T., & Heinze, T. (2002). Evaluation of molten inorganic salt hydrates as reaction medium for the derivatization of cellulose., *9*(3), 293-300.

Fukaya, Y., Asai, R., Kadotani, S., Nokami, T., & Itoh, T. (2016). Extraction of Polysaccharides from Japanese Cedar Using Phosphonate-Derived Polar Ionic Liquids Having Functional Groups. *Bulletin of the Chemical Society of Japan*, 89(8), 879-886.

Fukaya, Y., Hayashi, K., Wada, M., & Ohno, H. (2008). Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions. *Green Chemistry*, *10*(1), 44-46.

Fukaya, Y., Sugimoto, A., & Ohno, H. (2006). Superior Solubility of Polysaccharides in Low Viscosity, Polar, and Halogen-Free 1,3-Dialkylimidazolium Formates. *Biomacromolecules*, 7(12), 3295-3297.

Gao, Y., Zhang, L., Wang, Y., & Li, H. (2010). Probing Electron Density of H-Bonding between Cation-Anion of Imidazolium-Based Ionic Liquids with Different Anions by Vibrational Spectroscopy. The Journal of Physical Chemistry B, 114(8), 2828-2833.

Gupta, K. M., & Jiang, J. (2015). Cellulose dissolution and regeneration in ionic liquids: A computational perspective. *Chemical Engineering Science*, *121*, 180-189.

Hauru, L. K. J., Hummel, M., Nieminen, K., Michud, A., & Sixta, H. (2016). Cellulose regeneration and spinnability from ionic liquids. *Soft Matter*, *12*(5), 1487-1495.

Heinze, T., & Liebert, T. (2001). Unconventional methods in cellulose functionalization. *Progress in Polymer Science*, 26(9), 1689-1762.

Hesse-Ertelt, S., Heinze, T., Kosan, B., Schwikal, K., & Meister, F. (2010). Solvent Effects on the NMR Chemical Shifts of Imidazolium-Based Ionic Liquids and Cellulose Therein. *Macromolecular Symposia*, 294(2), 75-89.

Kosan, B., Michels, C., & Meister, F. (2008). Dissolution and forming of cellulose with ionic liquids. *Cellulose*, *15*(1), 59-66.

Laine, C., Asikainen, S., Talja, R., Stépán, A., Sixta, H., & Harlin, A. (2016). Simultaneous bench scale production of dissolving grade pulp and valuable hemicelluloses from softwood kraft pulp by ionic liquid extraction. *Carbohydrate Polymers*, *136*, 402-408.

Le, K. A., Rudaz, C., & Budtova, T. (2014). Phase diagram, solubility limit and hydrodynamic properties of cellulose in binary solvents with ionic liquid. *Carbohydrate Polymers*, *105*, 237-243.

Liebert, T. F., & Heinze, T. J. (2001). Exploitation of Reactivity and Selectivity in Cellulose Functionalization Using Unconventional Media for the Design of Products Showing New Superstructures. *Biomacromolecules*, 2(4), 1124-1132.

Liu, Z., Sun, X., Hao, M., Huang, C., Xue, Z., & Mu, T. (2015). Preparation and characterization of regenerated cellulose from ionic liquid using different methods. *Carbohydrate Polymers*, *117*, 99-105.

Long, J., Zhang, Y., Wang, L., & Li, X. (2016). Which is the determinant for cellulose degradation in cooperative ionic liquid pairs: dissolution or catalysis? *Science China Chemistry*, *59*(5), 557-563.

Luo, Z., Lu, X., Kong, X., Fu, X., Li, F., & Luo, F. (2013). Physicochemical properties of starch dispersed in 1-allyl-3-methylimidazolium chloride. *Industrial Crops and Products*, *46*, 197-204.

Majidi, M. R., Pournaghi-Azar, M. H., Fadakar Bajeh Baj, R., & Naseri, A. (2015). Formation of graphene nanoplatelet-like structures on carbon – ceramic electrode surface: application for simultaneous determination of sunset yellow and tartrazine in some food samples., *21*(3), 863-875.

Marekha, B. A., Bria, M., Moreau, M., De Waele, I., Miannay, F., Smortsova, Y., Takamuku, T., Kalugin, O. N., Kiselev, M., & Idrissi, A. (2015). Intermolecular interactions in mixtures of 1-n-butyl-3-methylimidazolium acetate and water: Insights from IR, Raman, NMR spectroscopy and quantum chemistry calculations. *Journal of Molecular Liquids*, 210, 227-237.

Mazza, M., Catana, D., Vaca-Garcia, C., & Cecutti, C. (2009). Influence of water on the dissolution of cellulose in selected ionic liquids. *Cellulose*, *16*(2), 207-215.

Minnick, D. L., Flores, R. A., DeStefano, M. R., & Scurto, A. M. (2016). Cellulose Solubility in Ionic Liquid Mixtures: Temperature, Cosolvent, and Antisolvent Effects. *The Journal of Physical Chemistry B*, *120*(32), 7906-7919.

