The Properties of Choline Chloride-based Deep Eutectic Solvents and their Performance in the Dissolution of Cellulose

Hongwei Ren,[a,b, #] Chunmao Chen,[a, #] Qinghong Wang,[a] Dishun Zhao,[b] and Shaohui Guo [a,]*

A series of choline chloride-based deep eutectic solvents (ChCl-DESs) were synthesized and characterized, and their performance in the dissolution of cellulose was investigated. The hydrogen-bond donors significantly (β-value) affected the properties of ChCl-DESs, causing differentiated dissolution performances. ChCl- imidazole (Im) showed the highest Hammett acidity function (1.869), hydrogen bond basicity (0.864), and dipolarity/polarizability effect (0.382) among the ChCl-DESs. The ChCl-Im showed the lowest pseudo-activation energy for viscous flow (31.76 kJ mol^{-1}) among the ChCl-DESs. The properties of ChCl-Im caused the highest solubility of cellulose (2.48 wt.%) relative to the other ChCl-DESs. Polyethylene glycol (PEG), as a co-solvent, significantly (β-value) enhanced the accessibility of ChCl-Im to cellulose by breaking the supramolecular structure of cellulose, promoting its dissolution. The decrystallization of ChCl-Im-coupled PEG approximately doubled the dissolving capabilities, and the solubility increased by more than 80% in comparison with only ChCl-Im. The cellulose was directly dissolved by ChCl-Im-coupled PEG, and no other derivatives were produced.

Keywords: Deep eutectic solvents; Cellulose; Dissolution; Choline chloride; Cosolvent

Contact information: a: State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, P. R. China; b: School of Science, Hebei University of Science and Technology, Shijiazhuang 050018, P. R. China;
** Corresponding author: cupgsh@163.com, # These authors contributed equally to this work.*

INTRODUCTION

As the most abundant biological polymer, cellulose has been widely used in the textile, chemical, pharmaceutical, and energy industries (Vitz *et al*. 2009; Yang *et al*. 2014; Ramamoorthy *et al*. 2015). Raw cellulose is insoluble in aqueous and common organic solvents because of its high crystallinity and supramolecular structure (Gümüskaya *et al*. 2003; Yanagisawa *et al*. 2004). Cellulose-derived products, including ester-, methyl-, dexy-, and ether-celluloses, are all produced *via* heterogeneous processing (Alvira *et al*. 2010). The weak contact between the two phases lowers the accessibility to cellulose of reactants. Harsh processing conditions, such as high pressure and temperature, are often required (Castro *et al*. 2015). Therefore, dissolution is the principal step in the processing of celluloses.

Conventional solvents, including sulfuric acid, phosphoric acid, lithium chloride/N, N-dimethylacetamide, sodium hydroxide/urea, and tetrabutylammonium fluoride trihydrate/dimethyl sulfoxide, can potentially cause severe pollution (Ruan *et al*. 2004; Ru *et al*. 2015). Therefore, a cleaner dissolution of cellulose requires “greener” solvents (Sun *et al*. 2011; Badgujar and Bhanage 2015). Deep eutectic solvents (DESs), formed by the combination of a hydrogen-bond acceptor (HBA) and a hydrogen-bond donor (HBD), have emerged as a novel generation of solvents (Abbott *et al*. 2003). The synthesis of DESs usually uses naturally derived raw materials, and no byproducts are produced. Therefore, DESs have been applied in the separation and synthesis of inorganic and organic matters because they are environmentally friendly (Dai *et al*. 2013; Paiva *et al*. 2014). The unique structure of HBD and HBA in DESs has been shown to benefit the dissolution of cellulose biomass (Vigier *et al*. 2015). Choline-based DESs exhibit the potential to dissolve refined cork, starch, and microcrystalline cellulose (Garcia *et al*. 2010; Hou *et al*. 2012; Ohira *et al*. 2012). However, the solubility of cellulose in choline-based DESs with HBDs, such as urea, amino acids, and glycerol, is very low (Abbott *et al*. 2004; Francisco *et al*. 2012). The development of a new and efficient HBD is needed.

The experiments in the present study were designed to synthesize environmentally friendly choline chloride (ChCl)-based DESs with various HBDs as the solvents, to dissolve cellulose. The ChCl-DESs were characterized and evaluated for their potential role in the dissolution of cellulose. Additionally, the dissolution behavior of the substrates was investigated.

EXPERIMENTAL

Materials

The cellulose used was a cotton linter pulp (size of 60 cm *25 cm), with a polymerization degree of 575.6 (Helon, China). The cotton linter pulp was cut into small pieces (size of 0.5 cm *1 cm). After drying at 100 °C for 12 h, the cellulose was prepared for use in the present study. The ChCl was recrystallized with ethanol, followed by filtering, and was dried under a vacuum prior to the experiment (Abbott *et al*. 2004). Imidazole (Im) was dried at 50 °C for 5 h prior to use. All chemical reagents were of analytical grade and purchased from Beijing Chemical Reagents Co. (Beijing, China).

Synthesis of ChCl-DESs

The ChCl-DESs were synthesized based on the previously described methods (Abbott *et al*. 2003; Morrison *et al*. 2009). The HBA (ChCl) and HBD (Im, urea (U), ammonium thiocyanate (AT), caprolactam (CA), or acetamide (AA)) were added to a flask at various molar ratios. The mixtures were heated with stirring until a homogeneous liquid phase formed. The product was dried under a vacuum at 60 °C for 24 h, and then the ChCl-Im, ChCl-U, ChCl-AT, ChCl-CA, and ChCl-AA were obtained. The conventional ionic liquid (IL) 1-allyl-3-methylimidazolium chloride ([AMIm]Cl) was synthesized according to previous literature (Liu *et al*. 2012) for a comparative study.

Analysis of ChCl-DESs

Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR) were used to analyze the structure of ChCl-DESs on a FTS-135 Fourier transform infrared spectroscope (Bio-Rad, Hercules, CA) and an AVANCE III NMR spectrometer (Bruker Corp., Germany), respectively. The thermogravimetric properties were measured using a TG209 TG/DSC thermal analysis instrument (Netzsch Inc., Germany).

The dipolarity/polarizability effects (π^*) and hydrogen bond basicity (β) were calculated using Eqs. 1 and 2, according to the Kamlet-Taft empirical polarity scale (Taft and Kamlet 1976),

$$\pi^* = 0.649\text{-}0.314\nu_{(\mathrm{NA})} \quad (1)$$

$$\beta = (1.035\ \nu_{(\mathrm{DENA})} + 2.64 - \nu_{(\mathrm{NA})}) / 2.80 \quad (2)$$

where $\nu_{(\mathrm{NA})}$ represents $(\lambda_{\max(\mathrm{NA})} \times 10^{-4})^{-1}$, $\nu_{(\mathrm{DENA})}$ represents $(\lambda_{\max(\mathrm{DENA})} \times 10^{-4})^{-1}$, $\lambda_{\max}$ represents the wavelength of maximum absorption, and NA and DENA are abbreviations for 4-nitroaniline and N,N-diethyl-4-nitroaniline, respectively.

