

Effects of anionic structure and lithium salts addition on the dissolution of cellulose in 1-butyl-3-methylimidazolium-based ionic liquid solvent systems†

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Cellulose is the most abundant biorenewable and biodegradable resource on the earth. However, the extent of its application is limited due to its inefficient dissolution in solvents. Thus, the development of new cellulose solvents continues to be an active area of investigation. In this work, a series of ionic liquids (ILs) have been synthesized by coupling the 1-*N*-butyl-3-methylimidazolium cation [C₄mim]⁺ with the Brønsted basic anions [CH₃COO][−], [HSCH₂COO][−], [HCOO][−], [(C₆H₅)COO][−], [H₂NCH₂COO][−], [HOCH₂COO][−], [CH₃CHOHCOO][−] and [N(CN)₂][−]. The solubilities of microcrystalline cellulose (MCC) in these ionic liquids were determined as a function of temperature. The effect of the anion structure on the solubility of cellulose has been estimated, and investigated by ¹H NMR and a solvatochromic UV/vis probe. It was found that the solubility of cellulose increases almost linearly with increasing hydrogen bond accepting ability of anions in the ionic liquids. At the same time, novel [C₄mim][CH₃COO]/lithium salt (LiCl, LiBr, LiAc, LiNO₃, or LiClO₄) solvent systems have been developed by adding 1.0 wt% of lithium salt into [C₄mim][CH₃COO]. It was shown that the addition of lithium salts significantly increased the solubility of the cellulose. This observation was studied by ¹³C NMR spectra, and the results suggested that the enhanced solubility of cellulose originated from the disruption of the intermolecular hydrogen bond, O(6)H ⋯ O(3) owing to the interaction of Li⁺ with the hydroxyl oxygen O(3) of cellulose. Furthermore, the cellulose materials regenerated from the ionic liquids were characterized by scanning electron micrograph, thermogravimetric analysis and Fourier transform infrared spectroscopy, and the degree of polymerization of the original and regenerated cellulose materials was also determined. Good thermal stability was found for the regenerated cellulose. It is expected that the above information is useful for the design of novel ionic liquids and ionic liquid-based solvent systems for cellulose.

Introduction

Cellulose is the most abundant biorenewable and biodegradable resource in the world, with an annual yield of over 1.0 × 10¹⁰ ton.¹ Cellulose can be derived from cellulose-rich starting materials like trees, cotton, and crop wastes. Cellulose and its derivatives have been widely used in our society in fibers, tissues, paper, membranes, polymers, paints and medicines.^{2,3} However, due to its close packing by numerous inter- and intramolecular hydrogen bonds, cellulose is extremely difficult to dissolve in water and most of the conventional organic solvents. Therefore, the main obstacle to the further application of cellulose is the lack of powerful solvent systems. Until now, only a limited number of solvent systems have been industrialized. However,

the dissolution processes using these solvent systems suffer from environmental, energy, safety, and other problems. For example, the viscose process, which is a traditional technology used in industry, sometimes causes serious environmental pollution and involves derivatization of cellulose products.⁴ Although the *N*-methylmorpholine-*N*-oxide (NMMO) process is a direct dissolution process commercialized for the manufacture of so-called lyocell fibres,⁴ this process also has some problems, such as the severe fibrillation of the manufactured fibres, a high dissolution temperature (130 °C), and the requirement of a major investment in safety technology because of its thermal instability. Other solvent systems investigated include DMAc/LiCl, DMSO/TBAF, DMF/N₂O₄, LiClO₄·3H₂O, and LiSCN·2H₂O,^{5–8} where DMAc, DMSO, TBAF, DMF, and N₂O₄ stand for *N,N*-dimethylacetamide, dimethyl sulfoxide, tetrabutyl ammonium fluoride, *N,N*-dimethylformamide and nitrous tetroxide, respectively. Such solvent systems still retain certain drawbacks such as high cost, toxicity, difficulty in solvent recovery or harsh processing conditions. Therefore, it is highly desirable to develop less energy consuming, more environmentally friendly, and highly efficient solvent systems for cellulose.

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Ionic liquids (ILs) are a novel class of green solvents. They have many distinct advantages such as chemical and thermal stability, non-flammability, non-detectable vapor pressures and chemical tunabilities,^{9–11} and promise widespread application in industry. In 2002, Rogers and coworkers¹² reported, for the first time, that cellulose could be efficiently dissolved in 1-*N*-butyl-3-methylimidazolium chloride [C₄mim]Cl, whereas the ILs containing [BF₄][−] and [PF₆][−] anions were poor solvents. ¹³C and ^{35/37}Cl NMR relaxation measurements demonstrated that the high solubility of cellulose in [C₄mim]Cl was attributable to the formation of hydrogen bonding between the hydroxyl protons of cellulose and the chloride anion of the IL.^{13,14} Since then, a series of researches has been conducted in this field. Zhang *et al.*¹⁵ reported that 1-*N*-allyl-3-methylimidazolium chloride [Amim]Cl was a powerful solvent for cellulose, in which microcrystalline cellulose could be dissolved quickly without activation or pretreatment. They also indicated that 1-*N*-ethyl-3-methylimidazolium acetate [C₂mim][CH₃COO], which has a lower melting point and viscosity, showed a much higher ability to dissolve cellulose.¹⁶ Ohno *et al.*^{17,18} found that *N,N'*-dialkylimidazolium formates, [RR'im][HCOO], and *N*-ethyl-*N'*-methylimidazolium alkylphosphates, [C₂mim][(MeO)₂PO₂], displayed superior solubility for a variety of polysaccharides, including cellulose. In the extended dissolution studies of Schubert *et al.*¹⁹ for cellulose in imidazolium-based ionic liquids, an odd–even effect was found for different alkyl side-chain lengths of the imidazolium chlorides, and 1-ethyl-3-methylimidazolium diethyl phosphate was found to be best suited to the dissolution of cellulose. It was also reported that wood and other biomasses such as bagasse and straw can be dissolved, at least partially, in ILs such as [Amim]Cl, [C₄mim]Cl and [C₂mim][CH₃COO].^{20–24} These encouraging results provide possibilities for the dissolution of cellulose and biomass by ILs instead of conventional organic solvents, as well as for solutions to the problems described above in the solvent systems of cellulose.

