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# Cellulose dissolution at ambient temperature: Role of preferential solvation of cations of ionic liquids by a cosolvent

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## ABSTRACT

Highly effective cellulose solvents for the dissolution of cellulose at ambient temperature have been designed by adding any aprotic polar solvent to 1-butyl-3-methylimidazolium acetate ([$C_4$mim][$CH_3COO$]). The effects of molar ratio of the aprotic polar solvents to [$C_4$mim][$CH_3COO$], anionic structure of the ionic liquids (ILs) and nature of the co-solvents on cellulose solubility have been studied in detail. The enhanced dissolution of cellulose is suggested to be mainly resulted from the preferential solvation of cations of the ILs by the aprotic polar solvents, and this has been supported by our conductivity measurements.

## 1. Introduction

As the most abundant biorenewable resource in the world, cellulose has been widely used in our society (Edgar et al., 2001; Klemm, Heublein, Fink, & Bohn, 2005; Moutos, Freed, & Guilak, 2007). Generally, processing of cellulose into desired products requires firstly the dissolution of cellulose. To this end, developing new efficient cellulose solvents never stops. Until now, the industrialized solvent systems include viscose process and *N*-methylmorpholine-*N*-oxide process (Hermanutz, Gähr, Uerdingen, Meister, & Kosan, 2008). Other typically investigated solvent systems comprise lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMA), tetrabutylammonium fluoride trihydrate/dimethyl sulfoxide (TBAF/DMSO), $LiClO_4{\cdot}3H_2O$ and among others (Fischer, Voigt, & Fischer, 1999; Heinze & Liebert, 2001; McCormick & Dawsey, 1990; Wang, Yokoyama, Chang, & Matsumoto, 2009). However, dissolution of cellulose in such solvents demands high processing temperature, and sometimes involves additional environmental, energy, safety, or other problems. Recently, alkylmethylimidazolium based ionic liquids (ILs) have been introduced as greener solvents for cellulose (Cao et al., 2009; Fukaya, Sugimoto, & Ohno, 2006; Fukaya, Hayashi, Wadab, & Ohno, 2008; Heinze & Liebert, 2001; Swatloski, Spear, John, Holbrey, & Rogers, 2002; Wang et al., 2009; Zhang, Wu, Zhang, & He, 2005) and other biomass (Sun et al., 2009) with high solubility, and 1-butyl-3-methylimidazolium chloride/1,3-dimethyl-2-imidazolidinone ([$C_4$mim]Cl/DMI) binaries have also been employed as efficient solvents for cellulose (Rinaldi, 2011). The main disadvantages of these solvents include high viscosity and/or higher dissolution temperature. Thus, it is still imperative to develop new cellulose solvents.

Herein, we report our novel cellulose solvents: 1-butyl-3-methylimidazolium acetate/dimethyl sulfoxide [$C_4$mim][$CH_3COO$]/DMSO, 1-butyl-3-methylimidazolium acetate/*N*,*N*-dimethylformamide [$C_4$mim][$CH_3COO$]/DMF, and 1-butyl-3-methylimidazolium acetate/*N*,*N*-dimethylacetamide [$C_4$mim][$CH_3COO$]/DMA. In addition to the desired advantages like non-derivatization, low viscosity, high dissolution speed and tolerance to water, the prominent feature of the novel solvents is that cellulose can readily be dissolved at ambient temperature (for example at 25 °C and even 17 °C) with high solubility. The possible mechanism for the dissolution of cellulose in these new solvents was investigated by conductivity measurements, and preferential solvation role of cations of the ionic liquids by a cosolvent was emphasized.

## 2. Experimental

### 2.1. Materials

1-Methylimidazole (99%) were purchased from Shanghai Chem. Co.; 1-chlorobutane (>99.0%), 1-bromobutane (98.0%), glycolic acid

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(98.0%) and anion exchange resin (Ambersep 900 OH) were from Alfa Aesar; acetic acid (>99.5%), benzoic acid (>99.5%) and lactic acid (85.0–90.0%) were obtained from Shanghai Shiyi Chem. Regent Co. Ltd.; Sodium dicyanamide (>98%) was purchased from Nanjing Chemlin Chem. Co. Ltd.; methanol (HPLC > 99.8%) was obtained from Sinopharm Chem. Co. Ltd.; deuterated DMSO (DMSO-$d_6$) used for NMR samples was purchased from Qingdao Weibo Tenglong Technol. Co. Ltd.; the above materials were used as received. 1,1,1-trichloroethane (95.0%) was obtained from Shanghai Shanpu Chem. Co. Ltd., and distilled before use.