The Hammett acidity function (H_0) was calculated according to Eq. 3 (Thomazeau *et al.* 2003),

$$H_0 = \mathrm{p}K\ (I)_{aq} + \log\ ([I]_s/[IH^+]_s) \quad (3)$$

where I represents the NA indicator, $\mathrm{p}K(I)_{aq}$ is a constant (0.99), $[I]_s/[IH^+]_s$ is determined according to the Beer-Lambert Law, based on wavelength of maximum absorption ($\lambda_{\max}$). $[IH^+]_s$ and $[I]_s$ represent the molar concentrations of the protonated and unprotonated forms of I, respectively.

The $\lambda_{\max}$ was measured using a U-2910 UV-vis spectrometer (Hitachi, Japan). The viscosity and conductivity were measured using a VS4450 rotational viscometer (Marimex Ind., Bottrop, Germany) and a DDS-307 conductivity meter (Leici, China), respectively.

The thermogravimetric properties of ChCl-DESs were measured by taking a portion mass of ChCl-DESs, and loading it into a TG209 TG/DSC thermal analyzer (Netzsch Inc., Germany). The sample was first cooled to the required temperature such as -20 °C, and then heated to 140 °C at a rate of 1 °C min^{-1}. The freezing temperature was obtained at the temperature when the ChCl-DESs solid began to melt.

Dissolution of Cellulose

The cellulose was first activated by ultrasonic-assisted saturated calcium chloride solution prior to dissolution. The activated cellulose, with a 65.4% degree of crystallinity, was gradually added to the ChCl-DESs or ILs in a flask. The solubility of cellulose in different ChCl-DESs or ILs was investigated from 20 to 120 °C at a rate of 10 °C intervals. The effects of the co-solvents, including aprotic solvents, quaternary ammonium salts (QASs), and polyethylene glycols (PEG) were investigated to promote the dissolution. The mass ratio of a co-solvent to a ChCl-DES was 5% in the dissolution experiment. The dissolving ended when a completely dark substance was observed under a polarization microscope (PLM; XP-203, Company, Changfang, China). The cellulose was generated by washing with ethanol three to five times.

Analysis of Cellulose

The structure of cellulose was analyzed according to a previously described FTIR method. The dissolution of cellulose in the ChCl-DESs was observed with the XP-203 polarization microscope (Company, Changfang, China). The surface morphology of cellulose was observed on an S-4800 scanning electron microscope (SEM; Hitachi Ltd., Tokyo, Japan). The crystal form was evaluated using an XRD-6000 X-ray powder diffraction apparatus (XRD; Shimadzu, Japan) with a 40.0 kV working voltage and 40.0 mA electric current of the cube target X-ray tube. The solubility of cellulose was calculated in terms of the mass of cellulose dissolved per gram of IL ($\mathrm{g\ g}^{-1}$) (Swatloski *et al*. 2002).

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

$$\mathrm{CrI}\ (\%) = (I_{002} - I_{\mathrm{am}}) \times 100/\ I_{002} \quad (4)$$

where CrI represents the degree of crystallinity and I_{002} is the maximum intensity of the principal peak (002) lattice diffraction. The 2θ was 22.6° for cellulose *I* and 20.8° for cellulose *II*. I_{am} is the diffraction intensity of amorphous cellulose between the plane (200) and (110). For cellulose *I*, 2θ was 18.0° and for cellulose *II* 2θ was 16.0°.

RESULTS AND DISCUSSION

Screening of ChCl-DESs

The type of HBD (Im, U, AT, CA, or AA) and the molar ratios of ChCl to HBD that affected the solvation properties of ChCl-DESs were investigated (Table 1). The eutectic freezing point (EFP) of DESs (T_f) and EFP of raw HBD (T_m) differed, suggesting that interactions existed between ChCl and HBDs. The ChCl-CA and ChCl-AA at any molar ratio of ChCl to HBD had negligible cellulose dissolving ability. The ChCl-Im, ChCl-U, and ChCl-AT showed relatively high cellulose solubilities at their optimized molar ratios (3:7, 1:2, and 1:1, respectively) (Supplementary Material Fig. A1-Fig. A5). Among these, ChCl-Im showed the best dissolving ability for cellulose (2.48 wt.%) in comparison with ChCl-AT (0.85 wt.%) and ChCl-U (1.43 wt.%), the most commonly used DESs.

Table 1. Properties of the Synthesized ChCl-DESs

ChCl-HBD	Optimized molar ratio	T_f (°C)	T_m (°C)	Δ (°C)	Appearance	Solubility of cellulose (wt%)	Dissolution time (h)
ChCl-Im	3: 7	56	91	35	Low viscosity, transparent	2.48	1.5
ChCl-U	1: 2	12	132.7	120.7	Medium viscosity, transparent	1.43	2.0
ChCl-AT	1: 1	58	149.6	91.6	Medium viscosity, translucent	0.85	3.0
ChCl-CA	1: 1	60	71	11	High viscosity, opaque	0.16	4.0
ChCl-AA	1: 2	68	82.3	15.3	High viscosity, opaque	0.22	24.0

ChCl-HBD: Choline chloride-hydrogen-bond donor; ChCl-Im: Choline chloride-Imidazole; ChCl-U: Choline chloride-Urea; ChCl-AT: Choline chloride-Ammonium thiocyanate; ChCl-CA: Choline chloride-Caprolactam; ChCl-AA: Choline chloride-Acetamide; EFP: Eutectic freezing point; T_f = EFP of ChCl- DESs; T_m = EFP of raw HBD; Δ = the difference between T_m and T_f

Structure of ChCl-DESs

The structure of three relatively high-performance ChCl-DESs, including ChCl-Im, ChCl-U, and ChCl-AT, were further analyzed. The ChCl-DESs were successfully synthesized, according to the results of FTIR and NMR analyses.

For ChCl-Im, the characteristic peaks, based on FTIR (KBr), were 3214.3 cm^{-1} (ν C-NH, Im, s), 3028.7 cm^{-1} and 2926.2 cm^{-1} (ν CH, CH_2, s), 2831.2 cm^{-1} (ν CH, CH_2, s), 1639.6 cm^{-1} (ν CH, C=C, w), 1482.4 cm^{-1} (ν CH, CH_3, m), 1362.2 cm^{-1} (ν CH, CN, w), 1257.8 cm^{-1} (ν CH, CH_3, w), 1087.4 cm^{-1} (ν OH, w), 1063.5 cm^{-1} (ν C-O, m), 955.2 cm^{-1} [ν $N(CH_3)_3$, m], 759.9 cm^{-1} (ν C-C, Im, m), and 664.3 cm^{-1} (ν CH, Im, s). The hydrogen shifts, based on ^{1}H NMR (500 MHz, $CDCl_3$), were at δ 7.645 (1H, s, N=C*H*-C), 7.009 (2H, d, N-C*H*=C*H*), 3.809 to 3.838 (2H, m, C*H*$_2$OH), 3.425 to 3.445 (2H, m, NC*H*$_2$), and 3.141 (9H, s, N(C*H*$_3$)$_3$). The carbon shifts, based on ^{13}C NMR (500 MHz, DMSO), were 135.6 ppm (C=N), 122.17 ppm (C=C), 67.41 ppm (CH$_2$OH), 53.56 to 53.63 ppm (CH$_2$N), and 39.46 to 40.46 ppm [(CH$_3$)$_3$N)].

