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Cation does matter: How cationic structure affects the dissolution of cellulose in ionic liquids

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As a kind of promising solvents, ionic liquids (ILs) have been used to dissolve cellulose and great progress has been made in recent years. However, the dissolution mechanism, especially the role of cations of ILs in the dissolution of cellulose, is still in debate. In this work, 13 kinds of ILs with a fixed anion [CH₃COO]⁻ but varied cationic backbones and alkyl chains have been prepared and characterized. Solubilities of cellulose in these ILs were measured at different temperatures. This allows us to systematically study the effect of cationic structures on the cellulose dissolution at a given temperature. In order to investigate the dissolution mechanism, Kamlet-Taft parameters of these ILs in the temperature range from 25 to 65°C and ¹³C NMR spectra of 1-benzyl-3-methylimidazolium acetate ([phC₁mim][CH₃COO]) + cellulose systems at 90°C were also determined. It was found that acidic protons on the heterocyclic rings of the cations are essential for the dissolution of cellulose in the ILs, but the van der Waals interaction of cation with cellulose is not important. These protons may form C-H···O hydrogen bonds with hydroxyl and ether oxygen of cellulose to increase cellulose solubility. Cations of the ILs may also decrease cellulose solubility by strong interaction with anions or steric hindrance effect of large size group in their alkyl chains. These interactions together with strong O-H…O hydrogen bonds between the anion and hydroxyl protons of cellulose resulted in the disruption of the inter- and

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intra-molecular hydrogen bonds and thus effective dissolution of cellulose.

Introduction

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In recent years, a great effort has been made to search for alternative and sustainable energy sources because of the rapidly growing demand for energy and high speed depletion of fossil fuels. As the most abundant biopolymer on the earth, cellulose is regarded as one of the most important biorenewable resource for fuels, chemicals and materials.¹ However, it is very difficult to convert cellulose into biofuels because cellulose is recalcitrant toward dissolution due to its highly ordered structure.² Conventional cellulose dissolution processes require harsh conditions and use uncommon and expensive organic solvents which usually have the drawbacks of toxicity, volatility and difficulty in solvent recovery.³⁻⁵

As a new class of greener solvents, ionic liquids (ILs) bring a bright prospect for cellulose dissolution. It has been found that some ILs can dissolve cellulose under relatively mild conditions and the ILs can be easily recycled.⁶⁻¹³ Unlike traditional organic solvents, ILs have many unique properties such as negligible vapor pressure, non-flammability, wide liquid range, high chemical and thermal stability, and strong dissolution ability for various organic and inorganic materials.^{14,15} Moreover, physical and chemical properties of ILs can be easily modulated by designing structures of their cations and/or anions. Provided that the roles of the cations and anions in the dissolving process can be understood clearly, it is possible to design highly efficient ILs for cellulose dissolution by coupling suitable cations and anions. Therefore, understanding the dissolving process of cellulose in ILs is imperative for the rational design of highly efficient cellulose solvents.

Up to now, the dissolution mechanism of cellulose in ILs is still under debate. Most of the researchers suggest that anions of ILs play a predominant part in the dissolution by forming hydrogen-bonds with hydroxyl protons of cellulose, and the stronger the hydrogen bond basicity of the IL, the stronger the ability of the IL to dissolve cellulose.¹⁶ As far as the role of the IL cation in the dissolution of cellulose is concerned, contradictory results have been reported. For example, Rogers *et al.*^{17,18} used NMR spectroscopy to study the mechanism of carbohydrates dissolution in 1-n-butyl-3-methylimidazolium chloride ([C₄mim]Cl),

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([C₂mim][CH₃COO]). It was shown that ¹³C and ^{35/37}Cl relaxation rates of acetate and chloride anions had a strong dependence on carbohydrate content. Conversely, there were only slight variations in the relaxation rates of carbon nuclei of the IL cations. Thus they concluded that the interactions between the IL anions and the carbohydrates are the main driving force in the dissolution, while the interactions between the IL cations and the solutes are nonspecific. By

using neutron scattering, NMR and molecular dynamics simulations, Youngs et al.^{19,20} investigated β-D-glucose dissolved in [C2mim][CH3COO] and 1,3-dimethylimidazolium chloride $([C_1mim]C])$. They also suggested that the principal interactions in the liquids are the hydrogen-bonding interactions between anions of the ILs and hydroxyl groups of glucose, and the cations have only a minor van der Waals interaction with the sugar. In the investigation of dissolution mechanism of cellobiose in [C₂mim][CH₃COO] by NMR spectroscopy under various solute concentrations and temperatures, Zhang and coworkers²¹ found that both anion and cation of the IL formed hydrogen bonds with the hydroxyl groups of cellobiose. The acetate anions prefer to form hydrogen bonds with hydroxyl protons in cellobiose, while protons of the cations, especially the most acidic H2 proton, interacted directly with the oxygen atoms of hydroxyls in cellobiose. When all the hydroxyls of cellobiose were acetylated, the interactions between cellobiose octa-acetate and the IL become very weak, and the acetylated cellobiose was almost insoluble in this IL even at 100°C. This indicated that hydrogen bonding of anion and cation with cellobiose was the major driving force for cellobiose dissolution in this system. However, based on the analysis for the interactions involved in cellulose dissolution process, Lindman et al.²² proposed that hydrophobic interactions between cations of ILs and cellulose (both are amphiphilic) are the predominant factor. Actually, literature survey reveals that almost all the previous investigations were focused on