Although previous investigations revealed some important aspects for the dissolution of cellulose in ILs, very few studies have been conducted to explore the influence of the structure of ILs on the dissolution performance of cellulose. Considering the fact that the dissolution of cellulose is significantly determined by the nature of the anions in ILs,^{13,14} we prepared a series of ionic liquids with a fixed cationic backbone and a fixed alkyl chain length, *i.e.* the 1-butyl-3-methylimidazolium cation [C₄mim]⁺, but with varied anion structures. This allowed us to examine the effect of the ILs' anion structure on the solubility of cellulose, as well as the related dissolution mechanism. In order to further enhance the dissolution of cellulose, several novel solvent systems have been developed by the addition of 1.0 wt% of a lithium salt (LiAc, LiCl, LiBr, LiClO₄, or LiNO₃) into [C₄mim][CH₃COO]. The dissolution of cellulose in the ILs and the [C₄mim][CH₃COO]/lithium salt solvent systems was studied by ¹H and ¹³C NMR spectroscopies and solvatochromic UV/vis probe. In addition, the regenerated cellulose materials were investigated by means of scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Fourier transform infrared (FT-IR), and the dissolution temperature and dissolution time effects on the degree of polymerization of the regenerated cellulose were also discussed.

Table 1 Solubility of microcrystalline cellulose in the ILs at different temperatures

Entry	IL	Solubility/wt%			
		40 °C	50 °C	60 °C	70 °C
1	[C ₄ mim][CH ₃ COO]	11.5	12.5	13.0	15.5
2	[C ₄ mim][HSCH ₂ COO]	<1.0	9.5	12.5	13.5
3	[C ₄ mim][HCOO]	7.5	8.5	9.0	12.5
4	[C ₄ mim][(C ₆ H ₅)COO]	<1.0	<1.0	<1.0	12.0
5	[C ₄ mim][H ₂ NCH ₂ COO]	<1.0	2.0	8.0	12.0
6	[C ₄ mim][HOCH ₂ COO]	— ^a	7.5	9.0	10.5
7	[C ₄ mim][CH ₃ CHOHCOO]	— ^a	— ^a	8.0	9.5
8	[C ₄ mim][N(CN) ₂]	— ^a	— ^a	— ^a	— ^a

^a Insoluble at the given temperature.

Results and discussion

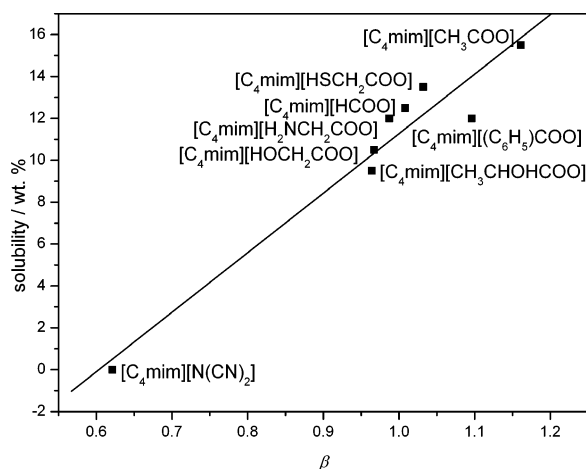
Influence of the ionic liquids' anion structure on the solubility of cellulose

The solubility values of microcrystalline cellulose in the studied ILs are shown in Table 1 as a function of temperature. It can be seen that the structure of the anions significantly affects the solubility of the cellulose. Among the investigated ILs, [C₄mim][CH₃COO] is the most efficient ionic liquid for the dissolution of cellulose. In contrast, cellulose is insoluble in [C₄mim][N(CN)₂]. This indicates that the anions of the ILs play a key role in the disruption of the inter- and intramolecular hydrogen bonds of cellulose. Generally, the solubility of cellulose in these ILs decreases in the order: [C₄mim][CH₃COO] > [C₄mim][HSCH₂COO] > [C₄mim][HCOO] > [C₄mim][(C₆H₅)COO] > [C₄mim][H₂NCH₂COO] > [C₄mim][HOCH₂COO] > [C₄mim][CH₃CHOHCOO] > [C₄mim][N(CN)₂]. It is interesting to note that replacing H in the CH₃COO[−] anion of the ionic liquid [C₄mim][CH₃COO] with electron-withdrawing groups such as OH, SH, NH₂ or CH₃OH leads to decreased solubility. Considering the fact that replacement of H in the CH₃COO[−] anion by an electron-withdrawing group would decrease the ability of CH₂XCOO[−] (X = OH, SH, NH₂ and CH₃OH) to form hydrogen bonds with the hydroxyl protons of cellulose, the decreased solubility observed is not difficult to understand. This suggests that the hydrogen bond accepting ability of the anions strongly dominates the ILs' capacity for the dissolution of cellulose. In addition, it is noted from Table 1 that the solubility of cellulose in these ILs is enhanced with increasing temperature. In the case of [C₄mim][CH₃COO], the solubility of cellulose at 70 °C (15.5 wt%) is higher than that at 40 °C (11.5 wt%) by about 35%. This is an indication that hydrogen bonds of the cellulose were also partially disrupted by the increased temperature.