For ChCl-U, the characteristic peaks, based on FTIR (KBr), were 3334.5 cm^{-1} (ν NH, NH$_2$, s), 1667.3 cm^{-1} (ν CO, CON$_2$H$_4$, s), 1621.9 cm^{-1} (ν CN, OCNH$_2$, s), 1476.1 cm^{-1} (ν CH, CH$_3$, m), 1083.3 cm^{-1} (ν OH, w), 954.4 cm^{-1} (ν NH, NH$_2$, w), and 587.8 cm^{-1} (ν CH, CH$_2$, w). The hydrogen shifts, based on ^{1}H NMR (500 MHz, CDCl$_3$), were at δ 7.260 [4H, s, CO(N*H*$_2$)$_2$], 4.460 (1H, s, O*H*), 3.925 (2H, m, C*H*$_2$OH), 3.497(2H, m, NC*H*$_2$), and 3.178 [9H, s, N(C*H*$_3$)$_3$].

For ChCl-AT, the characteristic peaks, based on FTIR (KBr), were 3290.0 cm^{-1} (ν NH, NH$_2$, s), 3021.0 cm^{-1} (ν CH, CH$_2$, w), 2361.1 cm^{-1} (ν CN, SCNH, s), 2054.2 cm^{-1} (ν CH, CH$_2$, s), 1479.7 cm^{-1} (ν CH, CH$_3$, m), 1410.1 cm^{-1} (ν OH, CH$_2$OH, w), 1083.1 cm^{-1} (ν OH, w), 1052.8 cm^{-1} (ν C-O, m), 954.7 cm^{-1} [ν N(CH$_3$)$_3$, m], and 861.7 cm^{-1} (ν NH, CNH, w). The hydrogen shifts, based on ^{1}H NMR (500 MHz, CDCl$_3$), were 3.310 (1H, s, N=C*H*-C), 7.009 (2H, d, N-C*H*=C*H*), 2.535 to 2.531 (2H, m, C*H*$_2$OH), 2.062 to 2.043 (2H, m, NC*H*$_2$), and 1.766 [9H, s, N(C*H*$_3$)$_3$].

Properties of ChCl-DESs

Thermostability of ChCl-DESs

The temperatures at 10% weight loss for ChCl-Im, ChCl-U, and ChCl-AT were 147, 143, and 199 °C, respectively, according to the results of thermogravimetric analysis (TGA; Fig. 1). The dissolution temperature of cellulose was usually below 120 °C to prevent carbonization (Wang *et al.* 2012). Therefore, these three ChCl-DESs showed sufficient thermostability for the dissolution of cellulose.

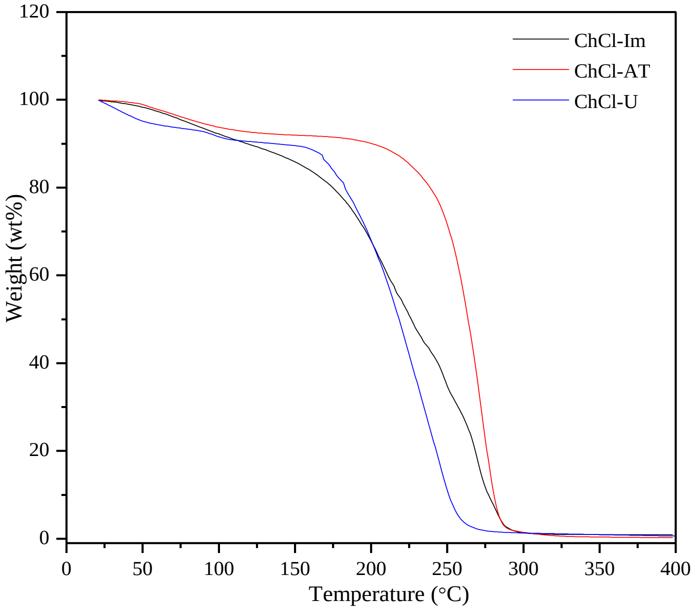
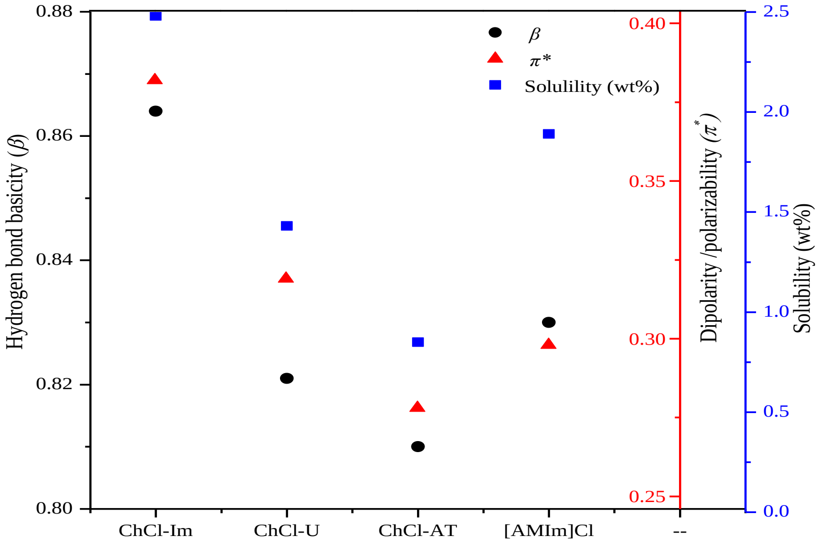


Fig. 1. Thermogravimetric analysis (in nitrogen) curves of ChCl-DESs

Solvation properties of ChCl-DESs

The Kamlet-Taft polarity model has been widely used to evaluate the solvation properties of solvents (Badgujar and Bhanage 2015). The β and π^* values of the three ChCl-

DESs and the [AMIm]Cl, a comparative ILs, were calculated and included in Fig. 2. The order of *β* values was ChCl-Im (0.864) > [AMIm]Cl (0.830) > ChCl-U (0.821) > ChCl-AT (0.810). The sequence of *π** values was ChCl-Im (0.382) > ChCl-U (0.319) > [AMIm]Cl (0.298) > ChCl-AT (0.258), differing from that of *β* values. The order of solubility of cellulose was ChCl-Im (2.48 wt. %) > [AMIm]Cl (1.89 wt. %) > ChCl-U (1.45 wt. %) > ChCl-AT (0.83 wt. %), consistently correlating with that of *β* values (Fig. 2). The essence of cellulose dissolving was the breaking of hydrogen bonds in the supramolecular structure. Based on the “electro donor-electron acceptor” mechanism (Pinkert *et al.* 2010; Liu *et al.* 2011), the accessibility of hydrogen bonds for a solvent is positively related to its dissolving ability. Therefore, the hydrogen bond basicity (*β*) of ChCl-DESs controls the solubility of cellulose compared to the dipolarity/polarizability effects (*π**). The *π*-*π* conjugative effect of the imidazole ring plays a key role in improving the hydrogen bond basicity of ChCl-Im and [AMIm]Cl (Ab Rani *et al.* 2011; Jessop *et al.* 2012); thus, better solubility is obtainable.