the anionic action of ILs in cellulose dissolution, and very few studies have been conducted to investigate the cationic effect of ILs. In this work, 13 kinds of ILs have been prepared which have a fixed anion [CH₃COO]⁻ but varied cationic backbones and alkyl chains such as 1-butyl-3-methylimidazolium $[C_4 mim]^+$, 1-methoxyethyl-3-methylimidazolium $[C_1 O C_2 mim]^+$, $[C_2OHmim]^+$, 1-hydroxyethyl-3-methylimidazolium 1-butyl-2,3-dimethylimidazolium

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View Article Online N-ethyl-N-methyino101936436441733F $[phC_1mim]^+$, $[C_4 dmim]^+$ 1-benzyl-3-methylimidazolium $[C_2 mmor]^+$, N-allyl-N-methylmorpholium $[C=C_2 mmor]^+$ N-allyl-N-methylpiperidium $[C=C_2mpip]^+$, N-butyl-N-methylpiperidium $[C_4 mpip]^+$, N-butyl-N-methylpyrrolidinium $[C_4 mpyr]^+$, 1-butyl-3-ethylbenzimidazolium $[C_4 ebim]^+$, 1,3-diethylbenzimidazolium $[C_2 ebim]^+$, and 1-butyl-3-ethylbenzotriazolium $[C_4ebt]^+$. Solubilities of microcrystalline cellulose (MCC) in these ILs were determined at different temperatures, and the effect of cationic structure on cellulose solubility was examined. In order to obtain new insight into the possible dissolution mechanism, Kamlet-Taft parameters for some of the ILs in the temperature range from 25 to ^{13}C 65 °C NMR [phC₁mim][CH₃COO] and spectra for and cellulose in [phC₁mim][CH₃COO]+cellulose mixtures at 90°C were also measured experimentally. The results have been discussed from hydrogen bond donor ability, hydrogen bond acceptor ability, polarizability of the ILs, and ¹³C NMR chemical shifts of the representative IL and cellulose.

Results and discussion

Chemical structures of cations and anion of the ILs prepared in the present work were shown in Scheme 1. All the ILs were characterized by ¹H NMR. Melting point (T_m) and glass transition temperature (T_g) of these ILs were determined by differential scanning calorimetry (DSC). Their thermal decomposition temperatures (T_d) were determined by thermogravimetric analysis (TGA). It was shown that the prepared ILs are all room temperature ILs and have reasonable thermal stability. The detailed spectral and thermal property data were given in Table S1 of Electronic Supplementary Information (ESI).

It has been reported that impurity contents in ILs may have a significant effect on their physical and chemical properties.²³ Considering the fact that in the synthesis process of our ILs, the main impurities would be water, halides and un-reacted organic starting materials such as 1-metheylimidazole, we determined the contents of these impurities in the ILs, and the detailed data were given in Table S2 (ESI). It can be seen that water content in these ILs was in the range of 300 - 600 ppm, chloride content varied from 0.0082 to 0.015 molkg⁻¹, and bromide content fell between 0.00028 molkg⁻¹ and 0.0030 molkg⁻¹. However, the content of the un-reacted 1-methylimidazole was found to be smaller than the detection limit of gas chromatograph. These

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results suggest that the quality of the ILs prepared in this work is reliable to investigate USHARSE1733F dissolution.

Cationic structure dependence of cellulose solubility

Table 1 shows the solubility data of microcrystalline cellulose in the studied ILs as a function of temperature. The cellulose used in the present work has a viscosity-average polymerization degree of 229. It was found that our solubility data of cellulose in $[C_4mim][CH_3COO]$ were in good agreement with the values reported by Xu *et al.*,⁸ although they used the unit of wt% to express cellulose solubility. Vitz *et al.*²⁴ also determined the solubility of cellulose in $[C_4mim][CH_3COO]$ at 100°C, but their value (24 g/mol) was significantly smaller than ours (54 g/mol). The most probable reason is that the cellulose (Alfa Aesar) we used is the same (same source and same polymerization degree) as that used by Xu *et al.*,⁸ however, different cellulose (Avicel PH-101, Fluka) was used by Vitz *et al.*²⁴ To the best of our knowledge, no solubility data of cellulose in the other ILs investigated in this work has been reported in literature.

