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Effects of anionic structure on the dissolution of cellulose in ionic liquids revealed by molecular simulation

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ABSTRACT

Although ionic liquids (ILs) have shown promise in the pretreatment of cellulose and lignocellulosic biomass, there is no established rule to guide the rational design of such ILs up to date. In this work, the mixtures of cellulose with a series of ILs having the same cation $[C_2mim]^+$ but different anions have been simulated to study the effect of anionic nature on the dissolution of cellulose. It was shown that hydrogen bonds (HBs) were formed between anions of the ILs and hydroxyl protons of cellulose. Cl^- anion and O atom of $[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$ are better HB acceptors. Furthermore, the effects of electronegativity of HB acceptor atoms, steric effect of alkyl chain length and electron-withdrawing group of the anions on their HB acceptor ability have been investigated. The obtained results are expected to be important for the rational design of novel ILs for efficient dissolution of cellulose.

1. Introduction

Cellulose is the most abundant biorenewable resource found on the Earth and is known to have very attractive properties such as biocompatibility, biodegradability, and thermal and chemical stability. Thus cellulose and its derivatives are extensively used in industries such as textiles, plastics, wood and paper products, coatings, cosmetics, pharmaceuticals and others (Wang, Gurau, & Rogers, 2012). Cellulose can be directly extracted from its raw biomass. However, it is extremely difficult to dissolve in water and conventional organic solvents due to its close packing by numerous intermolecular and intramolecular hydrogen bonds (HBs) (Pinkert, Marsh, Pang, & Staiger, 2009). In the recent years, some ionic liquids (ILs) have been used as the high-efficient green solvents to dissolve cellulose. Contrary to the conventional organic solvents, they have very low vapor pressure, high thermal stability, and tunable structures and properties (Pinkert, Marsh, & Pang, 2010).

Up to date, imidazolium ionic liquids, including those with halide (F^-, Cl^-, Br^- and I^-) (Vitz, Erdmenger, Haensch, & Schubert, 2009), phosphonate ($[R_1O(R_2O)PO_2]^-$, $[R_1O(R_2)PO_2]^-$ and $[R_1R_2PO_2]^-$) (Abe, Fukaya, & Ohno, 2010; Fukaya, Hayashi, Wada, & Ohno, 2008), carboxylate ($[XCOO]^-$, X = —R, —CH_2OH, —$CH_2C_6H_5$, —CH_2NH_2 and —CH_2SH) (Xu, Wang, & Wang, 2010) and thiocyanate ($[SCN]^-$) (Swatloski, Spear, Holbrey, & Rogers, 2002) as anions, have been reported for cellulose dissolution. Most of the current experimental studies suggest that the dissolution process is governed by the interactions between the anion and cellulose. Based on their NMR spectroscopy measurements, Remsing, Swatloski, Rogers, and Moyna (2006) reported that the solvation of cellulose by 1-butyl-3-methylimidazolium chloride involves stoichiometric hydrogen-bonding between the hydroxyl protons of the cellulose and the chloride anions of the IL. Remsing et al. (2008) studied the solvation of carbohydrates in 1-ethyl-3-methyl imidazolium acetate ($[C_2mim][CH_3COO]$), 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$), and 1-allyl-3-methyl imidazolium chloride ([Amim]Cl) by measuring the $^{35/37}Cl$ and ^{13}C relaxation rates of chloride and acetate anions. Their results indicate that the dissolution of cellulose is mainly due to the interactions between the ILs anions and the carbohydrates. Zhang et al. (2010) also used NMR spectroscopy to study the solvation of cellobiose in 1-ethyl-3-methylimidazolium acetate ($[C_2mim][CH_3COO]$) under various cellobiose concentrations and different temperatures. They found that the acetate anions favor the formation of HBs with protons of cellobiose hydroxyls, and the

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aromatic protons in bulky cation $[C_2mim]^+$, especially the most acidic H2, prefer to associate with the oxygen atoms of hydroxyls in cellobiose. It was suggested that the dissolution of cellulose was determined by the combination of cation and anion of the ILs, however, the hydrogen bonding interactions between anion and cellulose were predominant.

At the same time, molecular dynamics (MD) simulations and Quantum Mechanical (QM) calculations have also been conducted to investigate the interactions of cellulose with ILs at the molecular level. Youngs, Hardacre, and Holbrey (2007) and Youngs et al. (2006) studied dissolution of β-D-glucose in 1,3-dimethylimidazolium chloride ($[C_1mim]Cl$) and $[C_2mim][CH_3COO]$ by MD simulations. It was found that the overriding interaction in the mixture is the hydrogen-bonding interactions between anion (Cl^- and acetate) and hydroxyl protons of the sugar. Liu, Sale, Holmes, Simmons, and Singh (2010) and Liu, Zhou, Zhang, and Yu (2010) performed a series of MD simulations on (1–4) linked-D-glucose oligomers with different molecular weights in $[C_2mim][CH_3COO]$ and in other solvents, and the proposed dissolution mechanism involves the formation of HBs between the IL anions and the hydroxyl protons of the glucose. Cho, Gross, and Chu (2011) (Gross, Bell, & Chu, 2011) explained the reason why cellulose could be dissolved in ILs but not in water in the idea that Cl^- can strongly interact with hydroxyl protons, and the coupling of cations to side chains and linker oxygens is stronger in the peeled-off state. Recently, Balasubramanian co-workers (Payal, Bharath, Periyasamy, & Balasubramanian, 2012) conducted some QM calculations on a cluster of solvent molecules to solvate the cellulosic units. It was suggested that all the intramolecular HBs were removed in the explicit $[C_1mim][CH_3COO]$ medium due to strong H-bonding interactions between cellobiose and the IL.