The β parameter, introduced by Kamlet and Taft, has been established as a measure of the hydrogen bond accepting ability of anions of ionic liquids.^{25–27} Unfortunately, most of the β parameters for the ILs investigated in the present work are not available in the literature. Therefore, we determined these parameters and the results are given in Table 2. It is evident that the ILs with different anion structures exhibit a marked variation in the β parameter. As shown in Fig. 1, the solubility values of cellulose increase almost linearly with increasing β parameter of the ILs. This indicates that the solubility of the cellulose strongly depends on the hydrogen bond-accepting ability of the

Table 2 The β parameter values for the ILs investigated

Entry	IL	β
1	[C ₄ mim][CH ₃ COO]	1.161
2	[C ₄ mim][HSCH ₂ COO]	1.032
3	[C ₄ mim][HCOO]	1.008
4	[C ₄ mim][(C ₆ H ₅)COO]	0.987
5	[C ₄ mim][H ₂ NCH ₂ COO]	1.096
6	[C ₄ mim][HOCH ₂ COO]	0.967
7	[C ₄ mim][CH ₃ CHOHCOO]	0.964
8	[C ₄ mim][N(CN) ₂]	0.621

**Fig. 1** Linear correlation between solubility of microcrystalline cellulose at 70 °C and β Parameter of the ILs investigated.

anions of the ILs. The stronger the hydrogen bond accepting ability of the anions, the higher the solubility of cellulose in the IL. For example, the anion of [C₄mim][CH₃COO] has the strongest hydrogen bond accepting ability (highest β value) of the ILs investigated, and solubility of the cellulose is found to be the highest in [C₄mim][CH₃COO].

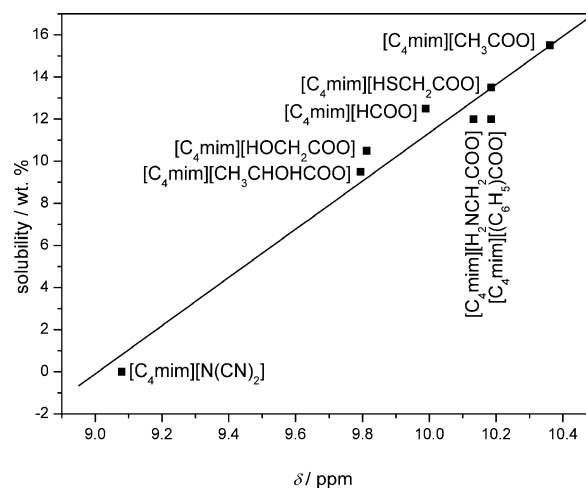
It is known that the ¹H NMR chemical shift (δ) of the proton in the 2-position of the imidazolium ring can be used as a measure of the capacity of the anion of an IL to form hydrogen bonds,²⁸ which is crucial to the breaking of the inter- and intramolecular hydrogen bonds of the cellulose chains,^{17,18} and thus to the dissolution of cellulose. Therefore, ¹H NMR chemical shifts of the proton in the 2-position of the imidazolium ring have been determined for the ILs under study, and the correlation between the solubility of cellulose and the chemical shift of this proton is shown in Fig. 2. As expected, the solubility of cellulose increases almost linearly with the chemical shift of the proton in the 2-position of the imidazolium ring. Hence, the solubility of cellulose in a certain IL can be predicted by using this linear correlation. According to our result, the ILs with a δ value smaller than 9.5 are not suitable solvents for the dissolution of cellulose.

Lithium salt-promoted dissolution of cellulose in [C₄mim][CH₃COO]

The solubility of cellulose in various [C₄mim][CH₃COO]/lithium salt solvent systems was investigated at different temperatures. Table 3 summarizes the results obtained for microcrystalline cellulose. It can be seen that solubility of

Table 3 Solubility of microcrystalline cellulose in [C₄mim][CH₃COO]/lithium salt solvent systems

Solvent system	Solubility (wt%) at different temperatures				
	40 °C	50 °C	60 °C	70 °C	80 °C
[C ₄ mim][CH ₃ COO]	11.5	12.5	13.0	15.5	19.0
[C ₄ mim][CH ₃ COO]/LiAc	12.0	16.0	17.5	19.0	20.0
[C ₄ mim][CH ₃ COO]/LiCl	12.0	14.5	16.0	18.5	20.0
[C ₄ mim][CH ₃ COO]/LiBr	11.5	13.5	15.0	18.0	19.5
[C ₄ mim][CH ₃ COO]/LiClO ₄	12.0	15.0	17.5	20.0	21.0
[C ₄ mim][CH ₃ COO]/LiNO ₃	12.0	15.0	18.5	19.5	21.0

**Fig. 2** Linear correlation between solubility of microcrystalline cellulose at 70 °C and the ¹H NMR chemical shifts of the proton in the 2-position of the imidazolium ring measured in DMSO-d₆ at a concentration of 1.0 mol kg⁻¹.

the cellulose is enhanced significantly after the addition of a small amount of lithium salt into [C₄mim][CH₃COO]. As reported in the literature,²⁹ some lithium salt hydrates have the capacity to dissolve cellulose through the hydroxyl groups of the cellulose taking part in the coordination of Li⁺. Compared to LiX·*n*H₂O, the lack of water molecules in LiX leads to more free coordination sites at the lithium cation. These sites can be occupied by other coordinating groups, *e.g.* the hydroxyl groups of cellulose, resulting in the breaking of some inter- and intramolecular hydrogen bonds of cellulose. This is a possible reason why higher solubility was observed for cellulose in [C₄mim][CH₃COO]/lithium salt solvent systems than in [C₄mim][CH₃COO] alone.