It is evident from Table 1 that cationic backbone of the ILs plays a crucial role in the cellulose dissolution. The imidazolium-based ILs (1-5) can readily dissolve cellulose with high solubility, some of the ILs with the cations of saturated heterocyclic ring (6-8) only have a certain extent of ability to dissolve cellulose at higher temperature, but all the other ILs (9-13) fail to dissolve cellulose even at the temperature of 120°C. For example, although [C₄mim][CH₃COO] (1), $[C_4 mpip][CH_3COO]$ (9) and $[C_4 mpyr][CH_3COO]$ (10) have the same cationic side chain, solubility of cellulose in these ILs decreased dramatically with their cationic backbones. At 90°C, solubility of cellulose in [C4mim][CH3COO] is as high as 49 g/mol, whereas that in [C₄mpip][CH₃COO] and [C₄mpyr][CH₃COO] is negligibly small. This finding may be understood from the fact that compared with the saturated piperidium and pyrrolidinium cations $([C_4mpip]^+ \text{ and } [C_4mpyr]^+)$, the conjugated imidazolium cations $[C_4mim]^+$ have acidic protons (H2, H4 and H5). Thus it is favorable for the more acidic proton to form hydrogen bonds with oxygen atoms of cellulose. This property of acidic proton in cationic backbones has been confirmed by comparing the solubility of cellulose in [C₄dmim][CH₃COO] (4) with that in [C₄mim][CH₃COO] (1). It was found that the solubility of cellulose in [C₄dmim][CH₃COO] was significantly decreased owing to the replacement of acidic H2 in $[C_4 mim]^+$ cation by a methyl

unit –CH₃. For example, solubility of cellulose in $[C_4mim][CH_3COO]$ is 25 g/m@Pat@30⁹C³GA^{1733F} only 5 g/mol is observed in $[C_4dmim][CH_3COO]$. Furthermore, the disability of $[C_4ebim][CH_3COO]$ (11), $[C_2ebim][CH_3COO]$ (12) and $[C_4ebt][CH_3COO]$ (13) for the dissolution of cellulose may be interpreted from the absence of acidic proton in the cationic backbone or the big steric hindrance in the bulky benzimidazolium and benzotriazolium cations which makes the cations difficult to access the oxygen atoms of cellulose.

It is also noted that nature of the functional groups bonded to the N-position in cationic backbone obviously affects the solubility of cellulose. For instance, replacement of $-C_4H_9$ in $[C_4 \text{mim}]^+$ by $-CH_2CH_2OCH_3$ and $-CH_2CH_2OH$ results in a decrease in cellulose solubility (see Table 1). This may be ascribed to the donating electron nature of $-OCH_3$ and -OH groups, which reduces the acidity of protons in cationic heterocyclic rings. As evidenced by α and β parameters and density functional calculations of Deng and coworkers,²⁵ hydroxyl proton of -CH₂CH₂OH may form hydrogen bond with oxygen of the anion, leading to the competition with the formation of hydrogen bond between anion and hydroxyl proton of cellulose. On the other hand, replacement of $-C_4H_9$ in $[C_4mim]^+$ by $-CH_2C_6H_5$ also leads to a decrease in cellulose solubility. This suggests that van der Waals interactions of ILs cations with cellulose are not important for cellulose dissolution. The insolubility of cellulose in [C₄ebim][CH₃COO] (11), the $[C_2ebim][CH_3COO]$ (12) and $[C_4ebt][CH_3COO]$ (13) strongly supports this suggestion. In addition, we found that at higher temperature (say 100°C), both [C=C₂mmor][CH₃COO] (7) and $[C=C_2mpip][CH_3COO]$ (8) can dissolve cellulose, but the solubility in $[C=C_2mmor][CH_3COO]$ is much higher than that in $[C=C_2mpip][CH_3COO]$. This might suggest that morpholium cation may have a stronger interaction with cellulose than piperidium cation although they all have saturated six-membered ring.

Based on the above analysis, it is reasonable to state that acidic protons in cationic backbones are indispensable for the dissolution of cellulose in ILs. Among the cations investigated here, imidazolium cation is the best for the dissolution of cellulose, in which acidic proton is involved in hydrogen bonding interactions between the cations and cellulose. However, the van der Waals interactions of ILs cations with cellulose are not important for the cellulose dissolution. For the rational design of efficient IL solvents for cellulose, cationic backbone with strong acidic protons

but without high electronegativity atoms (say oxygen atom) and bulky steric hindrane ogroups of A1733F the side chain should give top priority.

Effects of hydrogen bond acidity, hydrogen bond basicity and dipolarity / polarizability of the ILs on the solubility of cellulose

In order to study the microscopic mechanism for the cationic structure effect in cellulose dissolution, hydrogen bond acidity, hydrogen bond basicity and dipolarity / polarizability for 6 kinds of ILs which can efficiently dissolve cellulose, were determined in the temperature range from 25 to 65°C, and the results were included in Table 2. Unfortunately, we are unable to determine these parameters for the other ILs because they are generally not liquids within the investigated temperature range.

It is known that the most common method to describe the hydrogen bond acidity, hydrogen bond basicity and dipolarity / polarizability of ILs is the Kamlet-Taft equation:²⁶

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \tag{1}$$

where XYZ stands for a reaction rate or equilibrium constant, or a position or intensity of spectral absorption, XYZ₀ is a constant, α , β and π^* represent hydrogen bond acidity, hydrogen bond basicity and dipolarity / polarizability of ILs, respectively, and a, b and s are solvent-independent correlation coefficients. It can be seen from Table 2 that the temperature dependence of α parameter is much stronger than β and π^* parameters because of the strong thermochromism of the standard betaine dye in solution.²⁷ With increasing temperature, the β and π^* parameters keep invariable, whereas a good linear relationship exists between α parameter and the reverse of temperature (Figs S1–S3, ESI). Thus, values of α parameter at other temperatures can be calculated from this linear relationship.