All the studies on the mechanism of the cellulose dissolution in ILs agree that anions of the ILs are HB acceptor and the O—H···anion HBs have been formed in the dissolution process. However, most of the studies were focused on one or several ILs, no systematical work was conducted at a molecular level. On the other hand, hydrogen bonding acceptor ability of anions is also affected by many factors, such as type and structure of HB acceptor (Guo, Zhang, Duan, & Liu, 2010; Guo, Zhang, & Liu, 2010), alkyl chain length of ILs (Abe et al., 2010), electron-withdrawing property of chemical groups in ILs (Xu et al., 2010), interaction of anions with cations of the ILs, and so forth. Therefore, further investigations are needed for the rational design of anions of ILs used in the efficient dissolution of cellulose.

In this work, MD simulations have been performed to study cellulose dissolution in a series of ILs with the same cation of $[C_2mim]^+$ but different anions such as F^-, Cl^-, Br^-, I^-, $[H(CH_2)_nCOO]^-$ ($n = 1, 3, 5, 9$), $[HOCH_2COO]^-$, $[(CH_3O)_2PO_2]^-$, $[SCN]^-$ and $[PF_6]^-$. In order to investigate the effect of anionic structures on the dissolution of cellulose in the ILs, the mixture systems of $[C_2mim]Cl$, $[C_2mim][CH_3COO]$, $[C_2mim][(CH_3O)_2PO_2]$, $[C_2mim][SCN]$ or $[C_2mim][PF_6]$ with cellulose oligomer were computed and compared in detail. The systems of $[C_2mim]F$, $[C_2mim]Cl$, $[C_2mim]Br$ and $[C_2mim]I$ with cellulose were chosen to study the electronegativity effect in the HB acceptor atoms. Then the mixtures of $[C_2mim][H(CH_2)_nCOO]$ ($n = 1, 3, 5, 9$) with cellulose were used to understand the effect of alkyl chain length of the anions on the dissolution of cellulose. In addition, $[C_2mim][HOCH_2COO]$-cellulose system was simulated to investigate the role of electron-withdrawing group on the alkyl chain of anion in the cellulose dissolution, and the results were compared with $[C_2mim][CH_3COO]$-cellulose system. The conclusions obtained in the present work would be important for the rational design of novel ILs used for the efficient dissolution of cellulose.

2. Computational details

2.1. Force field parameters

All-atom force fields were used in our simulations. For cellulose with the degree of polymerization (DP) of 10, we used the GLYCAM force field (Kirschner et al., 2008). For the anions of F^-, Cl^- (Cornell et al., 1995), Br^-, I^-, $[CH_3COO]^-$, $[HOCH_2COO]^-$ (Liu et al., 2006), $[H(CH_2)_3COO]^-$, $[H(CH_2)_5COO]^-$, $[H(CH_2)_9COO]^-$, $[(CH_3O)_2PO_2]^-$ (Cornell et al., 1995), $[SCN]^-$ (Chaumont & Wipff, 2009) and $[PF_6]^-$ (Liu, Huang, & Wang, 2004) (see Fig. S1 for their chemical structures), the reported AMBER force field was used. Parameters for $[C_2mim]^+$ were obtained from Liu's work (Liu et al., 2004). Optimization of the isolated ion structures was performed by using the Gaussian 09 B.01 version (Dong et al., 2012) at the B3LYP/6-31+G* level. Atom charges were obtained by fitting the electrostatic potential calculated at the B3LYP/6-311++G* level, and one-conformation, two-step restraint electrostatic potential method (Liu, Zhou, Zhang, Wu, & Yu, 2007) was used for this purpose (see Fig. S2 for the results). Subsequently, more sophisticated 6-31++G** basis set was employed to obtain the optimal geometries of the isolated anions. The electrostatic potential surface for the optimized isolated anions of Cl^-, $[CH_3COO]^-$, $[(CH_3O)_2PO_2]^-$, $[SCN]^-$ and $[PF_6]^-$ was calculated at this level.