In order to further examine how the addition of lithium salts increases the solubility of cellulose, ¹³C NMR measurements of cellulose were carried out in solutions of [C₄mim][CH₃COO]/cellulose (9.0 wt%) and [C₄mim][CH₃COO]/LiCl (1.0 wt%)/cellulose (9.0 wt%) at 90 °C. The ¹³C NMR spectra are shown in Fig. 3, and the ¹³C NMR chemical shift data are presented in Table 4. It can be seen from Table 4 that the addition of LiCl produces a downfield shift (an increase in chemical shift) for C3 and upfield shifts (decrease in chemical shift) for the other C atoms. Based on the results reported in literature,^{30,31} the hydrogen bonds of cellulose are mainly the intramolecular hydrogen bonds, O(3)H...O(5) and O(2)H...O(6), present on both sides of the cellulose chain,

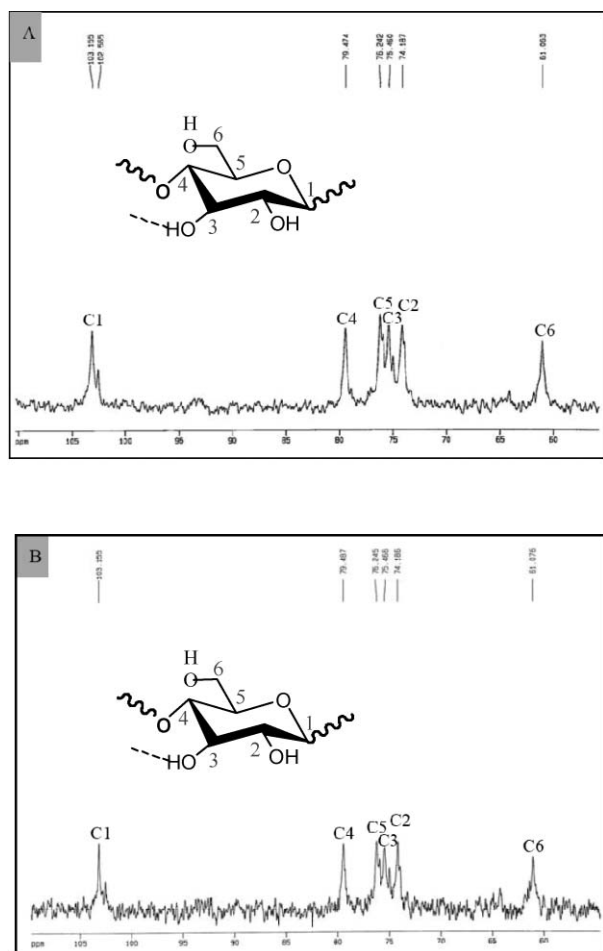


Fig. 3 ^{13}C NMR spectra of microcrystalline cellulose in IL and IL/lithium salt systems at 90 °C: (A) $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$; (B) $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}$.

and the intermolecular hydrogen bond, $\text{O}(6)\text{H}\cdots\text{O}(3)$, which builds a bridge between two neighboring molecules (Fig. 4). After the addition of LiCl into the $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$ /cellulose system, the intermolecular hydrogen bond, $\text{O}(6)\text{H}\cdots\text{O}(3)$, was broken owing to the interaction of Li^+ with the hydroxyl oxygen $\text{O}(3)$ of cellulose, and thus the electron cloud density of $\text{C}3$ bonded to the hydroxyl oxygen $\text{O}(3)$ of cellulose decreased. Consequently, the ^{13}C NMR signal of $\text{C}3$ shifts downfield, and the chemical shift of $\text{C}3$ increases correspondingly. At

Table 4 ^{13}C NMR chemical shifts (δ (ppm) relative to TMS) of cellulose in $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{cellulose}$ (9.0 wt%) and $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}$ (1.0 wt%)/cellulose (9.0 wt%) systems

Solvent system	δ (ppm)					
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
$[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$	103.165	74.188	75.468	79.488	76.242	61.063
$[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}$	103.146	74.182	75.478	79.467	76.189	61.034

the same time, disruption of this intermolecular hydrogen bond prompts further dissolution of the cellulose. However, the chemical shifts for the other C atoms of cellulose behave differently. This may be interpreted as the interactions of the Cl^- anion of LiCl with the hydroxyl proton of cellulose in the $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}$ /cellulose system, which leads to an increase of electron cloud density of the C atoms and an upfield shift of their ^{13}C NMR signals. The dissolution mechanism of cellulose in $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}$ reported here is somewhat similar to that in N,N -dimethylacetamide/ LiCl , and the breaking of intermolecular hydrogen bonds results from the direct interaction of lithium with the cellulosic hydroxyl oxygen.³² The difference is that $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$ in the $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}$ solvent system can dissolve cellulose, but N,N -dimethylacetamide in N,N -dimethylacetamide/ LiCl cannot.