To investigate the correlation between cellulose solubility and Kamlet-Taft parameters of the ILs, we used natural logarithm of the solubility (lnS) as XYZ in the Kamlet-Taft linear solvation free energy relationship (equation 1) and performed a multivariate linear regression²⁸ to determine the coefficients for the variables { α , β , π^* }. Using *p*-value as a test of significance, a maximum *p*-value (*p*<0.05) was set to indicate it. When a multivariate linear regression was

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$$\ln S = 3.82(0.32) + 1.91(0.17)^* \alpha + 1.97(0.13)^* \beta - 3.19(0.26)^* \pi^*$$
(2)

performed at 90°C using all variables { α , β , π^* }, we obtain:

The italic numbers in the parentheses present the *p*-values for each coefficient. It can be seen that no coefficient proved significant. Then, we performed a regression using each pair of variables in the three pairs $\{\alpha, \beta\}$, $\{\alpha, \pi^*\}$ and $\{\beta, \pi^*\}$, and the following equations were found:

$$\ln S = -0.48(0.68) + 3.21(0.0054)^* \alpha + 2.21(0.10)^* \beta$$
(3)

$$\ln S = 7.26(0.18) + 1.13(0.44) * \alpha - 4.16(0.30) * \pi *$$
(4)

$$\ln S = 9.41(0.011) + 1.54(0.26)^* \beta - 7.12(0.0094)^* \pi^*$$
(5)

Again there is not a relationship contained all significant coefficients, so we must test all three variables $\{\alpha\}$, $\{\beta\}$ and $\{\pi^*\}$ individually. Under these circumstances, we have:

$$lnS = 2.00(0.0020) + 2.97(0.0089)^* \alpha$$
(6)
$$lnS = 2.64(0.52) + 0.60(0.87) * \beta$$
(7)
$$lnS = 10.81(0.0016) - 6.89(0.0062)^* \pi^*$$
(8)

It is clear that the relationship presented by equation (6) contains all significant coefficients. This indicates that the solubility of cellulose depends on $\{\alpha\}$. As far as π^* parameter is concerned, because the range of its values is quite narrow (see Table 2), it is not safe to state that lnS has a linear correlation with π^* parameter, although the relationship (8) also contains all significant coefficients. Moreover, the relationship (7) does not contain any significant coefficients, indicating that β parameter is an insignificant variable in the present work. Similar results have been obtained at other temperatures under study.

It has been known that α parameter can be used as a measure of hydrogen bond donor ability (hydrogen bond acidity) of ILs and depends on the cationic structure.²⁹ A larger α parameter value indicates a stronger hydrogen bond acidity. It was noted from equation (6) that lnS has a linear correlation with α parameter, and cellulose solubility increases with the increase of α parameter of the ILs. Fig. 1 shows such a linear correlation at 90°C, and the same trend was observed at the other temperatures (Figs S4-S8, ESI). Considering the donor and acidity characteristics, this suggests that cations of the ILs may affect the cellulose solubility by forming hydrogen bonds with hydroxyl or ether oxygen of cellulose. The stronger the hydrogen bond acidity of IL cation, the stronger of its ability to form hydrogen bond with cellulose. This confirms the analysis of

experimental results discussed in the previous section.

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The β parameter has been established as a measure of the hydrogen bond accepting ability (hydrogen bond basicity) of ILs.^{30–32} To our knowledge, β parameters for most of the ILs investigated in the present work are not available in the literature. Therefore, we determined these parameters and the results were given in Table 2 as a function of temperature. It can be seen from the above linear regression analysis (eq. 7) that there has no correlation between solubility of cellulose and β parameter of the ILs at a given temperature. Considering the fact that these ILs have the same anion [CH₃COO]⁻, this suggests that the hydrogen bond accepting ability of these ILs is essentially controlled by their anion, and the ability of their cations to accept acidic protons for the formation of hydrogen bonds is very weak. The possible reason for the unusual behavior observed for [C₂OHmim][CH₃COO] is that the terminal hydroxyl proton in the alkyl chain of this IL forms hydrogen bond with the anion, lowering the hydrogen bond accepting ability of the anion for the hydroxyl protons of cellulose.^{25,33} Similar result has been reported for [C₂OHmim][(CH₃)₂PO₄] by Ohno and his coworkers.³⁴ Therefore, it is easy to understand why solubility of cellulose varies significantly with β values of the ILs which have the same cation but different anions.⁸

The π^* value of the ILs derives from two cumulative effects: ion pairing strength and polarizability of the cation and anion.²⁹ A large π^* value means strong interaction or strong association between cation and anion in the IL. It seems likely from equation (8) and Tables 1-2 that cellulose solubility roughly decreases with the increase of π^* parameter of the ILs at a given temperature although we are not sure if the variation is linear because of the reason mentioned above. This suggests that capacity of the ILs to dissolve cellulose decreases with the enhanced interaction between cation and anion of the ILs because the stronger cation-anion interactions in the ILs would decrease the self-diffusion ability of the ions, thus decreasing the possibility of hydrogen bond interaction of cellulose with anions and/or cations. On the other hand, for the ILs with the same anion, the increase in the delocalization degree of positive charges around the cationic ring will result in the increase of polarizability of the cation and the decrease of Coulomb interaction strength between cation and anion of the ILs, leading to the decrease of π^* values. Thus cations with highly delocalized positive charge would be preferred in the design of ILs for

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efficient dissolution of cellulose.