2.2. Molecular dynamics simulations

All simulations were performed with MDynaMix 5.2 package (Lyubartsev & Laaksonen, 2000). The double time-step algorithm (Tuckerman, Berne, & Martyna, 1992) was adopted with long and short time steps of 2 and 0.5 fs, respectively. Ewald summation method (Deleeuw, Perram, & Smith, 1983) was used to treat the long-range electrostatic interaction, in which the long-range parts were cut off at 15 Å. The simulations for the mixtures of cellulose with $[C_2mim]F$, $[C_2mim]Cl$, $[C_2mim]Br$, $[C_2mim]I$, $[C_2mim][(CH_3O)_2PO_2]$, $[C_2mim][SCN]$, $[C_2mim][PF_6]$, $[C_2mim][CH_3COO]$, $[C_2mim][HOCH_2COO]$, $[C_2mim][H(CH_2)_3COO]$, $[C_2mim][H(CH_2)_5COO]$ and $[C_2mim]$ $[H(CH_2)_9COO]$ were carried out at 373.15 K. Each simulation system consists of 256 ion pairs and one cellulose chain with DP = 10. The cellulose chain was aligned along the X-direction, and it was very close to the centre of the box in order to make it relax inside of the box. Referring to the mole fraction of cellulose used by Liu, Sale, et al. (2010) and Liu, Zhou, et al. (2010) and Xu, Pan, Wang, Zhang, and Liu (2012), a given mole fraction (0.0039) of cellulose in our simulated systems was used to compare the dissolution ability of the ILs adopt the same criterion. This mole fraction of cellulose is much lower than the experimental solubility of cellulose reported in literature (Wang et al., 2012); therefore, the cellulose chain could be sufficiently dissolved in the ionic liquids. The mass fraction, box size and volume for each system were given in Table S1 (Supporting information).

A typical simulation process (Liu et al., 2006; Zhao, Liu, Wang, & Zhang, 2012) was used as follows. In NVE ensemble, a starting simulation was executed from a face-centered cubic lattice at a very low density and high temperature, typically 0.1 g cm^{-3} and 700 K. After a relaxation for a few MD steps to reduce the possible overlapping in the initial configuration, the Nose–Hoover (Martyna, Tuckerman, Tobias, & Klein, 1996) NPT ensemble simulation was performed. Descending from 700 K to the sampling temperature of 373.15 K, a series of NPT simulations were carried out under the standard atmospheric conditions. At the sampling temperature point, the system was equilibrated for at least 5 ns, and then the production phase was lasted for 3 ns. The conformations in trajectories were dumped with an interval of 20 fs for further analysis.

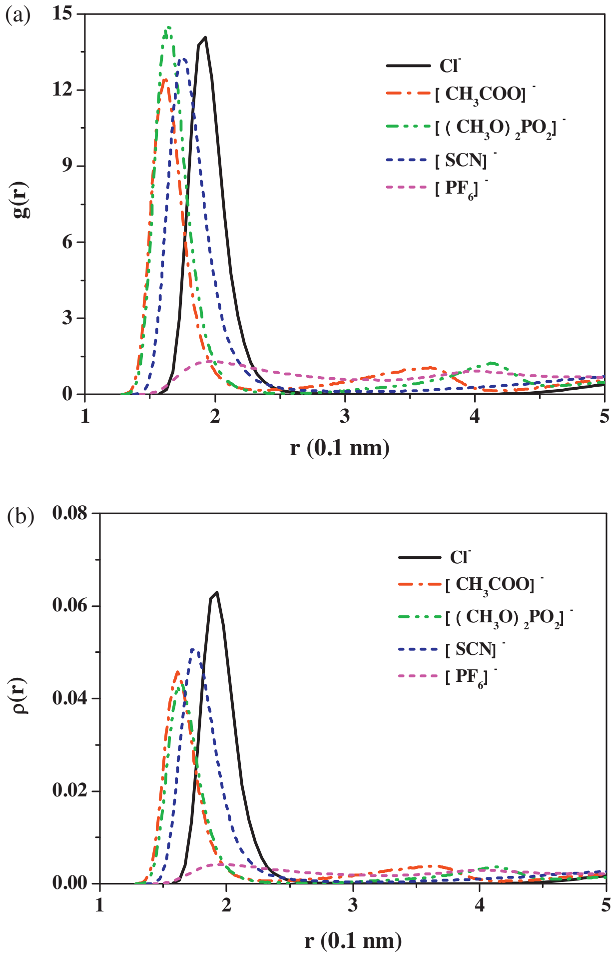


Fig. 1. The distribution of different anions around (O6) H of cellulose in the ILs-cellulose systems: (a) $g(r)$ and (b) $\rho(r)$.