Compared to other solvent systems for cellulose, the $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$ /lithium salt solvent systems reported in the present work have the advantages of higher solubility and lower dissolution temperature. For example, at 40 °C, the solubility of cellulose in $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiX}$ ($\text{X} = \text{Cl}, \text{NO}_3, \text{ClO}_4, \text{Ac}$) systems could be as high as 12.0 wt%, whereas only 8.0 wt% of cellulose was dissolved in $[\text{C}_2\text{mim}][(\text{MeO})\text{HPO}_2]$.¹⁸ At 60 °C, 18.5 wt% of cellulose can be dissolved in $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiNO}_3$, but only 10.0 wt% of cellulose has been dissolved in $[\text{C}_2\text{mim}][\text{HCOO}]$.¹⁷ On the other hand, cellulose cannot be dissolved in $[\text{Amim}]\text{Cl}$ at temperatures below 70 °C,¹⁵ and the temperature needs to be maintained at 130 °C for the dissolution of 10–15 wt% of cellulose in the NMMO system. In addition, our ILs and $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$ /lithium salt solvent systems can be used for the direct dissolution of cellulose without any pretreatment or activation. In contrast, in most of the conventional solvent systems for cellulose such

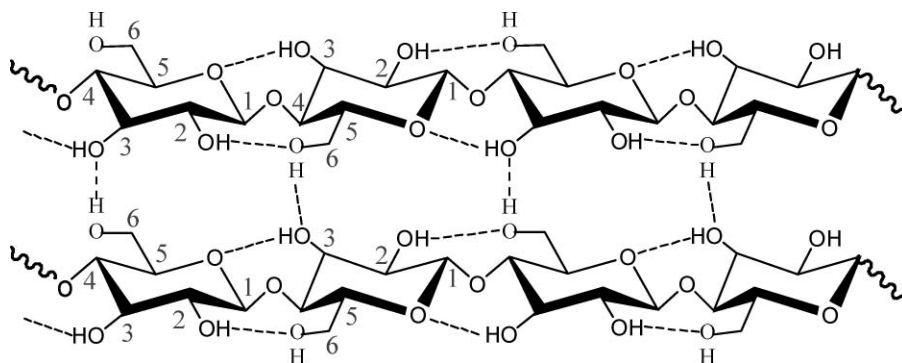


Fig. 4 Schematic structure and numbering of cellulose.

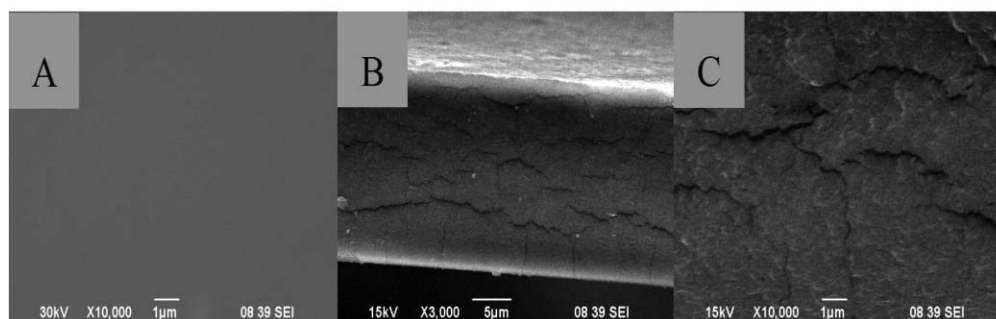


Fig. 5 SEM images of the free and fracture surfaces for the regenerated cellulose films from $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}/\text{cellulose}$ solution: (A) free surface at 10 000 \times magnification; (B), (C) fracture surface at 3000 \times magnification and 10 000 \times magnification, respectively.

as DMAc/LiCl and NaOH/ H_2O , pretreatment or activation of the original cellulose is often necessary.^{33,34}

Encouragingly, it is also found that absorbent cotton with a degree of polymerization as high as 1586 could be dissolved in the $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}$ system in high concentrations (up to 21 wt%) at 90 $^\circ\text{C}$. We have tried to increase the content of the lithium salts in $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$ to enhance the cellulose solubility further. However, we failed to do this because of the limited solubility of the lithium salts in the ILs.

Structure and properties of the regenerated cellulose

The cellulose regenerated from $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{lithium salt}$ solvent systems (see Experimental section) was characterized by SEM, TGA, and FTIR spectroscopy. The degree of polymerization of the original and the regenerated cellulose materials was also determined, and the dissolution temperature and the dissolution time effects were examined.

SEM images of the regenerated cellulose films from $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}$ solution are shown in Fig. 5. It can be seen that the free surface and fracture surface of the dried films display homogeneous structures from the interior to the surface, indicating a dense architecture, in which no undissolved original cellulose can be detected. The structure of the regenerated cellulose is quite similar to that reported by Zhang *et al.*¹⁵ and Zhang *et al.*,³⁵ but different from the porous structure regenerated from aqueous NaOH/thiourea solution.³⁶

FTIR spectra of the original and the regenerated cellulose materials are shown in Fig. S1 (see ESI†). It can be seen that all the spectra are quite similar and no new peaks are observed in the regenerated sample. This indicates that no chemical reaction takes place during the cellulose dissolution and regeneration processes. The absorption band at 1427 cm^{-1} in the regenerated cellulose was assigned to the CH_2 scissoring vibration. This band was weakened and shifted to a lower wavenumber compared to the peak at 1431 cm^{-1} for the original cellulose, suggesting the destruction of an intra-molecular hydrogen bond involving O6.³⁵ A new shoulder at 990 cm^{-1} was observed in the regenerated cellulose, which could be assigned to a C–O stretching vibration in the amorphous region.³⁷ The O–H vibration in the regenerated cellulose shifts to a higher wavenumber (3427 cm^{-1}), indicating the breaking of hydrogen bonds to some extent.^{38,39} The absorption bands in the range of 1164–1061 cm^{-1} are assigned to the C–O–C stretching of the original cellulose.⁴⁰ The presence of such bands in the absorption of the regenerated cellulose

suggests that the macromolecular structure of cellulose has not been destroyed.