From the above discussion, it is clear that for the investigated ILs, β parameter is mainly dependent on anionic structure, whereas α parameter is cation dependence. Cations can affect solubility of cellulose in the ILs in two ways: (i) acidic proton in the cationic heterocyclic rings forms hydrogen bonds directly with oxygen of cellulose, resulting in the increase of cellulose solubility; (ii), polarizability of the cation and its ion pairing strength with anion affect solubility of cellulose indirectly by influencing the ability of the IL anion to form hydrogen bonds with cellulose, high polarizability and weak ionic association would benefit the dissolution of cellulose in the ILs.

Interaction between cellulose and [phC₁mim][CH₃COO] and the possible dissolution mechanism

In order to further investigate the dissolution mechanism of cellulose in the ILs, ¹³C NMR measurements of $[phC_1mim][CH_3COO]$ and cellulose were carried out in the solutions of $[phC_1mim][CH_3COO]$ + cellulose at 90°C, and the NMR data were given in Table 3 and Table 4, respectively. For the sake of easy understanding, the schematic structure and numbering of C atoms in $[phC_1mim][CH_3COO]$ were shown in Fig. 2.

It is noted from Table 3 that with the increase of cellulose concentration, the signal of C2 atom of the imidazolium ring moves upfield (a decrease of chemical shift), whereas that of the carboxyl C15 atom downfield (an increase of chemical shift) significantly. This indicates that in the cellulose dissolution, the acidic H2 proton in imidazolium cation most probably interacts with the oxygen atoms in cellulose through hydrogen bonding, which leads to an increase of the electron cloud density of the C2, and thus an upfield chemical shift. Simultaneously, as a hydrogen bond acceptor, the oxygen atom in $[CH_3COO]^-$ of the IL forms hydrogen bond with the hydroxyl proton of cellulose. This results in the decrease of the electron cloud density of the C15, thus its chemical shift moves downfield. Moreover, it can be seen that the downfield shift value of C15 was greater than that of C2, indicating that the carboxyl oxygen atom has stronger interaction with cellulose than H2 proton. In addition, the observable but small upfield shift of C14 may be due to the redistribution of the electron cloud density around the carboxyl group after the interaction between carboxyl oxygen and hydroxyl proton. However, little changes have been

found for the chemical shifts of the other carbon atoms (C4-C13) in the imidazoium cation?/CF4451733F reveals that the interactions of the oxygen in cellulose with the C4 and C5 protons on the imidazolium ring are very weak, which is in agreement with the weak acidity of these protons. Also, this is an indicative for the very weak interaction between cellulose and the benzene unit in the IL cation.

Moreover, it can be seen from Table 4 that the increase of cellulose concentration results in the upfield shifts for C3 and C6 atoms, but downfield shifts for C1, C2 and C5 atoms in cellulose. It is generally accepted that the interaction network of cellulose consists of three components: intrachain, interchain and intersheet interactions, which contribute to the recalcitrance of cellulose to chemicals or enzymes.^{35,36} O(3)-H···O(5) and O(2)-H···O(6) hydrogen bonds were formed between neighboring residues of the same chain (intrachain), while O(6)-H···O(3) hydrogen bonds were formed at different chains in the same sheet (interchain) (Fig. 3). At the same time, numerous C-H...O contacts and van der Waals interactions connect the residues on neighboring sheets (intersheet).³⁷ In the dissolution process of cellulose in [phC₁mim][CH₃COO], the hydrogen bonding interactions of the oxygen on the carboxyl group of [CH₃COO]⁻ with the proton of the C3-OH and C6-OH units in cellulose disrupt the inter- and intra-chain hydrogen bonds in cellulose, and thus resulting in an increase of the electron cloud density of the C3 and C6 in cellulose and an upfield shift of their ¹³C signals. Meanwhile the acidic protons on the imidazolium cations, especially the H2 proton, interact with the C2-OH and the ether oxygen O, and disrupt the intersheet C-H...O bonds in cellulose, which leads to the decrease in the electron cloud density of the C1, C2 and C5 atoms in cellulose. Consequently, the ¹³C NMR signals of these carbon atoms shift downfield. These results are consistent with the conclusions drawn from molecular dynamic (MD) simulation.^{38,39}

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From the above analysis, it is evident that both the cation and anion of the IL play important roles in the cellulose dissolution. The anion of the IL forms hydrogen bonds with the hydroxyl proton of cellulose, while the acidic protons on the imidazolium cation contact with the hydroxyl oxygen and ether oxygen in cellulose through weak hydrogen bond C-H···O interactions. The

hydrogen bonding interactions of the hydroxyl protons of cellulose with anion of the IL were than those of the hydroxyl oxygen and ether oxygen of cellulose with protons on the IL cations. However, the contribution from cations of the ILs is indispensible although the role of their anion is predominant in the cellulose dissolution process.