3. Results and discussion

3.1. The effect of anionic structures on the dissolution of cellulose

To better understand the influence of nature of HB acceptors (anions) on the solubility of cellulose, five kinds of ILs with the same cation but different anions ([C_2mim]Cl, [C_2mim][CH_3COO], [C_2mim][$(CH_3O)_2PO_2$], [C_2mim][SCN] and [C_2mim][PF_6]) were chosen in the present work. Guo, Zhang, Duan, et al. (2010) and Guo, Zhang, & Liu (2010) reported that Cl^- anion, O atoms of $[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$, N atom of $[SCN]^-$ and F atom of $[PF_6]^-$ could form HBs with hydroxyl protons of cellulose. According to the structure of the anions, anion-cellulose HBs can be divided roughly into the following five types: (1) O—H···Cl, (2) O—H···O—C ($[CH_3COO]^-$), (3) O—H···O—P ($[(CH_3O)_2PO_2]^-$), (4) O—H···N ($[SCN]^-$), and (5) O—H···F ($[PF_6]^-$). In order to study the distribution of these anions around cellulose, site-site radial distribution functions (RDFs) were calculated. As the HBs were mainly formed by (O2) H, (O3) H and (O6) H of cellulose with different anions (Xu et al., 2010), the (O6) H was chosen as a representative hydroxyl proton of cellulose to analyse the RDFs of H proton and anions in these ILs-cellulose systems. Fig. 1a shows the RDFs of H—Cl (Cl^-), H—O ($[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$), H—N ($[SCN]^-$) and H—F ($[PF_6]^-$). It is clear that HBs were formed between anions of the ILs and hydroxyl protons of cellulose around the first peak position. The Cl, O, N and F atom of anions are HB acceptors, while hydroxyl protons are HB donors. The height of the first peak for $[PF_6]^-$ is significantly lower than that of the other four peaks, which means that only a few $[PF_6]^-$ anions formed HBs with cellulose. The positions of these peaks were estimated and the results were given in Table 1. These values represent the distance of the (O6) H proton of cellulose from the anions of ILs which has the largest probability around cellulose in the first solvation shell. It can be seen that the peak positions for the different HB types increase in the order: O—H···O—C ($[CH_3COO]^-$, 1.615 Å) < O—H···O—P ($[(CH_3O)_2PO_2]^-$, 1.645 Å) < O—H···N ($[SCN]^-$, 1.725 Å) < O—H···F($[PF_6]^-$, 1.875 Å) < O—H···Cl^- (Cl^-, 1.925 Å). This simulation result is in close agreement with that obtained from QM calculations (Guo, Zhang, Duan, et al., 2010; Guo, Zhang, & Liu, 2010).

Table 1
The max peak position of site-site RDFs in the first solvation shell.

IL	HB type	Peak position	QM result[18,31]
[C_2mim]Cl	O—H···Cl	1.925	2.073
[C_2mim][CH_3COO]	O—H···O—C	1.615	1.629
[C_2mim][$(CH_3O)_2PO_2$]	O—H···O—P	1.645	1.667
[C_2mim][SCN]	O—H···N	1.725	–
[C_2mim][PF_6]	O—H···F	1.875	1.838

To compare the local density of the HB acceptor around the H proton of cellulose in different ILs-cellulose systems, the concept of local density distribution $\rho(r)$ was proposed. Considering an atomic liquid, $\rho(r)$ at a distance r of a given particle is defined as $\rho g(r)$, i.e.

$$\rho(r) = \rho g(r) \tag{1}$$

here ρ is the average number density in the fluid which can be presented by $\rho = N/V$, and $g(r)$ is the radial distribution function. Thus, we have:

$$\rho(r) = g(r) \times \frac{N}{V} \tag{2}$$

The average number densities N/V for these systems are shown in Table S1 (Supporting information). Fig. 1b illustrates the average local density of the anions around cellulose as a function of distance r in the IL-cellulose systems. It is evident that the height of the first peak decreases in the order: Cl^- > $[SCN]^-$ > $[CH_3COO]^-$ > $[(CH_3O)_2PO_2]^-$ > $[PF_6]^-$. This suggests that the density of Cl^-, $[SCN]^-$, $[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$ anions is higher than that of $[PF_6]^-$ around cellulose.

To quantitatively study the strength of the interactions between these anions and cellulose, the interaction energies were calculated by averaging the energies in every time step, and the results were shown in Fig. 2a. Here, interaction energy of the anion with cellulose is the sum of electrostatic and Van de Waals energies, and stands for the interaction energy of anion with cellulose per mole of solution (IL + cellulose) at a given mole fraction. A comparison of the interaction energies reveal that the interactions of the anions with cellulose decrease in the order: Cl^- > $[CH_3COO]^-$ > $[(CH_3O)_2PO_2]^-$ > $[SCN]^-$ > $[PF_6]^-$. The ratio of anion–cellulose interaction energy to anion–cation interaction energy was also calculated to understand the balance between solute–solvent and solvent–solvent interactions. The results were given in Table S3, and it can be seen that the ratios of the systems containing Cl^-, $[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$ anions are higher than that of the systems containing $[SCN]^-$ and $[PF_6]^-$ anions. This suggests that the interactions of Cl^-, $[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$ anions with cellulose are stronger than $[SCN]^-$ and $[PF_6]^-$ anions. From the interaction energies between the anions and cellulose and their ratios to anion–cation interaction energies in the studied systems, it is clear that the dissolving capacity of [C_2mim]Cl, [C_2mim][CH_3COO] and [C_2mim][$(CH_3O)_2PO_2$] for cellulose are stronger than [C_2mim][SCN] and [C_2mim][PF_6].