●: *β*, ▲: *π**, ■: Solubility of cellulose (wt. %)

Fig. 2. *β* and *π** values of the ChCl-DESs and the solubility of cellulose

The acidity of a solvent is greatly associated with the dissolving ability (Badgujar and Bhanage 2015). The Hammett acidity function (H_0) was used to express the acidity of a solvent (Thomazeau *et al.* 2003). The order of H_0 values was [AMIm]Cl (2.189) > ChCl-Im (1.869) > ChCl-U (1.732) > ChCl-AT (1.575), based on the UV-vis spectra in Fig. 3. The ChCl-Im showed a high acidity relative to [AMIm]Cl, which agreed with the order of *β* values. The high polarity promoted the dissociation of cations and anions in the ChCl-DESs, providing high ion activity and acidity. Therefore, the ChCl-Im showed higher solubility of cellulose than [AMIm]Cl. Though the acidity was relatively low, the ChCl-Im dissolved more cellulose relative to ChCl-U and ChCl-AT. The reason was probably related to the existence of an active hydrogen bond network in the ChCl-Im (Montes *et al.* 2003; Turner *et al*. 2003; Payal *et al*. 2015).

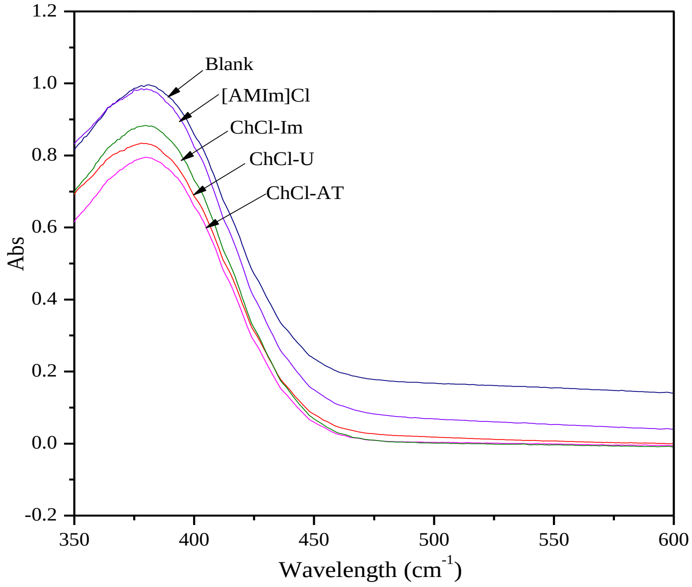


Fig. 3. UV-vis spectra of the ChCl-DESs and ILs

Viscosity of ChCl-DESs

The viscosity of the ChCl-DESs decreased with increasing temperature (Fig. 4). The ChCl-Im showed the lowest viscosity and the highest solubility among the ChCl-DESs at the same temperature. The viscosity of ChCl-Im decreased from 124 cP to 5.1 cP in a range of 20 to 120 °C. The high solubility at 2.48 wt.% of cellulose in the ChCl-Im was obtained under a viscosity below 10 cP. The solubility was dynamically dependent on the viscosity. Low viscosity benefited the accessibility between the solvent with hydrogen bonds in cellulose (Badgujar and Bhanage 2015; Cruz *et al.* 2012). The low viscosity of ChCl-Im would make the imidazole moiety and anion of chlorine into a charge delocalized system through hydrogen bonds. A similar effect has been found in imidazolium-based ILs (Alcalde *et al.* 2015).

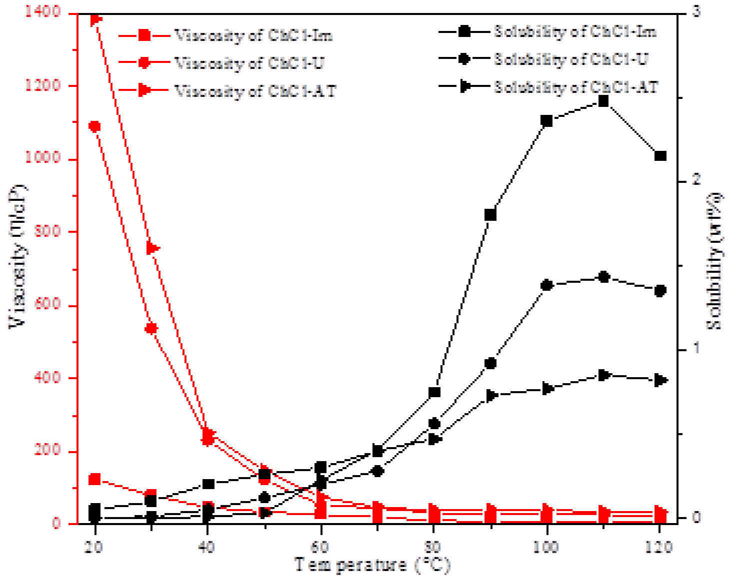


Fig. 4. Viscosity-temperature relationship and the solubility of cellulose for ChCl-DESs

The viscosity-temperature relationship of the three ChCl-DESs is well-described by the Arrhenius equation (Eq. 5) (Abbott *et al.* 2004; Zhang *et al.* 2012a),

$$\ln\eta = \ln\eta_0 + E_\eta / RT \qquad (5)$$

where η represents the value of viscosity, T is the absolute temperature, E_η is the pseudo-activation energy for viscous flow, and η_0 is a constant. The values of η_0, E_η, and R^2 are listed in Fig. 5.

A good linear correlation was observed between ln η and $1/T$ values over the three ChCl-DESs ($R^2 > 0.97$). The ChCl-Im showed the lowest E_η value (31.76 kJ mol^{-1}), compared with ChCl-U (52.21 kJ mol^{-1}) and ChCl-AT (53.92 kJ mol^{-1}). A low E_η value suggests weaker entanglement of the hydrogen bonds between the anions and the HBD in the ChCl-DESs (Abbott *et al.* 2004). The ChCl-Im may release more free active ions to react with the hydrogen bonds in cellulose to promote dissolution.

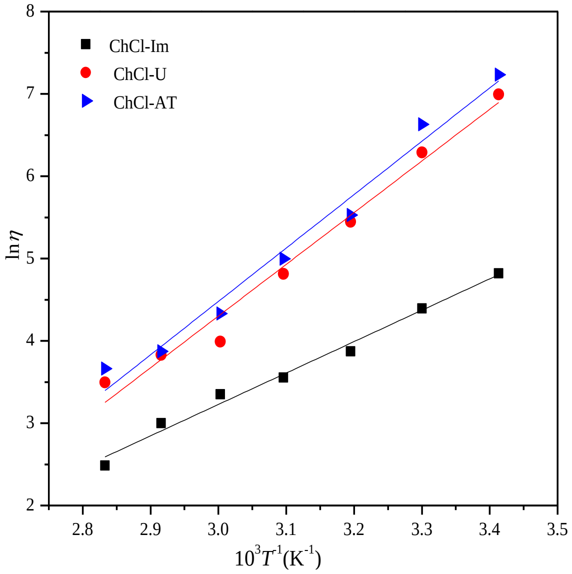


Fig. 5. Arrhenius-fitted curves of lnη *versus* $1/T$ for the ChCl-DESs. ChCl-Im: η_0 = 9.51, E_η =31.76 kJ mol^{-1}, $R^2 > 0.99$; ChCl-U: η_0 =15.56, E_η = 52.21 kJ mol^{-1}, $R^2 > 0.98$; ChCl-AT: η_0 =16.12, E_η =53.92 kJ mol^{-1}, $R^2 > 0.98$

Solubilization of Co-Solvents

Co-solvents can improve solubility by reducing the hydrophobicity of cellulose or enhancing the reactive activity of solvents (Gericke *et al.* 2012; Zhao *et al.* 2013). Three classes of co-solvents, including aprotic co-solvents, QASs, and PEG (Supplementary Material Fig. A6), were evaluated, and the solubilization effects are shown in Fig. 6. The aprotic co-solvents dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and N,N-dimethylacetamide (DMA) had negligible solubilization to ChCl-Im. The QASs (surfactants) showed better solubilization to ChCl-Im, which was in agreement with a previous report (Zhang *et al.* 2012b). The solubility of cellulose was increased from 2.48 wt.% to 3.12 wt.%, 2.69 wt.%, and 3.80 wt.%, respectively, with the addition of tetrabutylammonium bromide (TBAB), tetraethylammonium bromide (TEAB), and tributylmethylammonium chloride ([TBMA]Cl), respectively. The [TBMA]Cl, having the structure of an asymmetric long chain alkyl, displayed strong amphiphilicity, which promoted the accessibility between the hydrophilic ChCl-Im and hydrophobic cellulose (Gümüskaya *et al.* 2003; Yanagisawa *et al.*2004).