Conclusions

In this work, 13 kinds of ILs which have the same $[CH_3COO]^-$ anion but varied cationic backbones and substituent groups have been prepared and characterized to investigate how the cations of the ILs affect cellulose dissolution. It was found that cations of the ILs significantly affect cellulose dissolution. Acidic protons of their cations may form C-H...O hydrogen bonds with hydroxyl oxygen and ether oxygen of cellulose to increase cellulose solubility. These cations may also decrease cellulose solubility by strong association with anions, existence of high electronegativity atoms (like oxygen and/or nitrogen) in the cationic backbone or large sized group (like phenyl group) in the alkyl chain. These factors decrease the ability of anion and cation to form hydrogen bonds with cellulose by anionic competition or steric hindrance. Thus the dissolution of cellulose was determined by both the anion and the cation of the ILs. Depending on the structures of ILs, sometimes the anions predominate and sometimes the cations do. For example, if there is a big steric hindrance group in the alkyl chain and/or there is not an acidic proton in the cationic backbone, it is very difficult for the ILs to dissolve cellulose. Therefore, to design ILs with efficient dissolution capacity for cellulose, anions with strong hydrogen bond basicity and cations with acidic protons but without high electronegativity atoms (like oxygen and/or nitrogen) in the cationic backbone and large sized group in the alkyl chain would be a rational choice. The above findings provide new insight into the role of cationic structure of ILs in cellulose dissolution, and would be useful for the rational design of ILs used in the highly efficient dissolution of cellulose. Nonetheless, duo to the narrow range of π^* values of the ILs investigated in this work, the correlations of cellulose solubility with π^* and $\{\alpha, \pi^*\}$ cannot be determined definitely. More data are needed to confirm these correlations.

Experimental

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Materials

1-Methylimidazole (99%) was purchased from Shanghai Chem. Co., and 1,2-dimethylimidazole (98%), N-methylmorpholine (99%), benzimidazole (99%), bromoethane (98%), 1-chlorobutane (99%), 2-chloroethyl methyl ether (98%), 4-nitroaniline (97.0%), microcrystalline cellulose and anion exchange resin (Ambersep 900 (OH), Amberlite IRA-400 (Cl)) were from Alfa Aesar. 1-Methylpiperidine (97%), 1-methylpyrrollidine (98%), 1H-benzotriazole (99%), allyl chloride (98%), benzyl chloride (AR) and tetrabutyl ammonium bromide (98%) were obtained from Aladdin Chem. Co. Ltd. 2,6-Dichloro-4-(2,4,6-triphenyl-1-pyridinio) phenolate (≥97.0%) were purchased from Sigma-Aldrich. 2-Chloroethanol (AR) and acetic acid (>99.5%) were obtained from Shanghai Shiji Chem. Reagent Co. Ltd. N.N-diethyl-4-nitroaniline (97.0%) and deuterated DMSO (DMSO-d₆) were from Nanjing Chemlin Chem. Industrial Co. Ltd. and Oingdao Weibo Tenglong Technol. Co. Ltd., respectively. Among the above materials, 1-methylimidazole was distilled, microcrystalline cellulose was dried under vacuum for 12h at 70°C, 4-nitroaniline was recrystallized from methanol and then dried under vacuum for 12h at 40°C before use, and the others were used as received. The viscosity-average polymerization degree of 229 was determined for the cellulose by Ubbelohde viscometer in cupriethylenediamine hydroxide solutions.

Synthesis of the ILs

The imidazolium-based ILs [C₄mim][CH₃COO], [phC₁mim][CH₃COO], [C₁OC₂mim][CH₃COO], [C₂OHmim][CH₃COO] and [C₄dmim][CH₃COO] were synthesized from 1-methylimidazole and corresponding chloralkanes by using the procedures described in the literature.⁸ [C₄mpip][CH₃COO], [C=C₂mpip][CH₃COO] and [C₄mpyr][CH₃COO] were also prepared by a similar way.

 $[C_2mmor][CH_3COO]$ was synthesized by fellowing the procedure reported by Yeon.⁴⁰ In a typical procedure, 1-bromoethane (0.22 mol) was added dropwise to a round-bottom flask containing N-methyl morpholine (0.2 mol) and acetonitrile (100 ml) at room temperature, and the mixture was stirred for 72h to produce a pale yellow solid. This solid was then recrystallized with acetone at room temperature to obtain $[C_2mmor][Br]$ (white solid). Aqueous $[C_2mmor][OH]$

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solution was obtained by passing an aqueous $[C_2mmor][Br]$ solution through a column fitted with 1733F anion exchange resin (Ambersep 900 (OH)). Then the aqueous $[C_2mmor][OH]$ solution was neutralized with equal mole of acitic acid. Water in the solution was removed by rotary evaporation and $[C_2mmor][CH_3COO]$ was then dried under vacuum for 72h at 60°C. $[C=C_2mmor][CH_3COO]$ was prepared by the same procedure.