Microcrystalline cellulose (MCC) with a viscosity-average degree of polymerization (DP) of 229 was purchased from Alfa Aesar. Absorbent cotton and native cotton with a viscosity-average degree of polymerization of 1586 and 2179, respectively, were purchased from Shanghai Chem. Co. The cellulose samples were used directly after being dried at 60 °C under vacuum for 10 h. Degree of polymerization of the cellulose samples was determined by using an Ubbelohde viscometer in cupriethylenediamine hydroxide solutions (Xu, Wang, & Wang, 2010).

### 2.2. Synthesis of the ILs

1-Butyl-3-methylimidazolium acetate [$C_4$mim][$CH_3COO$], 1-butyl-3-methylimidazolium glycolate [$C_4$mim][$HOCH_2COO$], 1-butyl-3-methylimidazolium lactate [$C_4$mim][$CH_3CHOHCOO$] and 1-butyl-3-methylimidazolium benzoate [$C_4$mim][($C_6H_5$)COO] were prepared and purified by using the procedure described in the literature (Xu et al., 2010). Briefly, an aqueous solution of [$C_4$mim]Br was allowed to pass through a column filled with anion exchange resin to obtain [$C_4$mim][OH]. The aqueous [$C_4$mim][OH] solution was then neutralized with equal molar acetic acid. After removing water by evaporation under reduced pressure, the viscous liquid [$C_4$mim][$CH_3COO$] was thoroughly washed with diethyl ether, and finally dried under vacuum for 72 h at 70 °C. The other carboxylate ionic liquids have been prepared by a similar process as described for the preparation of [$C_4$mim][$CH_3COO$]. 1-Butyl-3-methylimidazolium dicyanamide [$C_4$mim][$N(CN)_2$], and [$C_4$mim]Cl were prepared and purified according to the procedure reported in literatures (Huddleston & Rogers, 1998; Liu, Janssen, Rantwijk, & Sheldon, 2005; Xu et al., 2010). The $^1$H NMR data of the above ILs were summarized in Supplementary Information. They were in good agreement with those available in literature (Xu et al., 2010; Liu et al., 2005; Huddleston & Rogers, 1998).

### 2.3. Dissolution of cellulose

In a typical dissolution experiment, microcrystalline cellulose was added into a 20 mL colorimetric tube which contained 2.0 g of [$C_4$mim][$CH_3COO$]/DMSO, and the tube was sealed with parafilm. The tube was then immersed in an oil bath (DF-101S, Gongyi Yingyu Instrument Factory), and the bath temperature was controlled to be 25 ± 0.5 °C. The mixture was heated and stirred at a given temperature. Additional cellulose was added until the solution became completely clear under polarization microscope (Nanjing Jiangnan Novel Optics Co. Ltd.). When cellulose became saturated, judged by the fact that cellulose could not be dissolved further within 1–2 h, its solubility (expressed by gram per 100 g of solvent) at the given temperature could be calculated from the amount of the solvent and cellulose added. All cellulose solubility values are presented in Table S1 in the Supplementary Information.

### 2.4. Conductivity measurements

Conductivity measurements of [$C_4$mim][$CH_3COO$]/DMSO solvents were performed at 25.00 °C by a DDS-12A conductometer (Xiaoshan Experimental Instrument Factory, China) at a fixed frequency of 1100 Hz. In order to prevent the ILs from picking up moisture from the environment, all measurements were performed under dry nitrogen atmosphere. The conductance cell was equipped with a water circulating jacket, and the temperature was controlled within ±0.01 °C with a DC-2006 low temperature thermostat (Shanghai Hengping Instrument Factory, China). The cell was calibrated with aqueous KCl solutions at different concentrations, and the cell constants at different temperatures were determined. The uncertainty of the conductivity measurements was estimated to be about 0.05%. Also, every datum has been measured at least twice for different samples to ensure its reproducibility within 10% in absolute value. To obtain each datum, we wait until the temperature of the sample was constant before electrical conductivity measurement. The cell constants at different temperatures were calculated by the procedure described in literature (Vila, Varela, & Cabeza, 2007). The conductivity data of [$C_4$mim][$CH_3COO$]/DMSO solutions at 25 °C are given in Table S2 in the Supplementary Information.