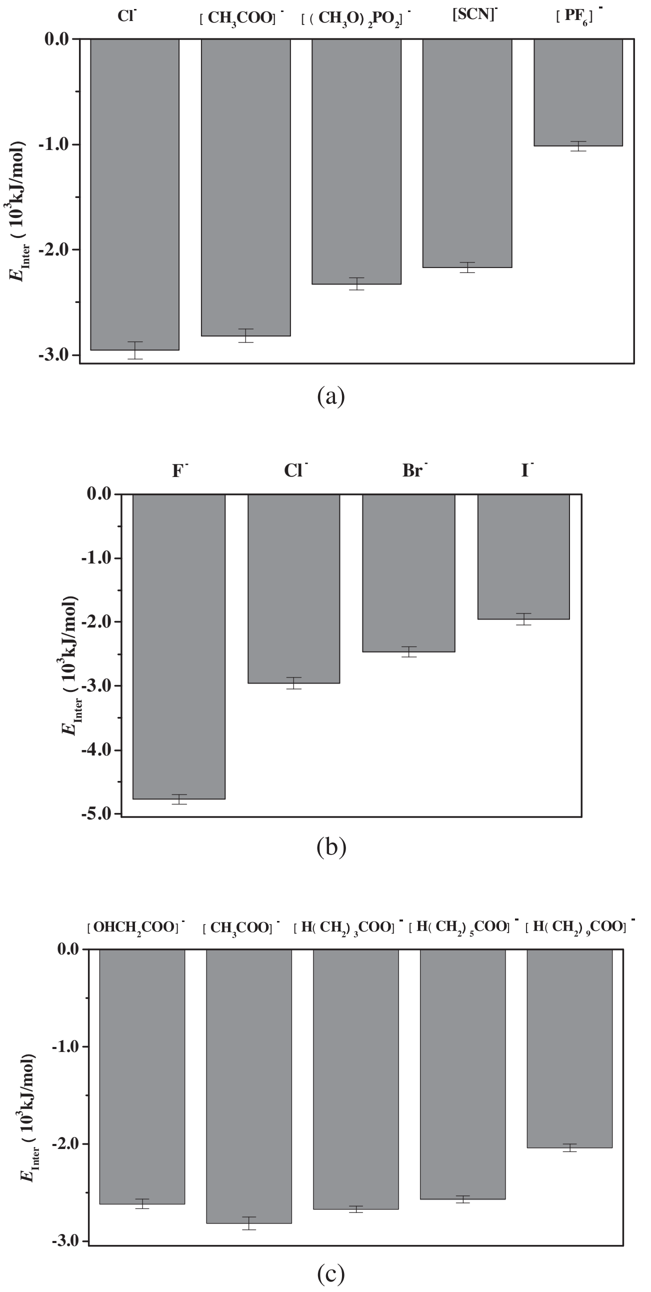


Fig. 2. The interaction energies of different anions with cellulose at 373.15 K.

Next, the average HB number formed between the anions and cellulose was calculated to investigate the HB accepting ability of the different anions. The criterion (Taylor & Kennard, 1982) for the formation of HBs was defined as: the distance from a donor hydrogen to an acceptor is less than 2.7 Å and the angle of acceptor–hydrogen–donor is larger than 150°. The average HB number for the anions with each —OH of cellulose was shown in Table 2. It is found that the HB number decreases in the order: $Cl^- > [CH_3COO]^- > [(CH_3O)_2PO_2]^- > [SCN]^- > [PF_6]^-$. From these results, we can see that the order of local density distribution is not the same as that of interaction energy and HB number. Though a lot of $[SCN]^-$ anions distributed around cellulose, the HB accepting ability of its N atom is weaker than that of Cl^- and O atoms of $[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$ because of the different electron densities for the five HB acceptors. The electrostatic potential surfaces for the anions were constructed to compare the densities of negative charges. From Fig. 3, it is clear that the most favorable sites of the anions (red regions) for proton attack are Cl, O ($[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$), N ($[SCN]^-$) and F ($[PF_6]^-$) where HBs can be formed with hydroxyl proton of cellulose. Obviously, the electron densities of N and F atoms are lower than the other HB acceptors, leading to the formation of weak HBs. This indicates that as an excellent IL for the dissolution of cellulose, its anion, as a HB acceptor, must have a high electron density in order to interact strongly with the hydroxyl proton of cellulose. Based on the above analysis, it is found that the HB accepting ability of the five HB types decreases in the order: O—H···Cl > O—H···O—C ($[CH_3COO]^-$) > O—H···O—P ($[(CH_3O)_2PO_2]^-$) > O—H···N ($[SCN]^-$) > O—H···F ($[PF_6]^-$).

Generally, the transport properties of ILs also influence the solvation of cellulose. To explore the mobility of the ions, self-diffusion coefficients of different ILs were calculated using the Einstein relation (Liu, Sale, et al., 2010; Liu, Zhou, et al., 2010):

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\langle|ri(t) - ri(0)|^2\rangle \tag{3}$$

The quantity in braces is the ensemble-averaged mean square displacement (MSD) of the molecules, and *ri* is the vector coordinate of the center of mass of ion *i*. Thus obtained values of self-diffusion coefficients for the ILs are given in Table S2. It is clearly indicated that the self-diffusion coefficients increase in the order: $Cl^- < [PF_6]^- < [(CH_3O)_2PO_2]^- < [CH_3COO]^- < [SCN]^-$. Therefore, although Cl^-, $[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$ are better HB acceptors as compared with $[SCN]^-$ and $[PF_6]^-$, diffusion of Cl^- is the slowest in these anions that may limit the dissolution efficiency of cellulose.