TGA curves for both the original cellulose and the regenerated cellulose are shown in Fig. 6. It is noted that the two TGA curves nearly overlapped at lower temperatures, and rapid decomposition occurred in the temperature range from 313 to 351 $^\circ\text{C}$ for the original cellulose and from 301 to 341 $^\circ\text{C}$ for the regenerated cellulose. The regenerated sample exhibits a slightly lower onset temperature (301 $^\circ\text{C}$) for the decomposition compared to the original cellulose (313 $^\circ\text{C}$), and gives a slightly higher char yield (nonvolatile carbonaceous material) on pyrolysis, indicated by the slightly higher residual mass after the decomposition step. This result indicates that the cellulose regenerated from the $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{lithium salts}$ solvent systems has good thermal stability. This is significantly different from the cellulose regenerated from the reported solvent systems^{12,15} in which a large difference in the decomposition temperature was observed between the regenerated and the original materials.

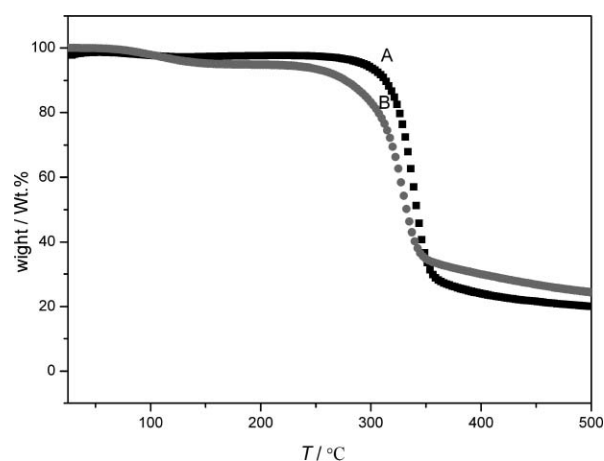


Fig. 6 Thermal decomposition profiles of the original cellulose and the regenerated cellulose materials: (A) the original cellulose; (B) the cellulose regenerated from $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}/\text{cellulose}$ after 1 h of dissolution at 60 $^\circ\text{C}$.

The effects of the dissolution temperature and dissolution time on the degree of polymerization (DP) of the regenerated cellulose are shown in Fig. 7 and 8, respectively. In the temperature range from 40 to 80 $^\circ\text{C}$, the DP values (from 215 to 209) of the regenerated cellulose are slightly smaller than that of the original cellulose (DP = 229). Only at 100 $^\circ\text{C}$ was a slight degradation of

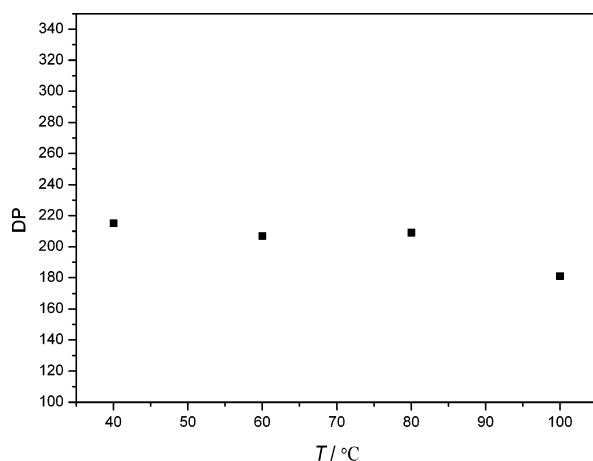


Fig. 7 Degree of polymerization for the cellulose regenerated from $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}/\text{cellulose}$ after 1 h of dissolution at different temperatures.

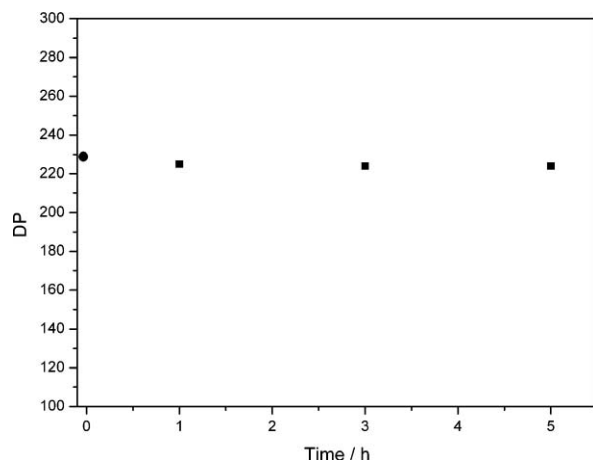


Fig. 8 Degree of polymerization for the original cellulose and the cellulose regenerated from $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{LiCl}/\text{cellulose}$ at 40 °C as a function of the dissolution times: (●) the original cellulose; (■) the regenerated cellulose.

cellulose observed, with the DP value of the regenerated cellulose being 181. It is worth noting that at 40 °C, the DP value of the regenerated cellulose hardly changed, even if the dissolution time was prolonged to as much as 5 h. This result indicates that no cellulose degradation took place at 40 °C during 5 h of dissolution in the $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{lithium salt}$ solvent systems. Obviously, the $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{lithium salt}$ solvent systems of cellulose are superior to some of the reported systems in which cellulose degradation definitely occurred.^{15,41} All of these facts suggest that our new solvent systems are excellent solvents for cellulose, and they could provide a new platform for the homogeneous processing of cellulose and the production of advanced cellulose materials under mild conditions.

Conclusions

In this work, solubility, ^1H and ^{13}C NMR and solvatochromic UV/vis probe measurements have been performed to study the effects of the structure of the anion in selected ILs and the effect of adding lithium salts to $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$ on the solubility of microcrystalline cellulose. It was shown that the structure of

the anion and the addition of lithium salts significantly affected the solubility of cellulose. The hydrogen bond accepting ability of the anions of the ILs, as characterized by the chemical shift values of the proton in the 2-position of the imidazolium ring, and the β parameter of the ILs, are closely linked to the solubility of cellulose. Thus, replacement of H in the CH_3COO^- anion of $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$ by an electron-withdrawing group such as OH, SH, NH_2 or CH_3OH leads to decreased solubility. The nature the enhanced dissolution achieved with lithium salts is suggested to result from the interaction of Li^+ with the hydroxyl oxygen O(3) of the cellulose, which disrupts the intermolecular hydrogen bond $\text{O}(6)\text{H}\cdots\text{O}(3)$. Such information is expected to be useful for the design of novel ILs and IL-based solvent systems for cellulose.