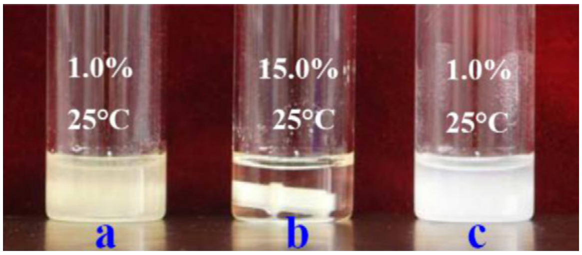

**Fig. 1.** Appearance of cellulose dissolution in: (a) [$C_4$mim][$CH_3COO$]; (b) [$C_4$mim][$CH_3COO$]/DMSO ($R_{DMSO}$ = 2.54:1); and (c) DMSO at 25 °C.

## 3. Results and discussion

### 3.1. Design of cellulose solvents and dissolution behavior of cellulose in these solvents

It has been reported that: (i) strong ion pairs are formed in neat ILs (Fraser, Izgorodina, Forsyth, Scott, & Macfarlane, 2007; Paul, Kumar, & Samanta, 2005; Tokuda et al., 2006; Wang & Voth, 2005; Yokozeki, Kasprzak, & Shiflett, 2007); (ii) aprotic polar solvents, such as DMSO, serve to mainly solvate cation and less likely anion of electrolyte (Fawcett, Brooksby, Verbovy, Bakó, & Pálinkás, 2005; Hanke, Atamas, & Lynden-Bell, 2002); and (iii) anions of the ILs play a predominant role in cellulose dissolution by disrupting inter- and intra-molecular hydrogen bonds in cellulose (Moulthrop, Swatloski, Moyna, & Rogers, 2005; Remsing, Swatloski, Rogers, & Moyna, 2006; Xu et al., 2010) although their cations are also important for the dissolution (Wang, Gurau, & Rogers, 2012). Based on these information, it is speculated that addition of aprotic polar solvents in [$C_4$mim][$CH_3COO$] will result in the further dissociation of [$C_4$mim][$CH_3COO$] to produce more solvated [$C_4$mim]$^+$ cations and "free" [$CH_3COO$]$^-$ anions. Therefore, [$CH_3COO$]$^-$ anions in [$C_4$mim][$CH_3COO$]/aprotic polar solvent systems are more accessible to the hydroxyl proton of cellulose than those in neat [$C_4$mim][$CH_3COO$], and this is beneficial to the disruption of the hydrogen bonds in cellulose and thus to the cellulose dissolution.

Promoted by the above concept, we initially designed [$C_4$mim][$CH_3COO$]/DMSO ($R_{DMSO}$ = 2.54:1) solvent (where $R$ is the molar ratio of DMSO to [$C_4$mim][$CH_3COO$]), and examined the dissolution behavior of microcrystalline cellulose (degree of polymerization DP ≈ 229) in such a solvent. It is interesting to find from Fig. 1 that at 25 °C, regardless of in a neat DMSO or neat [$C_4$mim][$CH_3COO$], cellulose is insoluble at all even though dissolution time was prolonged to 24 h. Strikingly, as DMSO is added

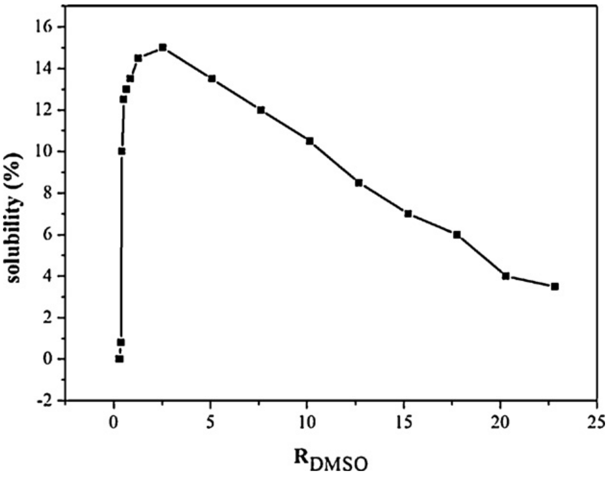

**Fig. 2.** The dependence of cellulose solubility on the molar ratio of DMSO to $[C_4mim][CH_3COO]$ in the $[C_4mim][CH_3COO]$/DMSO solvents at 25 °C.