The PEG significantly promoted the dissolving ability of ChCl-Im, and the solubility of cellulose was dramatically enhanced from 2.48 wt. % to 4.57 wt. %. The ample flexible alkoxy groups [–(CH_2–CH_2–O)–] in PEG were hydrophobic, and they could easily absorb on the surface of cellulose. At the same time, the hydroxyl groups of PEG were hydrophilic, making cellulose more accessible with DES. Thus the hydrophobicity of cellulose decreased, which was consistent with previous studies (Lindman *et al*. 2010; Tang *et al.* 2012a; Ohira *et al.* 2012). The oxygens of alkoxy group (CH_2-CH_2-O) units could behave as hydrogen-bond acceptor. They could react with the hydrogen of hydroxyl group in cellulose (Zhao *et al.* 2008; Tang *et al.* 2012b). The two effects of PEG jointly improved the dissolution of cellulose in DES.

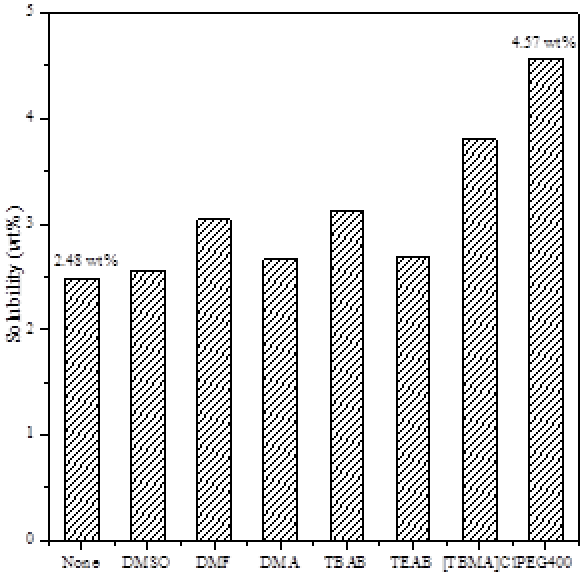


Fig. 6. Effect of co-solvents on solubility of cellulose (mass ratio of ChCl-Im to co-solvent of 20:1)

Dissolving Behavior of Cellulose in ChCl-Im

The dissolving of cellulose in ChCl-Im-coupled PEG was observed under the polarizing microscope. The fibrils of the original cellulose were tightly intertwined (Fig. 7a). The fibrils swelled after 20 min of dissolving, suggesting that a reaction occurred between the solvents and the hydrogen bonds in cellulose (Fig. 7b). The fibrils had become shortened after 45 min of dissolving, indicating the breaking of hydrogen bonds in cellulose (Fig. 7c). The dark sight in the PLM at the end of dissolving demonstrated that all of the hydrogen bonds were broken down (Fig. 7d).

The original cellulose showed the characteristic diffraction curves of cellulose I. The strong crystalline peaks at 14.93° (101 plane), 16.57° (101' plane), and 22.84° (002 plane) of cellulose were observed. The CrI of the original cellulose was 65.4%, which indicated that the crystalline structure dominated. Broader and weaker diffraction peaks appeared in the regenerated cellulose, which was dissolved by the single ChCl-Im. A shifting of the peaks (to a 2θ value of 28.60 degrees), a decrease in CrI (to a value of 41.6%), and a greatly reduced peak intensity all suggested that the crystal form had changed from cellulose I to a portion of cellulose II combined with a majority of essentially amorphous cellulose.

The regenerated cellulose, which was dissolved by the ChCl-Im-coupled PEG, retained its crystalline form, *II*. The peak shifted to 2θ of 22.31, and the CrI was reduced to 21.83%, suggesting that the PEG enhanced the breaking of crystallinity in cellulose (Fig. 8). No marked change happened for the FTIR characteristic peak (3449 cm^{-1}) of the original, single ChCl-Im and ChCl-Im-coupled PEG dissolved cellulose (Fig. 9). Accordingly, the cellulose was directly dissolved by ChCl-Im or ChCl-Im-coupled PEG, and no other derivatives were generated.

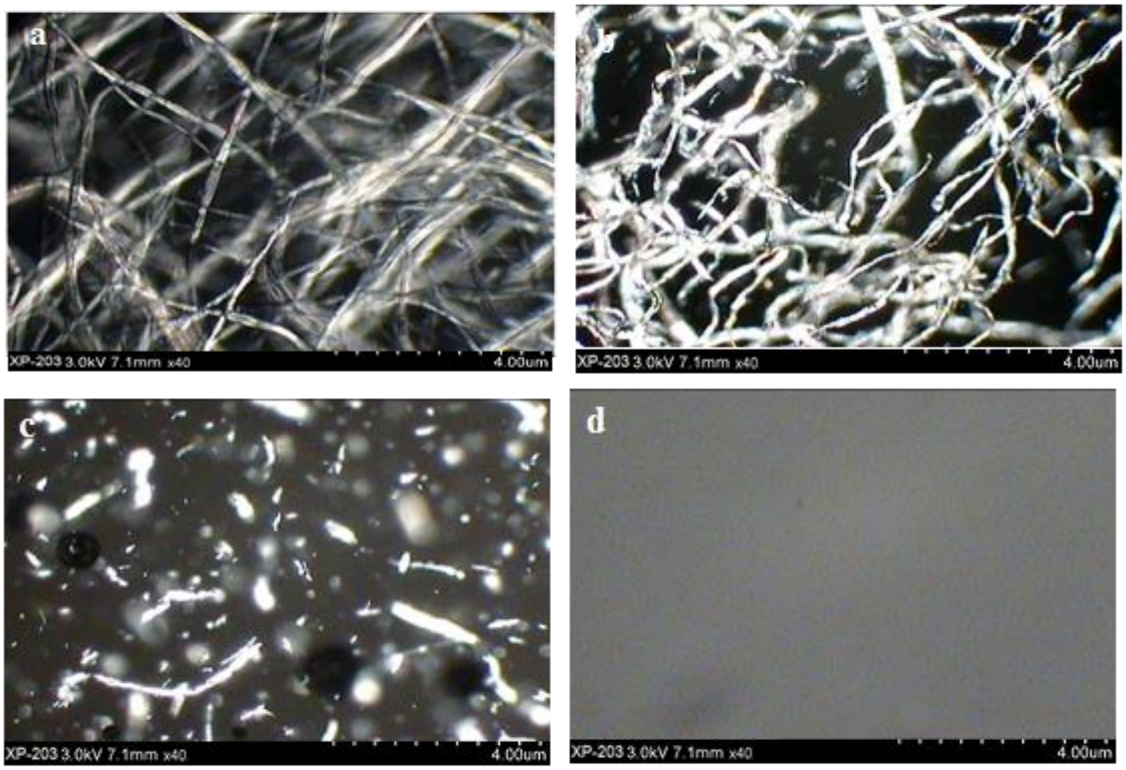


Fig. 7. Polarizing microscope images of cellulose in ChCl-Im-coupled PEG dissolving at different time frames (110 °C): a) 0 min; b) 20 min; c) 45 min; d) 90 min