For a brief and qualitative comparison, the reported experimental solubility of cellulose in the ILs with $[C_2mim]^+$ and $[C_4mim]^+$ as cations was shown in Table 2. As recommended by Rogers co-workers (Wang et al., 2012), the cellulose solubilities in the ILs have been expressed by gram per mole of ionic liquid ($g\,mol^{-1}$). It can be seen that the experimental solubilities of cellulose in the ILs with Cl^-, $[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$ as anions are higher than those with $[SCN]^-$ and $[PF_6]^-$. This agrees well with our simulation results. Therefore, Cl^- anion and O atom of $[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$ are better HB acceptors, as they have high electron density in order to interact strongly with the hydroxyl proton of cellulose

3.2. The factors affecting the dissolution capacity of cellulose in the ILs

In this part, we will discuss the main factors that affect the HB formation ability of anions, such as electronegativity of the HB acceptor atoms, steric hindrance of the alkyl chains and electron-withdrawing property of chemical groups in the anions. Firstly, four simple monatomic anions F^-, Cl^-, Br^- and I^- were chosen to examine the effect of electronegativity of the HB acceptor atoms on the solubility of cellulose. The interaction energies and HB number between anions of the ILs and the hydroxyl protons of cellulose were calculated, and the results were shown in Table 2 and Fig. 2b. It is clear from Fig. 2b that the interaction energies are negative and their values increase in the order: $[C_2mim]F < [C_2mim]Cl < [C_2mim]Br < [C_2mim]I$. Considering the fact that the order of the electronegativity for these HB acceptor atoms is F > Cl > Br > I, these results suggest that the HB interactions between the anions and cellulose increase with increasing electronegativity of the HB acceptor atoms. The average HB number of the anions with per —OH of cellulose further demonstrates that HB formation ability of the HB acceptors would be expected to change reasonably with their electronegativity. Therefore, in the design of anions of ILs for the efficient dissolution of cellulose, the atom with stronger electronegativity should be chosen as the HB

Table 2
The number of HBs formed between the anions and each —OH of cellulose at 373.15 K and experimental solubility data available in literatures (Wang et al., 2012).

Anion	HB number (per —OH)	Experimental solubility with $[C_2mim]^+$cation (g mol^{-1} IL)	Experimental solubility with $[C_4mim]^+$cation (g mol^{-1} IL)
Cl^-	0.95	14.7–20.5[a] (373 K)	17.5–34.9[a] (373 K)
$[CH_3COO]^-$	0.94	13.6–25.5[a] (373 K)	23.8[a] (373 K)
$[(CH_3O)_2PO_2]^-$	0.91	23.6[b] (338 K)	–
$[SCN]^-$	0.71	–	9.9–13.8[c] (NM)
$[PF_6]^-$	0.39	–	Insoluble[c] (NM)
F^-	1.00	2.6[a] (373 K)	–
Cl^-	0.95	14.7–20.5[a] (373 K)	17.5–34.9[a] (373 K)
Br^-	0.85	1.9–3.8[a] (373 K)	4.4–4.6[a] (373 K)
I^-	0.70	–	2.7–5.3[a] (373 K)
$[CH_3COO]^-$	0.94	13.6–25.5[a] (373 K)	30.7[b] (343 K)
$[H(CH_2)_3COO]^-$	0.93	–	–
$[H(CH_2)_5COO]^-$	0.89	–	–
$[H(CH_2)_9COO]^-$	0.71	–	–
$[CH_3COO]^-$	0.94	13.6–25.5[a] (373 K)	30.7[b] (343 K)
$[OHCH_2COO]^-$	0.92	–	22.5[b] (343 K)

[a] Avicel.
[b] MCC.
[c] Pulp cellulose; NM: not mentioned.