[C₄ebim][CH₃COO], [C₂ebim][CH₃COO] and [C₄ebt][CH₃COO] were synthesized by the following steps: (i) the synthesis of 1-ethylbenzimidazole or 1-Butylbenzotriazole; (ii) the synthesis of [C4ebim][C1], [C2ebim][Br] and [C4ebt][Br];^{41,42} and (iii) the synthesis of [C4ebim][CH3COO], [C2ebim][CH3COO] and [C4ebt][CH3COO]. For example, for the synthesis of [C₄ebim][CH₃COO], benzimidazole (bim, 0.3mol) and tetrabutyl ammonium bromide (2% mole percent of bim) were dissolved in an aqueous solution of 30% sodium hydroxide (100ml) under vigorous stirring, then bromoethane (0.3mol) was added dropwise at room temperature. After the dropping was finished, the mixture was stirred at 50°C for 24h until two phases were formed. Then the upper organic phase was separated and washed with deionized water and ethyl acetate. The remaining ethyl acetate was removed by rotary evaporation to give 1-ethylbenzimidazole. Then 1-ethylbenzimidazole and 1-chlorobutane were mixed (molar ratio 1:1.05) in a round bottom flask, and stirred at 70°C for 72h. The gray solid product [C₄ebim][Cl] was collected and washed repeatedly with ethyl acetate and then dried under vacuum at 60°C for 48h. Finally, the aqueous $[C_4ebim][CH_3COO]$ solution was prepared by passing an aqueous [C₄mim][Cl] solution through a column filled with CH₃COO⁻ anion exchange resin (obtained by exchanging Amberlite IRA-400(Cl) with aqueous CH₃COONa solution). Removing water in the solution by rotary evaporation, the product [C4ebim][CH3COO] was collected and dried under vacuum at 60°C for 24h. [C₂ebim][CH₃COO] and [C₄ebt][CH₃COO] were prepared by similar procedures.

Characterization of the ILs

All the ILs prepared in this work were characterized by ¹H NMR spectroscopy at room temperature on a Bruker Avance-400 NMR spectrometer. Melting temperature (T_m) and glass transition temperature (T_g) of the ILs were determined using a differential scanning calorimeter (Netzsch DSC 204F1) at a cooling and heating rate of 10°C min⁻¹ under dry N₂ atmosphere. The

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thermal decomposition temperatures (T_d) of the ILs were measured by using a Net**29th STA**/**4496**^{1733F} thermal gravimetric analyzer (TGA). All samples were heated up to 600°C in aluminium pans at a heating rate of 10°C min⁻¹ under nitrogen atmosphere. The temperatures reported from TGA data were the onset temperatures, which were determined from the step tangent.

Determination of impurity contents in the ILs

Based on the procedure described by Seddon and his co-workers,²³ chloride and bromide contents were determined by means of a PCl-1 chloride-selective electrode and a PBr-1 bromide-selective electrode (both, Shanghai Precision & Scientific Instrument Co., Ltd.), respectively. To this end, a 232 saturated calomel reference electrode and a PHS-25 digital pH meter (both, Shanghai Precision & Scientific Instrument Co., Ltd.) were used. The measurements were conducted at 25°C, and calibration curves were obtained from aqueous solutions of the corresponding precursor halide ionic liquids. Triplicate measurements were performed and the reproducibility was within 2%.

Water contents in the ILs were measured by coulometric Karl-Fischer titration with a Metrohm 851 moisture titrator. 1-Methylimidazole is also a possible impurity in the ILs, its content was determined by gas chromatograph using the standard addition method. Analysis was performed on an Agilent 7890A gas chromatograph equipped with a PONA column and a FID detector, and the procedure reported in the literature⁴³ was closely followed.

Dissolution of cellulose in the ILs

Dried microcrystalline cellulose (0.5wt% of the IL) was added into a dried IL (2.0g) which was sealed in a colorimetric tube. The mixture was then heated and stirred at a given temperature in an oil bath (DF-101S, Gongyi Yingyu Instrument Factory). After the solution became optically clear under a polarization microscope (Nanjing Jiangnan Novel Optics Co. Ltd.), additional cellulose was added. When the cellulose could not be dissolved further within 2h, it could be judged as becoming saturated. Solubility of cellulose at the given temperature could be calculated from the amount of solvent and cellulose added. The solubility value of cellulose in each IL was measured at the temperature range from 40°C to 120°C with 10°C intervals. According to the recommendation by Rogers *et al*,¹⁶ the solubility data of cellulose were reported in terms of mass

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of cellulose dissolved in per mole of IL (g.mol⁻¹).