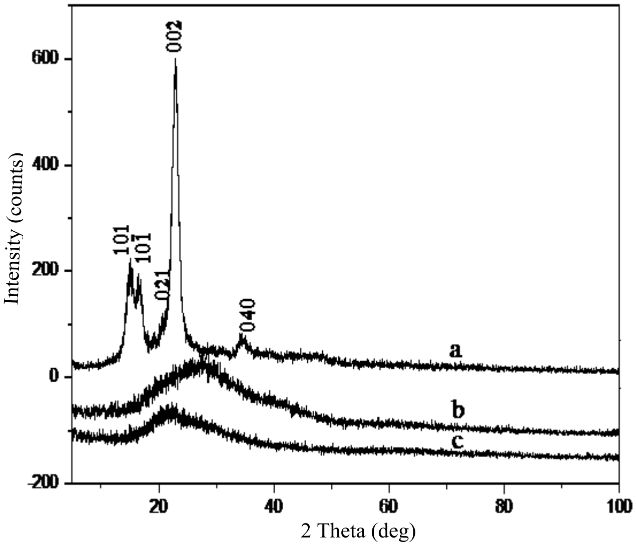


Fig. 8. X-ray diffraction patterns of the original and regenerated celluloses: a) original cellulose; b) regenerated cellulose after dissolving in ChCl-Im; c) regenerated cellulose after dissolving in ChCl-Im coupled with PEG

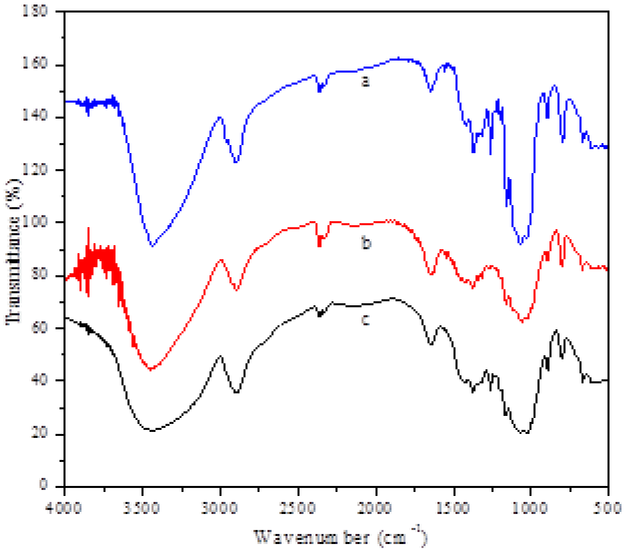


Fig. 9. Fourier transform infrared spectra of the original and regenerated cellulose: a) original cellulose; b) regenerated cellulose after dissolving in ChCl-Im; c) regenerated cellulose after dissolving in ChCl-Im coupled with PEG

The surface of the original cellulose appeared ordered and condensed under SEM (Fig. 10). The rough and disordered surface of regenerated cellulose appeared after dissolving in ChCl-Im (Fig. 10). The ChCl-Im-coupled PEG co-solvent further loosened the surface (Fig. 10). A more accessible surface facilitates the further processing of regenerated cellulose (Singh *et al.* 2009).

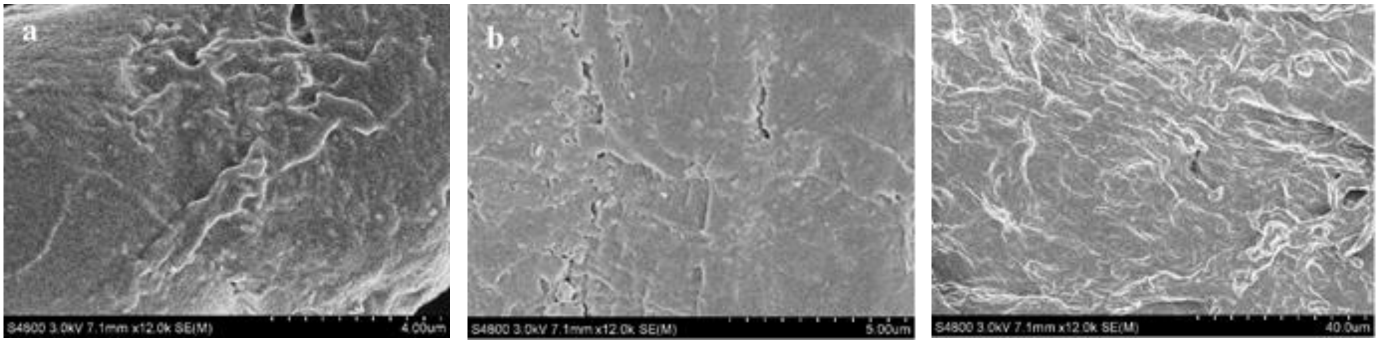


Fig. 10. Scanning electron micrographs of the a) original cellulose; b) regenerated cellulose after dissolving in ChCl-Im; c) regenerated cellulose after dissolving in ChCl-Im coupled with PEG

CONCLUSIONS

1. This study demonstrated the properties of the choline chloride deep eutectic solvents (ChCl-DESs) and their performance in the “green” dissolution of cellulose. Five different types of ChCl-DES, with various hydrogen bond donors (HBDs), were successfully synthesized.
2. The ChCl-Imidazole (ChCl-Im) exhibited the best dissolving ability of cellulose because of its high hydrogen bond basicity, dipolarity/polarizability effects, and Hammett acidity function, as well as a low viscosity and a high conductivity.

3. The polyethylene glycol (PEG) displayed great solubilization to ChCl-Im, and the dissolution of cellulose was improved by employing ChCl-Im-coupled PEG.
4. The study showed the potential of ChCl-DESs for the dissolution of cellulose in an environmentally friendly way.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No. 20976107 and No.21306229) and the Science Foundation of China University of Petroleum, Beijing (2462014YJRC001).