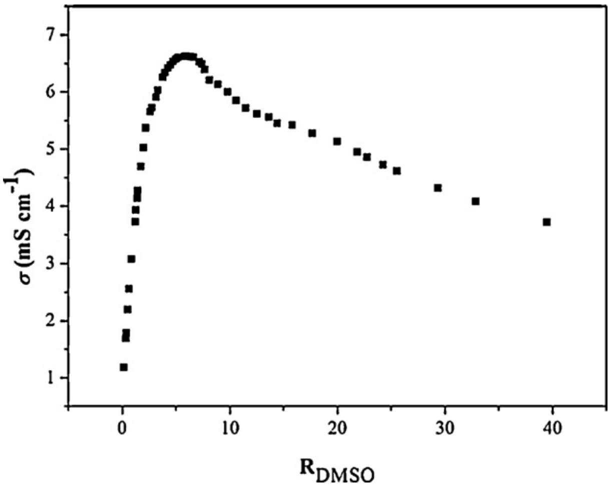

**Fig. 3.** The dependence of IL conductivity on the molar ratio of DMSO to $[C_4mim][CH_3COO]$ in the $[C_4mim][CH_3COO]$/DMSO solvents at 25 °C.

into $[C_4mim][CH_3COO]$, cellulose becomes readily soluble, and the solubility reaches 15.0% at 25 °C. Additionally, 8.0% of cellulose solution in $[C_4mim][CH_3COO]$/DMSO ($R_{DMSO}$ = 12.69:1) can be obtained even at 17 °C. Taken together, dissolution of cellulose in high concentration can be accomplished successfully at ambient temperature. However, this is impossible in the reported solvents except for *N*-ethyl-*N*′-methylimidazolium dimethylphosphate $[C_2mim][RR'PO_2]$ in which the solubility of cellulose was reported to be 2–4% at 25 °C (Fukaya et al., 2008). Furthermore, we found that absorbent cotton (DP = 1586) and native cotton (DP = 2179), which are very difficult to dissolve in conventional solvents, can also be dissolved in $[C_4mim][CH_3COO]$/DMSO ($R_{DMSO}$ = 2.54:1) to attain a 6.0% absorbent cotton solution and a 3.5% native cotton solution at 35 °C, and a 12.5% absorbent cotton solution and a 11.0% native cotton solution at 85 °C, respectively. Also, the solubility of cellulose remarkably increases with increasing temperature. For example, in the solvent of $[C_4mim][CH_3COO]$/DMSO ($R_{DMSO}$ = 2.54:1), solubility of cellulose is 15.0% at 25 °C, but reaches 21.0% at 65 °C. Additionally, we found that $[C_4mim][CH_3COO]$/DMSO solvents display high dissolution speed for cellulose. For example, 9.0% cellulose can be completely dissolved in $[C_4mim][CH_3COO]$/DMSO ($R_{DMSO}$ = 7.61:1) within 15 min at 25 °C, and only 5 min is needed at 40 °C.

### *3.2. Influence of molar ratio of DMSO to $[C_4mim][CH_3COO]$ on cellulose solubility*

Fig. 2 shows the dependence of cellulose solubility on the molar ratio of DMSO to $[C_4mim][CH_3COO]$ in $[C_4mim][CH_3COO]$/DMSO solvents. Remarkably, the solubility of cellulose increases with increasing DMSO concentration in the molar ratio range from 0 to 2.54, then decreases with further increase of DMSO content. This can be explained by the assumption that concentration of the "free" $[CH_3COO]^-$ increases with addition of DMSO before the maximum solubility, and then it is diluted owing to the further increase of DMSO content in the IL. This assumption has been supported by our conductivity measurements shown in Fig. 3 in which conductivity shows a variation trend similar to that observed for cellulose solubility with increasing molar ratio of DMSO to the IL. However, it is found from Fig. 2 that the maximum cellulose solubility appears at $R_{DMSO}$ = 2.54 (mole fraction of DMSO in the binary $\chi_{DMSO}$ = 0.72) which is lower than the molar ratio of $R_{DMSO}$ = 5.81 ($\chi_{DMSO}$ = 0.85) for the maximum conductivity shown in Fig. 3. This suggests that not only anions but also cations of the IL are involved in the favorable interactions of IL with cellulose. Similar conclusion has been reported by Zhang and his coworkers from NMR spectroscopic studies (Zhang et al., 2010). These combined interactions make it possible to dissolve cellulose at a lower molar ratio of DMSO to the IL. Nevertheless, it seems reasonable, from these results, to emphasize that although cations of the IL do have an important contribution to the dissolution of cellulose, the hydrogen bonds of cellulose are mainly disrupted by $[CH_3COO]^-$, and the DMSO serves to solvate cations and promotes the IL to dissociate into solvated $[C_4mim]^+$ cations and "free" anions.