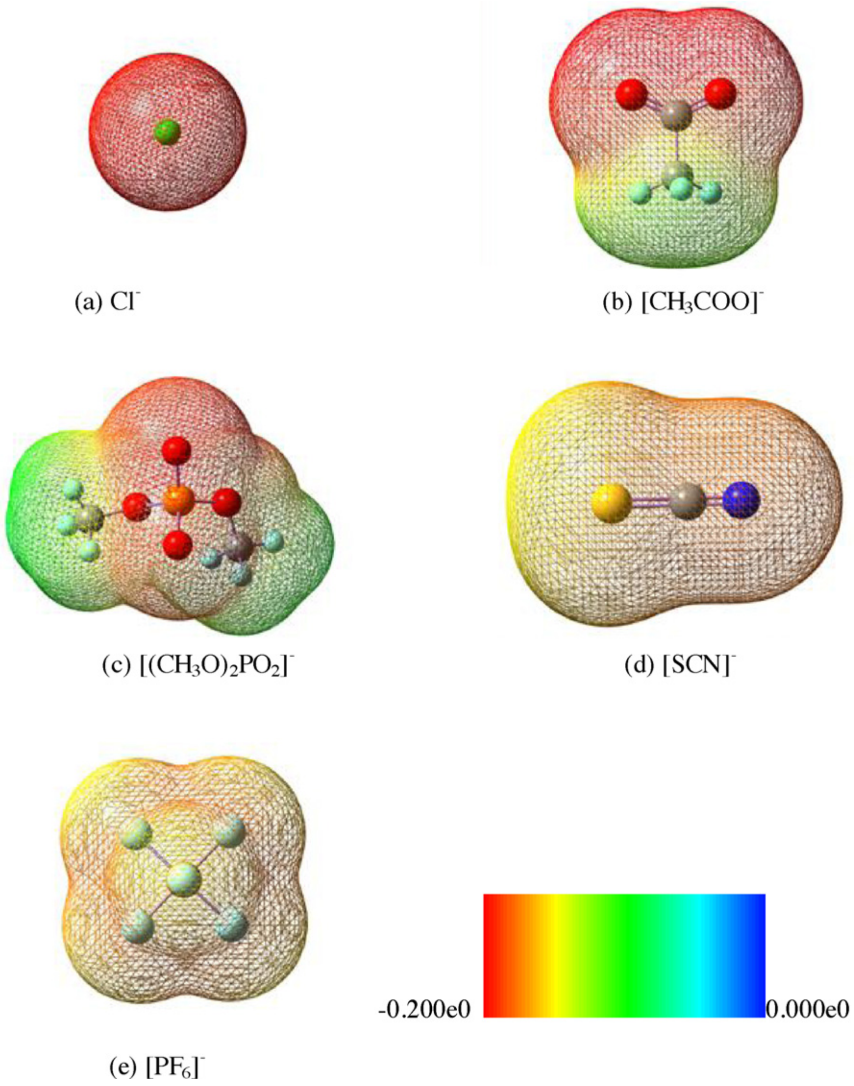
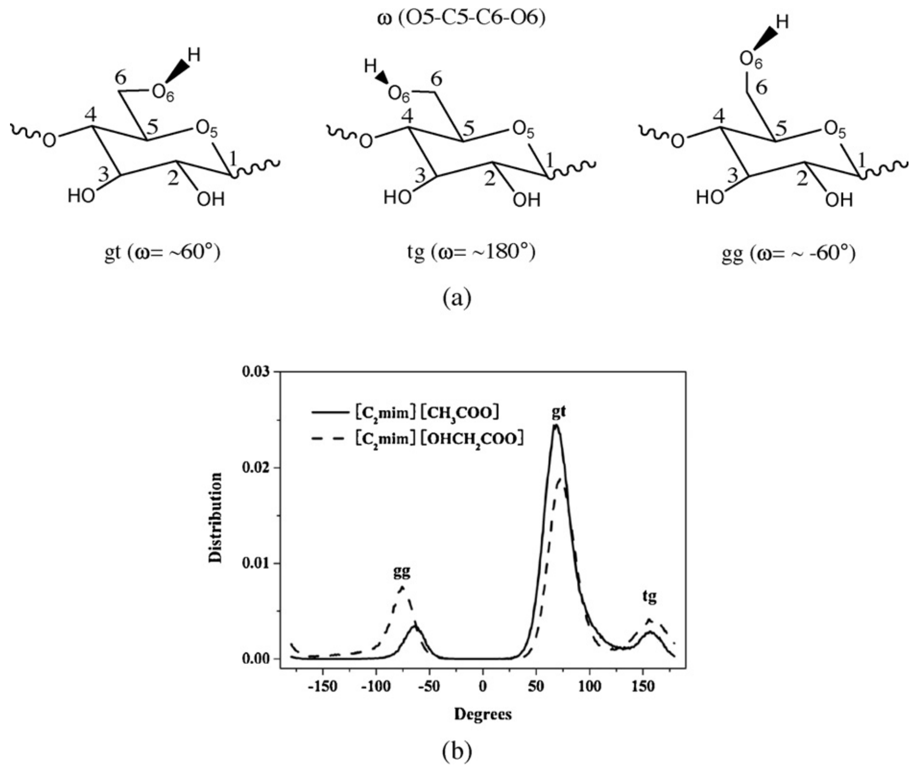

(a) Cl^-
(b) $[CH_3COO]^-$
(c) $[(CH_3O)_2PO_2]^-$
(d) $[SCN]^-$
(e) $[PF_6]^-$

Fig. 3. The electrostatic potential surfaces for the five optimized isolated anions at b3lyp/6-31++G** level where the red colors indicate the regions with more negative charges. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

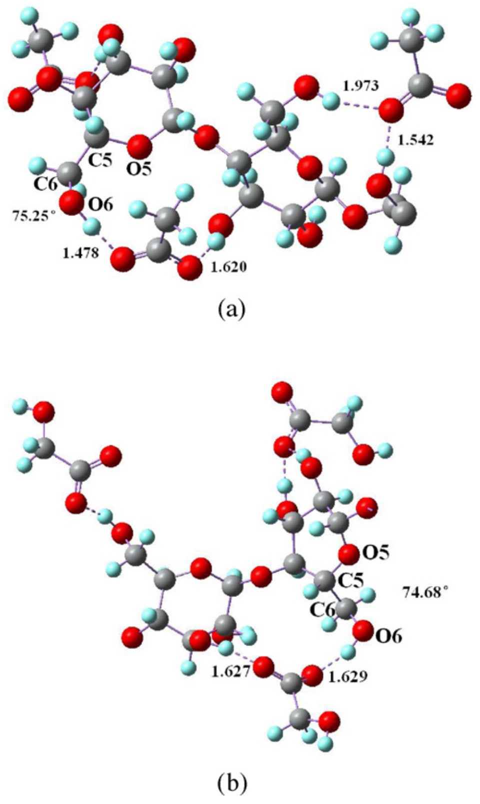


(a)