REFERENCES CITED

Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., and Tambyrajah, V. (2003). "Novel solvent properties of choline chloride/urea mixtures," *Chem. Commun.* 2003(1), 70-71. DOI: 10.1039/B210714G

Abbott, A. P., Boothby, D., Capper, G., Davies, D. L., and Rasheed, R. K. (2004). "Deep eutectic solvents formed between choline chloride and carboxylic acids: Versatile alternatives to ionic liquids," *J. Am. Chem. Soc.* 126(29), 9142-9147. DOI: 10.1021/ja048266j

Ab Rani, M. A., Brant, A., Crowhurst, L., Dolan, A., Lui, M., Hassan, N. H., Hunt, P. A., Niedermeyer, H., Perez-Arlandis, J. M., Schrems, T., *et al*. (2011). "Understanding the polarity of ionic liquids," *Phys. Chem. Chem. Phys*. 13(37), 16831-16840. DOI: 10.1039/C1CP21262A

Alcalde, R., García, G., Atilhan, M., and Aparicio, S. (2015). "Systematic study on the viscosity of ionic liquids: Measurement and prediction," *Ind. Eng. Chem. Res*. 54(43), 10918-10924. DOI: 10.1021/acs.iecr.5b02713

Alvira, P., Tomás-Pejó, E., Ballesteros, M., and Negro, M. J. (2010). "Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review," *Bioresour. Technol.* 101(13), 4851-4861. DOI: 10.1016/j.biortech.2009.11.093

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

Castro, M. C., Arce, A., Soto, A., and Rodríguez, H. (2015). "Influence of methanol on the dissolution of lignocellulose biopolymers with the ionic liquid 1-ethyl-3-methylimidazolium acetate," *Ind. Eng. Chem. Res.* 54(39), 9605-9614. DOI: 10.1021/acs.iecr.5b02604

Cruz, H., Fanselow, M., Holbrey, J. D., and Seddon, K. R. (2012). "Determining relative rates of cellulose dissolution in ionic liquids through *in situ* viscosity measurement," *Chem. Commun.* 48(45), 5620-5622. DOI: 10.1039/C2CC31487H

Dai, Y., van Spronsen, J., Witkamp, G. J., Verpoorte, R., and Choi, Y. H. (2013). "Ionic liquids and deep eutectic solvents in natural products research: Mixtures of solids as extraction solvents," *J. Nat. Prod.* 76(11), 2162-2173. DOI: 10.1021/np400051w

Francisco, M., van den Bruinhorst, A., and Kroon, M. C. (2012). "New natural and renewable low transition temperature mixtures (LTTMs): Screening as solvents for lignocellulosic biomass processing," *Green Chem.* 14(8), 2153-2157. DOI: 10.1039/C2GC35660K

Garcia, H., Ferreira, R., Petkovic, M., Ferguson, J. L., Leitao, M. C., Nimal, G. H. Q., Seddon, K. R., Rebelo, L. P. N., and Pereira, C. S. (2010). "Dissolution of cork biopolymers in biocompatible ionic liquids," *Green Chem.* 12(3), 367-369. DOI: 10.1039/B922553F

Gericke, M., Schaller, J., Liebert, T., Fardim, P., Meister, F., and Heinze, T. (2012). "Studies on the tosylation of cellulose in mixtures of ionic liquids and a co-solvent," *Carbohydr. Polym.* 89(2), 526-536. DOI: 10.1016/j.carbpol.2012.03.040

Gümüskaya, E., Usta, M., and Kirci, H. (2003). "The effects of various pulping conditions on crystalline structure of cellulose in cotton linters," *Polym. Degrad. Stab*. 81(3), 559-564. DOI: 10.1016/S0141-3910(03)00157-5

Hou, X., Smith, T. J., Li, and Zong, M. (2012). "Novel renewable ionic liquids as highly effective solvents for pretreatment of rice straw biomass by selective removal of lignin," *Biotechnol. Bioeng*. 109(10), 2484-2493. DOI: 10.1002/bit.24522

Jessop, P. G., Jessop, D. A., Fu, D., and Phan L. (2012). "Solvatochromic parameters for solvents of interest in green chemistry," *Green Chem*. 14(5), 1245-1259. DOI: 10.1039/C2GC16670D

Lindman, B., Karlström, G., and Stigsson, L. (2010). "On the mechanism of dissolution of cellulose," *J. Mol. Liq*. 156(1), 76-81. DOI: 10.1016/j.molliq.2010.04.016

Liu, D.- T., Xia, K.- F., Cai, W.- H., Yang, R.- D., Wang, L.- Q., 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

Liu, H., Sale, K. L., Simmons, B. A, and Singh, S. (2011). "Molecular dynamics study of polysaccharides in binary solvent mixtures of an ionic liquid and water," *J. Phys. Chem. B* 115(34), 10251-10258. DOI: 10.1021/jp111738q

Montes, I., Lai, C., and Sanabria, D. (2003). "Like dissolves like: A classroom demonstration and a guided-inquiry experiment for organic chemistry," *J. Chem. Educ.* 80(4), 447-452. DOI: 10.1021/ed080p447

Morrison, H. G., Sun, C., and Neervannan, S. (2009). "Characterization of thermal behavior of deep eutectic solvents and their potential as drug solubilization vehicles," *Int. J. Pharm.* 378(1-2), 136-139. DOI: 10.1016/j.ijpharm.2009.05.039

Ohira, K., Abe, Y., Kawatsura, M., and Suzuki, K. (2012). "Design of cellulose dissolving ionic liquids inspired by nature," *ChemSusChem* 5(2), 388-391. DOI: 10.1002/cssc.201100427

Paiva, A., Craveiro, R., Aroso, I., Martins, M., Reis, R. L., and Duarte, A. R. C. (2014). "Natural deep eutectic solvents – Solvents for the 21st century," *ACS Sust. Chem. Eng.* 2(5), 1063-1071. DOI: 10.1021/sc500096j

Payal, R. S., Bejagam, K. K., Mondal, A., and Balasubramanian, S. (2015). "Dissolution of cellulose in room temperature ionic liquids: Anion dependence," *J. Phys. Chem. B* 119(4), 1654-1659. DOI: 10.1021/jp512240t

Pinkert, A., Marsh, K. N., and S. Pang. (2010). "Reflections on the solubility of cellulose," *Ind. Eng. Chem. Res*. 49(22), 11121-11130. DOI: 10.1021/ie1006596

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

Ruan, D., Zhang, L., Mao, Y., Zeng, M., and Li, X. (2004). "Microporous membranes prepared from cellulose in NaOH/thiourea aqueous solution," *J. Membr. Sci.* 241(2), 265-274. DOI:10.1016/j.memsci.2004.05.019

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

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

Singh, S., Simmons, B. A., and Vogel, K. P. (2009). "Visualization of biomass solubilization and cellulose regeneration during ionic liquid pretreatment of switchgrass," *Biotechnol. Bioeng.* 104(1), 68-75. DOI: 10.1002/bit.22386

Sun, N., Rodríguez, H., Rahman, M., and Rogers, R. D. (2011). "Where are ionic liquid strategies most suited in the pursuit of chemicals and energy from lignocellulosic biomass?" *Chem. Commun.* 47(5), 1405-1421. DOI: 10.1039/C0CC03990J

Swatloski, R. P., Spear, S. K., Holbrey, J. D., and Rogers, R. D. (2002). "Dissolution of cellose with ionic liquids," *J. Am. Chem. Soc*. 124(18), 4974-4975. DOI: 10.1021/ja025790m

Taft, R.W., and Kamlet, M. J. (1976). "Solvatochromic comparison method II. Alpha-scale of solvent hydrogen-bond donor (Hbd) acidities," *J. Am. Chem. Soc.* 98(10), 2886-2894. DOI: 10.1021/ja00426a036

Tang, S., Baker, G. A., and Zhao, H. (2012a). "Ether- and alcohol-functionalized task-specific ionic liquids: attractive properties and applications," *Chem. Soc. Rev*., 41, 4030-4066. DOI: 10.1039/C2CS15362A