### *3.3. Influence of anionic structure of the ionic liquids on the solubility of cellulose*

Table 1 gives the results for the dissolution of cellulose in various ILs/DMSO ($R_{DMSO}$ = 2.54:1) solvents at 25 °C as a function of anions of the ILs. Clearly, solubility of cellulose depends strongly on the nature of the anions in such solvents. $[C_4mim][CH_3COO]$/DMSO and $[C_4mim][(C_6H_5)COO]$/DMSO give 15.0% and 9.0% of cellulose solution, respectively, whereas cellulose is insoluble in the other ILs/DMSO solvents at the same molar ratio of DMSO to the ILs. To better understand the anionic effect in cellulose solubility, $\beta$ parameters (Table 1) are used to measure hydrogen bond accepting capacity of the ILs. It is known that ILs with higher $\beta$ value could dissolve more cellulose (Xu et al., 2010). A comparison of the $\beta$ parameters of the ILs and the solubilities of cellulose in the ILs/DMSO solvents (Table 1) reveals that in the ILs/DMSO solvents, only the ILs having high $\beta$ parameter value (for example $\geq$0.987) is good candidates as cellulose solvent. This further emphasizes the importance of anions of the ILs in the destruction of hydrogen bonds of cellulose, and thus in the promotion of cellulose dissolution at room temperature.

It is interesting to find that the $[C_4mim][CH_3COO]$/DMSO ($R_{DMSO}$ = 2.54:1) solvent containing 5.0% water still gives 6.5% cellulose solubility. This differs clearly from the neat $[C_4mim]Cl$, in which ca. 1 wt% of water would make cellulose insoluble (Swatloski et al., 2002). Actually, this is understandable because interaction of partial DMSO in the system with water lowers, to some degree, the opportunity of the direct interaction of the $[CH_3COO]^-$ with water. This means that the solvent and cellulose feedstock are not necessary to be sufficiently dried before dissolution, which would make cellulose processing simple.

**Table 1**
The solubility (%) of microcrystalline cellulose in ILs/DMSO ($R_{DMSO}$ = 2.54:1) solvents and the $\beta$ parameters of the ILs at 25 °C.

| Solvent[a] | Cellulose solubility (%) | IL | $\beta$[b] |
|---|---|---|---|
| $[C_4mim][CH_3COO]$/DMSO ($R_{DMSO}$ = 2.54:1) | 15.0 | $[C_4mim][CH_3COO]$ | 1.161 |
| $[C_4mim][(C_6H_5)COO]$/DMSO ($R_{DMSO}$ = 2.54:1) | 9.0 | $[C_4mim][(C_6H_5)COO]$ | 0.987 |
| $[C_4mim][HOCH_2COO]$/DMSO ($R_{DMSO}$ = 2.54:1) | Insoluble | $[C_4mim][HOCH_2COO]$ | 0.967 |
| $[C_4mim][CH_3CHOHCOO]$/DMSO ($R_{DMSO}$ = 2.54:1) | Insoluble | $[C_4mim][CH_3CHOHCOO]$ | 0.964 |
| $[C_4mim]Cl$/DMSO ($R_{DMSO}$ = 2.54:1) | Insoluble | $[C_4mim]Cl$ | 0.840 |
| $[C_4mim][N(CN)_2]$/DMSO ($R_{DMSO}$ = 2.54:1) | Insoluble | $[C_4mim][N(CN)_2]$ | 0.621 |

[a] $R_{DMSO}$ is the mole ratio of DMSO to IL.
[b] Ref. Xu et al.