(b)

Fig. 4. The distribution of gt, tg and gg rotamers of glucose conformation for ω torsion angle.

acceptor atom. On the other hand, we can see from the experimental solubility data shown in Table 2 that the order of the dissolving ability of these anions for cellulose is $Cl^- > Br^- > I^- > F^-$. Obviously, the dissolving ability of $[C_2mim]F$ is out of prediction from our MD simulations. Actually, the related studies involving $[C_nmim]F$ are seldom in literature, mainly because their synthetic process is very complicated. This inconsistent result may be explained from impurities in this IL.



(a)

(b)

Fig. 5. Configurations for the interaction between the anions and cellulose extracted from the trajectory file: (a) $[CH_3COO]^-$ and (b) $[OHCH_2COO]^-$.

To understand the effect of alkyl chain length of anions of the ILs on the dissolution of cellulose, the interactions of cellulose with $[C_2mim][H(CH_2)_nCOO]$ ($n = 1, 3, 5, 9$) were also analyzed by calculating the interaction energies and the HB number. It was found from Fig. 2c that the interaction energies of these anions with cellulose decrease with increasing alkyl chain length. Furthermore, the HB number (Table 2) is also influenced by the alkyl chain length in a similar way. These results indicate that the anions with a longer alkyl chain may have a negative effect on the interaction between the HB acceptors and the hydroxyl protons of cellulose because of the steric effect. The same experimental conclusions have been reported for the effect of alkyl chain length of the anions (Abe et al., 2010) and imidazolium cations (Swatloski et al., 2002) on the cellulose dissolution ability.

A comparable investigation of $[C_2mim][CH_3COO]$ – cellulose and $[C_2mim][OHCH_2COO]$ – cellulose systems has been made to examine the effect of electron-withdrawing groups of the anions on the dissolution ability of ILs for cellulose. In this context, interaction energies and HB number between the anions and cellulose were calculated at 373.15 K, and the results were shown in Fig. 2c and Table 2. It is evident that the interaction energy of $[C_2mim][CH_3COO]$ with cellulose is lower than that of $[C_2mim][OHCH_2COO]$ with cellulose. This indicates that the interaction between anion and cellulose becomes weaker when the electron-withdrawing group such as —OH is added in the anion, leading to the reduced HB number.

It is known that the cellulose polysaccharide chains contain an additional rotatable bond, which may be characterized by the O5—C5—C6—O6 torsion angle (ω-angle). The orientations of the ω-angle mainly include three staggered rotamers (Fig. 4a): gauche–trans (gt), trans–gauche (tg), and gauche–gauche (gg)

(Kirschner & Woods, 2001). It can be seen from distribution of the three rotamers that the addition of any electron-withdrawing group decreases the population of the gt rotamer (Fig. 4b). We extracted a gt rotamer in both systems from the trajectory files, and the result was shown in Fig. 5. In this form of the rotamer, oxygen atom of the anion interacts with two hydroxys of cellulose. However, the distance between O atom of $[CH_3COO]^-$ and —OH of cellulose is closer than that in $[OHCH_2COO]^-$ – cellulose system. This suggests that the presence of an electron-withdrawing group tends to increase the distance between HB acceptor and —OH. This makes their electrostatic interaction to be weaker, leading to the drop of the population of the gt rotamer. Thus, the addition of electron-withdrawing group to anion can decrease the HB formation ability of the acceptor. This conclusion is in good agreement with our previously published experimental results (Xu et al., 2010) (Table 2).

4. Conclusions

In this work, the effect of anionic structures on the dissolution of cellulose in ILs was systematically investigated. It was found that the interactions of anions of the ILs with cellulose decrease in the order: $Cl^- > [CH_3COO]^- > [(CH_3O)_2PO_2]^- > [SCN]^- > [PF_6]^-$, suggesting that Cl^- and O atom of $[CH_3COO]^-$ and $[(CH_3O)_2PO_2]^-$ are better HB acceptors than N atom of $[SCN]^-$ and F atom of $[PF_6]^-$ because of higher electron density. Furthermore, the effects of electronegativity of the HB acceptor atoms, alkyl chain length and electron-withdrawing group of the anions on the dissolution ability of cellulose have been investigated. Guided by the analysis of these results, we can conclude that for the design of ILs used to dissolve cellulose efficiently, the following factors should be considered: (i) the HB acceptors of anions must have enough high electron density in order to interact strongly with H of hydroxyl in cellulose and the electronegativity of HB acceptor atom itself should be stronger, (ii) the alkyl chain of the anions would be shorter to decrease the steric hindrance effect, and (iii) any electron-withdrawing groups should be avoided in the anions. The above information is expected to be valuable for the design of novel ILs solvents used in the efficient dissolution of cellulose.

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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.2013.02.011.

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