Cellulose can be regenerated from the ILs and the $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{lithium salt}$ solvent systems by precipitation with water. The regenerated cellulose was studied by SEM, TGA, FTIR and degree of polymerization measurements. It was found that no chemical reaction took place between cellulose and the ILs or the $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{lithium salt}$ systems during the dissolution and precipitation processes. The regenerated cellulose exhibited a quite similar thermal stability to the original cellulose. Therefore, the $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{Li salt}$ solvent systems reported here are expected to provide a possible platform for the homogeneous processing of cellulose and the production of advanced cellulose materials under mild conditions. However, it should be pointed out that the recovery and reuse of the ILs and the lithium salts are the key issue for the practical application of the new solvent systems mentioned above. Although both of them can be recovered by simple evaporation from their aqueous solutions and then dried under vacuum, this method is energy consuming and thus expensive. Therefore, alternative low-cost methods for the recovery of the ILs and the lithium salts from the aqueous solutions need to be developed.

Experimental

Materials

Absorbent cotton and 1-methylimidazole (99%) were purchased from Shanghai Chem. Co.; 1-chlorobutane (>99.0%), 1-bromobutane (98.0%), mercaptoacetic acid (>97.0%), glycolic acid (98.0%), glycine (>99.0%), microcrystalline cellulose (MCC) and anion exchange resin (Ambersep 900 OH) were from Alfa Aesar; acetic acid (>99.5%), formic acid (>88.0%), benzoic acid (>99.5%) and lactic acid (85.0–90.0%) were obtained from Shanghai Shiyi Chem. Reagent Co. Ltd.; *N,N*-diethyl-4-nitroaniline (97.0%) was purchased from Nanjing Chemlin Chemical Industrial 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. 4-Nitroaniline (98.0%) from Alfa Aesar was dissolved in methanol, and the mixture was stirred and then filtered to remove insoluble impurities. The methanol in the filtrate was evaporated, and 4-nitroaniline was dried under vacuum for 12 h at 40 °C. $\text{LiCl}\cdot 3\text{H}_2\text{O}$, $\text{LiBr}\cdot 2\text{H}_2\text{O}$, $\text{LiAc}\cdot 2\text{H}_2\text{O}$, $\text{LiClO}_4\cdot 3\text{H}_2\text{O}$ and $\text{LiNO}_3\cdot 3\text{H}_2\text{O}$ were obtained from Shanghai Chem. Co. and dried under vacuum before use to remove the crystallization water.

Synthesis of 1-butyl-3-methylimidazolium bromide [C₄mim]Br and 1-butyl-3-methylimidazolium chloride [C₄mim]Cl

[C₄mim]Br was prepared and purified by using the procedure described in the literature.⁴² Briefly, the reaction of 1-methylimidazole with an excess of 1-bromobutane was performed in 1,1,1-trichloroethane at 70 °C for 48 h. The solid product of [C₄mim]Br was washed with 1,1,1-trichloroethane and then filtered. The residual solvent was removed by rotary evaporation, and the resulting product was dried under vacuum for 24 h. [C₄mim]Cl was prepared similarly, but ethyl acetate was used instead of 1,1,1-trichloroethane.⁴³

Synthesis of 1-butyl-3-methylimidazolium acetate [C₄mim][CH₃COO], 1-butyl-3-methylimidazolium formate [C₄mim][HCOO], 1-butyl-3-methylimidazolium lactate [C₄mim][CH₃CHOHCOO], 1-butyl-3-methylimidazolium glycolate [C₄mim][HOCH₂COO], 1-butyl-3-methylimidazolium thioglycolate [C₄mim][HSCH₂COO], and 1-butyl-3-methylimidazolium benzoate [C₄mim][(C₆H₅)COO]

An aqueous solution of [C₄mim]Br was allowed to pass through a column filled with anion exchange resin to obtain [C₄mim][OH].¹⁷ The aqueous [C₄mim][OH] solution was then neutralized with equal molar acetic acid. After removing water by evaporation under reduced pressure, the viscous liquid [C₄mim][CH₃COO] was thoroughly washed with diethyl ether, and finally dried under vacuum for 72 h at 70 °C. The other ionic liquids were prepared by a similar process.

Synthesis of 1-butyl-3-methylimidazolium aminoethanoic acid salt [C₄mim][H₂NCH₂COO]

This IL was prepared by a similar procedure to that reported by Ohno *et al.*⁴⁴ Aqueous [C₄mim][OH] solution was thoroughly mixed with a slight excess of aqueous amino acid solution. After 12 h of reaction under cooling, water in the mixture was evaporated at 50 °C, and a slightly viscous liquid was obtained. After addition of acetonitrile-methanol (9 : 1, v/v), the mixture was stirred and then filtered to remove the excess amino acid. The organic solvents in the filtrate were evaporated and the product was dried under vacuum for 72 h at 80 °C.

Synthesis of 1-butyl-3-methylimidazolium dicyanamide [C₄mim][N(CN)₂]

This IL was synthesized and purified by using the procedure described by Sheldon and coworkers.⁴⁵ Briefly, to a solution of [C₄mim]Cl in acetone, Na[N(CN)₂] was added. The mixture was stirred for 24 h and the solid NaCl was removed by filtration. After removing acetone by evaporation under reduced pressure, the viscous liquid [C₄mim][N(CN)₂] was washed with dichloromethane, and dried under vacuum for 24 h at 60 °C.