### 3.4. Influence of co-solvent nature on the solubility of cellulose

Encouraged by the above results, we have used other aprotic polar solvents to see whether their addition in the $[C_4mim][CH_3COO]$ can enhance the solubility of cellulose. DMF and DMA are selected for this purpose. It is found that at 25 °C, solubility of cellulose in $[C_4mim][CH_3COO]$/DMF ($R_{DMSO}$ = 2.54:1) and $[C_4mim][CH_3COO]$/DMA ($R_{DMSO}$ = 2.54:1) solvents also increases markedly compared with that of cellulose in $[C_4mim][CH_3COO]$. Generally, the cellulose solubility follows the order: $[C_4mim][CH_3COO]$/DMSO (15.0%) > $[C_4mim][CH_3COO]$/DMF (12.5%) > $[C_4mim][CH_3COO]$/DMA (5.5%) at the same molar ratio of the aprotic polar solvents to the IL. Considering the fact that cations of the ILs could be preferentially solvated by aprotic polar solvents through ion–dipole interaction (Hanke et al., 2002), and the difference in cellulose solubility would partially be ascribed to the difference in the dipole moment of these aprotic polar solvents. According to the literature (Covington & Dickinson, 1973), dipole moment of the aprotic polar solvents we used follows the order: DMSO (3.96D) > DMF (3.86D) > DMA (3.81D). Thus, the solvated strength of the $[C_4mim]^+$ cations by the aprotic polar solvents and the corresponding concentration of "free" $[CH_3COO]^-$ anions in the solvent systems should follow the same order. Consequently, under the same conditions, $[C_4mim][CH_3COO]$/DMSO gives the highest cellulose solubility, and the lowest cellulose solubility is observed in $[C_4mim][CH_3COO]$/DMA solvent.

Furthermore, based on our concept mentioned above, if a protic polar solvent is added into an ionic liquid, solubility of cellulose will decrease in such a solvent because anions rather than cations of the ILs will be solvated preferentially by formation of hydrogen bonding. In order to examine this speculation, we tried to measure solubilities of cellulose in $[C_4mim][CH_3COO]$/water and $[C_4mim][CH_3COO]$/methanol solvents at 25 °C. It was found that in the presence of 1 wt% water or methanol, the solubilities of cellulose in these solvents were too small to be determined. This is why the protic polar solvents, like water and methanol, are often used as precipitants to regenerate cellulose from ILs solutions (Swatloski et al., 2002; Xu et al., 2010). Alternatively, we determined cellulose solubility at 25 °C in $[C_4mim][CH_3COO]$/DMSO (1:2.54) with addition of 1.0% methanol, then 20.0% decrease in the cellulose solubility was observed. This confirms the role of preferential solvation of anions of ionic liquids by protic polar solvents in the decrease of cellulose solubility.

Additionally, it is always observed that solubility of cellulose in an IL from different sources is sometimes quite variable. This has been a problem which is difficult to understand. Actually, such phenomenon can be explained from the fact that IL from different companies/labs contains different kinds and/or different contents of impurities. If the impurity is an aprotic polar solvent, such as unreacted *N*-methylimidazole, the solubility of cellulose in the IL will increase. On the other hands, if the impurity is a protic polar solvent, such as water, the solubility of cellulose in the IL will decrease (Swatloski et al., 2002). For example, our experimental result shows that at 25 °C, although cellulose is insoluble in 1-allyl-3-methylimidazolium acetate $[Amim][CH_3COO]$, addition of 10% *N*-methylimidazole into $[Amim][CH_3COO]$ gives 14% solubility.

## 4. Conclusions

The novel solvents designed in this work can directly dissolve cellulose in high concentration without heating. The conductivity results confirm that the enhanced dissolution of cellulose is mainly ascribed to the increased concentration of the "free" $[CH_3COO]^-$ anions from the dissociated IL owing to the preferential solvation of $[C_4mim]^+$ by the aprotic polar solvents. This supports the conclusion that cellulose solubility in ILs is mainly determined by the hydrogen bond accepting ability of their anions, and explains why protic polar solvents such as water and methanol can be used to precipitate cellulose from ILs solutions. This finding opens up new horizons in the design of cellulose solvents, and provides a new platform for the practical use of the cellulose processing at ambient temperature.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.09.028.

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