Tang, S., Baker, G. A., Ravula, S., Jones, J. E., and Zhao, H. (2012b). "PEG-functionalized ionic liquids for cellulose dissolution and saccharification," *Green Chem*. 14(10), 2922-2924. DOI: 10.1039/C2GC35631G

Thomazeau, C., Olivier-Bourbigou, H., 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

Turner, E. A., Pye, C. C., and Singer, R. D. (2003). "Use of ab initio calculations toward the rational design of room temperature ionic liquids," *J. Phys. Chem. A* 107(13), 2277-2288. DOI: 10.1021/jp021694w

Vigier, K. D. O., Chatel, G., and Jérôme, F. (2015). "Contribution of deep eutectic solvents for biomass processing: Opportunities, challenges, and limitations," *ChemCatChem.* 7(8), 1250-1260. DOI: 10.1002/cctc.201500134

Vitz, J., Erdmenger, T., Haensch, C., and Schubert, U. S. (2009). "Extended dissolution studies of cellulose in imidazolium based ionic liquids," *Green Chem.* 11(3), 417-424. DOI: 10.1039/B818061J

Wang, H., Gurau, G., and Rogers, R. D. (2012). "Ionic liquid processing of cellulose," *Chem. Soc. Rev.* 41(4), 1519-1537. DOI: 10.1039/C2CS15311D

Yanagisawa, M., Shibata, I., and Isogai, A. (2004). "SEC–MALLS analysis of cellulose using LiCl/1,3-dimethyl-2-imidazolidinone as an eluent," *Cellulose* 11(2), 169-176. DOI: 10.1023/B:CELL.0000025388.92043.ec

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

Zhang, Q., Vigier, K. D. O., Royer, S., and Jérôme, F. (2012a). "Deep eutectic solvents: Syntheses, properties and applications," *Chem. Soc. Rev.* 41(21), 7108-7146. DOI: 10.1039/C2CS35178A

Zhang, Q., Benoit, M., De, O. V. K., Barrault, J., and Jérôme, F. (2012b). "Green and inexpensive choline-derived solvents for cellulose decrystallization," *Chem. Eur. J.* 18, 1043-1046. DOI: 10.1039/B210714G

Zhao, H., Baker, G. A., Song, Z. Y., Olubajo, O., Crittle, T., and Peters, D. (2008). "Designing enzyme-compatible ionic liquids that can dissolve carbohydrates," *Green Chem*. 10(6), 696-705. DOI: 10.1039/B801489B

Zhao, Y., Liu, X., Wang, J., and Zhang, S. (2013). "Insight into the cosolvent effect of cellulose dissolution in imidazolium-based ionic liquid systems," *J. Phys. Chem. B.* 117(30), 9042-9049. DOI: 10.1021/jp4038039

Article submitted: February 19, 2016; Peer review completed: April 10, 2016; Revised version received and accepted: April 25, 2016; Published: May 3, 2016.
DOI:

APPENDIX

Supplementary Material, Part 1

The curves of melting point *vs.* molar ratio for DESs

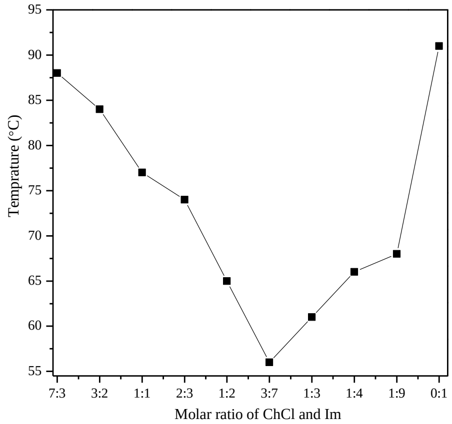


Fig. A1. Freezing point of ChCl and Im as a function of composition

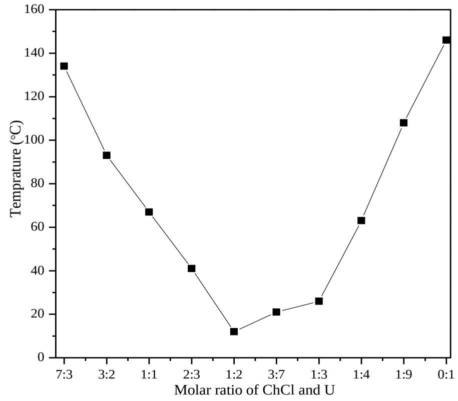


Fig. A2. Freezing point of ChCl and U as a function of composition

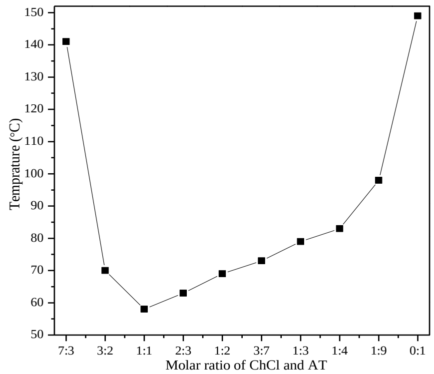


Fig. A3. Freezing point of ChCl and AT as a function of composition

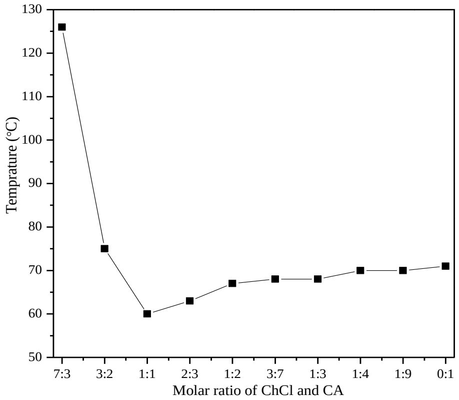


Fig. A4. Freezing point of ChCl and CA as a function of composition

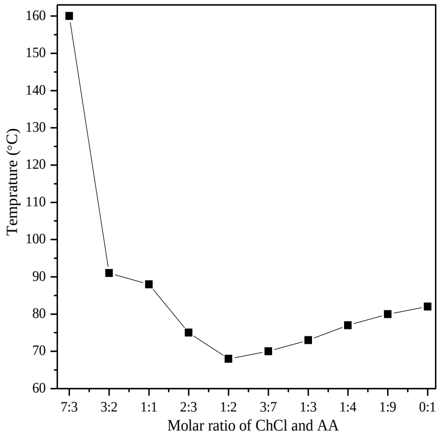


Fig. A5. Freezing point of ChCl and AA as a function of composition

Supplementary Material, Part 2

Effect of chain lengths of PEG on solubility of cellulose

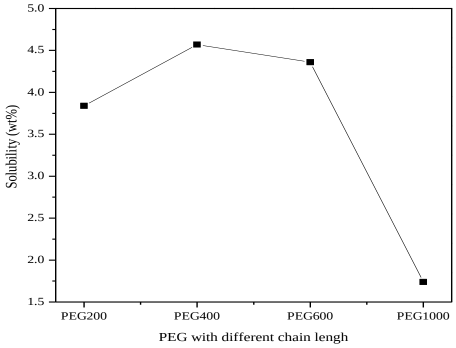


Fig. A6. Effect of chain lengths of PEG on solubility of cellulose
(110 °C, 1.0 h, ChCl-Im 10 g and PEGs 0.001 mol)