The ¹H NMR data of the above ILs are summarized in the supporting information. They were in good agreement with those available in literature.^{42,43,45}

Preparation of [C₄mim][CH₃COO]/lithium salt solvent systems

1.0% (w/w) of LiCl, LiBr, LiAc, LiNO₃ or LiClO₄ was dissolved in [C₄mim][CH₃COO] to prepared the [C₄mim][CH₃COO]/

lithium salt solvent systems. These solvent mixtures were prepared immediately before use to minimize moisture uptake.

Dissolution of cellulose in the ILs and [C₄mim][CH₃COO]/lithium salt solvent systems

In a typical dissolution experiment, microcrystalline cellulose or absorbent cotton sample was added into a 20 mL colorimetric tube which contained 2.0 g of the dried IL or the IL/lithium salt, and the tube was sealed with parafilm. The tube was then immersed in an oil bath (DF-101S, Gongyi Yingyu Instrument Factory); the instability of the bath temperature was estimated to be ± 0.5 °C. The mixture was heated at a given temperature and stirred under argon atmosphere. Additional cellulose was added until the solution became optically clear under a polarization microscope (Nanjing Jiangnan Novel Optics Co. Ltd.). When cellulose became saturated, judged to be the point where cellulose could not be dissolved further within 1 h, its solubility (expressed in g per 100 g of IL) at the given temperature could be calculated from the amount of solvent and cellulose added. For each IL or [C₄mim][CH₃COO]/lithium salt solvent, the solubility values of cellulose were measured at different temperatures with 10 °C intervals.

Measurements of ¹H NMR and ¹³C NMR spectra

¹H NMR spectra of the ILs were collected at room temperature on a Bruker Avance-400 NMR spectrometer operating at 400.13 MHz. Measurements of ¹³C NMR spectra for the cellulose in [C₄mim][CH₃COO]/cellulose (9.0 wt%) and [C₄mim][CH₃COO]/LiCl (1.0 wt%)/cellulose (9.0 wt%) were performed on a Bruker DMX 300 spectrometer at 90 °C. Chemical shifts were given in ppm downfield from TMS.

Measurements of the β parameter for the ILs

The β parameter of the ILs, introduced as a measure of the hydrogen bond accepting ability of a solvent, was determined by following the procedure reported by Ohno *et al.*¹⁸ To calculate the β parameter, two different dyes, 4-nitroaniline (NA) and *N,N*-diethyl-4-nitroaniline (DENA) were employed. In a dry box, a given amount of the dried IL and a concentrated solution of NA or DENA in dry methanol were added into a vial and mixed homogeneously. The methanol was then carefully removed by drying under vacuum at 40 °C for 12 h. To avoid aggregation of the dyes, concentrations of NA or DENA in the ILs were selected to give an absorbance between 0.15 and 0.30. The IL containing NA or DENA was added into a quartz cell in a dry box and the cell was capped and sealed. The visible spectra of the ILs containing NA or DENA were recorded on a TU-1810 ultraviolet-visible spectrophotometer at 25.0 ± 0.1 °C. The wavelength at the maximum absorption (λ_{max}) was determined and used to calculate the β values by the following equations:¹⁸

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

$$\nu_{(\text{DENA})} = 1/(\lambda_{\text{max}(\text{DENA})} \times 10^{-4}) \quad (2)$$

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

Recovery and recycling of [C₄mim][CH₃COO]/Li salt solvent systems

After the complete dissolution of cellulose in the [C₄mim][CH₃COO]/Li salt solvent systems, cellulose can be regenerated and the [C₄mim][CH₃COO]/Li salt solvent mixtures can be recovered by addition of water or ethanol. In a typical recovery trial, 2.0 g of [C₄mim][CH₃COO]/LiCl solvent and 5.0 wt% cellulose solution were used. The cellulose solution was poured into a 100 mL beaker containing 10 mL of water. The beaker was sealed with preservative film and the mixture was stirred for 30 min at ambient temperature. The precipitated cellulose was separated by filtration through a ceramic funnel with Nylon filter paper on a Büchner flask under vacuum. The cellulose was washed four times to ensure that all the [C₄mim][CH₃COO]/LiCl solvent had been washed out. The filtrates were combined in a round bottomed flask, and water was removed by rotatory evaporation under reduced pressure. The resulting [C₄mim][CH₃COO]/LiCl solvent mixture was dried under vacuum for 24 h at 70 °C, and then could be used in the next dissolution process. In each dissolution–recovery cycle, the recovery percentage of [C₄mim][CH₃COO]/LiCl solvent is approximately 99.2 wt%, and the dissolving capacity of the recovered solvent for cellulose is equivalent to the original solvent.

Characterization of the regenerated cellulose

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus spectrometer with KBr pellets. A total of 16 scans were taken for each sample at a resolution of 2 cm⁻¹. Scanning electron micrographs were taken with a JEOL JSM-6390LV scanning electron microscope. The regenerated cellulose films in the dry state were frozen in liquid nitrogen, immediately snapped, and then dried under vacuum. The free surface (side in direct contact with the coagulant) and the fracture surface of the films were sputtered with gold, and then photographed. TGA was carried out with a NETZSCH STA 449 C thermal analyser using alumina crucibles. The sample mass was ca. 10–15 mg per measurement. The measurements were carried out under flowing N₂ at a heating rate of 10 °C min⁻¹. The viscosity-average degree of polymerization (DP) for the original and regenerated cellulose materials was determined by using an Ubbelohde viscometer in cupriethylenediamine hydroxide solutions.

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