Ohira, K., Yoshida, K., Hayase, S., & Itoh, T. (2012). Amino Acid Ionic Liquid as an Efficient Cosolvent of Dimethyl Sulfoxide to Realize Cellulose Dissolution at Room Temperature. *Chemistry Letters*, *41*(9), 987-989.

Ohno, H., & Fukumoto, K. (2007). Amino Acid Ionic Liquids. Accounts of Chemical Research, 40(11), 1122-1129.

Payal, R. S., Bejagam, K. K., Mondal, A., & Balasubramanian, S. (2015). Dissolution of Cellulose in Room Temperature Ionic Liquids: Anion Dependence. *The Journal of Physical Chemistry B*, 119(4), 1654-1659.

Pinkert, A., Marsh, K. N., Pang, S., & Staiger, M. P. (2009). Ionic Liquids and Their Interaction with Cellulose. *Chemical Reviews*, 109(12), 6712-6728.

Reddy, K. O., Maheswari, C. U., Dhlamini, M. S., Mothudi, B. M., Zhang, J., Zhang, J., Nagarajan, R.,
& Rajulu, A. V. (2017). Preparation and characterization of regenerated cellulose films using borassus fruit fibers and an ionic liquid. *Carbohydrate Polymers*, *160*, 203-211.

Remsing, R. C., Hernandez, G., Swatloski, R. P., Massefski, W. W., Rogers, R. D., & Moyna, G. (2008). Solvation of Carbohydrates in N,N' -Dialkylimidazolium Ionic Liquids: A Multinuclear NMR Spectroscopy Study. *The Journal of Physical Chemistry B*, *112*(35), 11071-11078.

Remsing, R. C., Swatloski, R. P., Rogers, R. D., & Moyna, G. (2006). Mechanism of cellulose dissolution in the ionic liquid 1-n-butyl-3-methylimidazolium chloride: a 13C and 35/37Cl NMR relaxation study on model systems. *Chemical Communications*(12), 1271.

Rinaldi, R. (2011). Instantaneous dissolution of cellulose in organic electrolyte solutions. *Chemical Communications*, 47(1), 511-513.

Sasaki, K., Matsumura, S., & Toshima, K. (2004). A novel glycosidation of glycosyl fluoride using a designed ionic liquid and its effect on the stereoselectivity. *Tetrahedron Letters*, *45*(38), 7043-7047.

Suzuki, T., Kono, K., Shimomura, K., & Minami, H. (2014). Preparation of cellulose particles using an ionic liquid. *Journal of Colloid and Interface Science*, *418*, 126-131.

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of Cellose with Ionic Liquids. *Journal of the American Chemical Society*, *124*(18), 4974-4975.

Taft, M. J. K. A. (1975). The Solvatochromic Comparison Method. I. The  $\beta$ -Scale of Solvent Hydrogen-Bond Acceptor (HBA) Basicities. *Journal of the American Chemical Society*, 377-383.

Takada, A., Imaichi, K., Kagawa, T., & Takahashi, Y. (2008). Abnormal Viscosity Increment Observed for an Ionic Liquid by Dissolving Lithium Chloride. *The Journal of Physical Chemistry B*, *112*(32), 9660-9662.

Vitz, J., Erdmenger, T., Haensch, C., & Schubert, U. S. (2009). Extended dissolution studies of cellulose in imidazolium based ionic liquids. *Green Chemistry*, 11(3), 417.

Wang, H., Gurau, G., & Rogers, R. D. (2012). Ionic liquid processing of cellulose. Chemical Society

Reviews, 41(4), 1519.

Xiong, B., Zhao, P., Hu, K., Zhang, L., & Cheng, G. (2014). Dissolution of cellulose in aqueous NaOH/urea solution: role of urea. *Cellulose*, *21*(3), 1183-1192.

Xu, A., Cao, L., & Wang, B. (2015). Facile cellulose dissolution without heating in [C4mim][CH3COO]/DMF solvent. *Carbohydrate Polymers*, *125*, 249-254.

Xu, A., Wang, J., & Wang, H. (2010). Effects of anionic structure and lithium salts addition on the dissolution of cellulose in 1-butyl-3-methylimidazolium-based ionic liquid solvent systems. *Green Chemistry*, *12*(2), 268-275.

Xu, A., & Zhang, Y. (2015). Insight into dissolution mechanism of cellulose in [C4mim][CH3COO]/DMSO solvent by 13C NMR spectra. *Journal of Molecular Structure, 1088*, 101-104.

Yajuan Zhang, A. X. B. L. (2015). Dissolution of cellulose in 1-allyl-3-methylimizodalium carboxylatesat room temperature: A structure – property relationship study. *Carbohydrate Polymers*(117), 666-672.

Zhang, H., Wu, J., Zhang, J., & He, J. (2005). 1-Allyl-3-methylimidazolium Chloride Room Temperature Ionic Liquid: A New and Powerful Nonderivatizing Solvent for Cellulose. *Macromolecules*, *38*(20), 8272-8277.

Zhang, Y., Li, H., Li, X., Gibril, M. E., & Yu, M. (2014). Chemical modification of cellulose by in situ reactive extrusion in ionic liquid. *Carbohydrate Polymers*, *99*, 126-131.