Measurements of the Kamlet-Taft parameters for the ILs

The Kamlet-Taft parameters were determined by following the procedure reported by Ohno et al.⁴⁴ То solution given amount of IL, a concentrated а of 4-nitroaniline. N,N-diethyl-4-nitroaniline or 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio) phenolate (Reichardt's dye 33) in dry methanol was added. The methanol was then removed under vacuum at 40°C for 6h. This solution was added into a quartz cell with 2mm light-path length, and the cell was capped and sealed. Temperature of the sample cell was controlled by water circulation. Using a TU-1810 ultraviolet-visible spectrophotometer, the wavelength at the maximum absorption (λ_{max}) was determined and used to calculate the α , β and π^* values by the following equations:

$$v_{(dye)} = 1/(\lambda_{max (dye)} \times 10^{-4})$$
 (9)

$$E_{\rm T}(30) = 0.9986 \times (28592/\lambda_{\rm max \ (Reichardt's \ dye \ 33)}) - 8.6878 \tag{10}$$

$$\pi^* = 0.314 \times (27.52 - \nu_{(N,N-\text{diethyl-4-nitroaniline})})$$
(11)

$$\alpha = 0.0649 E_{\rm T}(30) - 2.03 - 0.72\pi^* \tag{12}$$

$$\beta = (1.035v_{(N,N-\text{diethyl-4-nitroaniline})} + 2.64 - v_{(4-\text{nitroaniline})})/2.80$$
(13)

Measurements of ¹³C NMR spectra of the [phC₁mim][CH₃COO] + cellulose mixtures

Samples used for the ¹³C NMR experiments were prepared by adding different amounts of MCC into solution of $[phC_1mim][CH_3COO] + DMSO-d_6$ (15 wt% of the IL) under stirring at 40°C. After the cellulose was dissolved completely, the sample was transferred into a 5mm NMR tube. Measurements of ¹³C NMR spectra were acquired on a Bruker DMX 300 spectrometer at 90°C.

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References

- A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484-489.
- 2 M. E. Himmet, S. Y. Ding, D. K. Johnson, W. S. Adney, M. R. Nimlos, J. W. Brady and T. D. Foust, *Science*, 2007, **315**, 804-807.
- F. Hermanutz, F. Gähr, E. Uerdingen, F. Meister and B. Kosan, *Macromol. Symp.*, 2008, 262, 23-27.
- 4 Z. Wang, T. Yokoyama, H. M. Chang and Y. Matsumoto, *J. Agric. Food Chem.*, 2009, **57**, 6167-6170.
- 5 S. Fischer, W. Voigt and K. Fischer, Cellulose, 1999, 6, 213-219.
- 6 R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, J. Am. Chem. Soc., 2002, 124, 4974-4975.
- 7 M. Abe, Y. Fukaya and H. Ohno, Green Chem., 2010, 12, 1274-1280.
- 8 A. R. Xu, J. J. Wang and H. Y. Wang, Green Chem., 2010, 12, 268-275.
- 9 Y. Fukaya, A. Sugimoto and H. Ohno, *Biomacromolecules*, 2006, 7, 3295-3297.
- 10 H. Zhang, J. Wu, J. Zhang and J. S. He, *Macromolecules*, 2005, 38, 8272-8277.
- 11 J. Vitz, T. Erdmenger, C. Haensch and U. S. Schubert, Green Chem., 2009, 11, 417-424.
- 12 B. Kosan, C. Michels and F. Meister, Cellulose, 2008, 15, 59-66.
- W. Lan, C. F. Liu, F. X. Yue, R. C. Sun and J. F. Kennedy, *Carbohydr. Polym.*, 2011, 86, 672-677.
- 14 A. Pinkert, K. N. Marsh, S. S. Pang and M. P. Staiger, Chem. Rev., 2009, 109, 6712-6728.
- 15 N. Sun, H. Rodriguez, M. Rahman and R. D. Rogers, Chem. Comm., 2011, 47, 1405-1421.
- 16 H. Wang, G. Gurau and R. D. Rogers, Chem. Soc. Rev., 2012, 41, 1519–1537.
- 17 R. C. Remsing, R. P. Swatloski, R. D. Rogers and G. Moyna, *Chem. Commun.*, 2006, 1271-1273.
- 18 R. C. Remsing, G. Hernandez, R. P. Swatloski, W. W. Massefski, R. D. Rogers and G. Moyna, J. Phys. Chem. B, 2008, 112, 11071-11078.
- 19 T. G. A. Youngs, J. D. Holbrey, C. L. Mullan, S. E. Norman, M. CristinaLagunas, C.

D'Agostino, M. D. Mantle, L. F. Gladden, D. T. Bowrond and C. Hardacre, *Cher*^{AOS}^{EG.1020}^{EG.1020}^{EG.1733F} 1594.

- 20 T. G. A. Youngs, C. Hardacre, and J. D. Holbrey, J. Phys. Chem. B, 2007, 111, 13765-13774.
- J. M. Zhang, H. Zhang, J. Wu, J. Zhang, J. S. He and J. F. Xiang, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1941-1947.
- 22 B. Lindman, G. Karlström and L. Stigsson, J. Mol. Liq., 2010, 156, 76-81.
- 23 K. R. Seddon, A. Stark and M. Torres, Pure Appl. Chem., 2000, 72, 2275–2287.
- 24 J.Vitz, T.Erdmenger, C.Haensch and U.S.Schubert, Green Chem., 2009, 11, 417–424.
- 25 Sh. Zhang, X. Qi, X. Ma, L. Lu and Y. Deng, J. Phys. Chem. B, 2010, 114, 3912–3920.
- 26 M. J. Kamlet, J. L. M. Abboud, M. H. Abraham and R. W. Taft, J. Org. Chem., 1983, 48, 2877–2887.
- 27 C. Reichardt, Chem. Soc. Rev., 1992, 21, 147-153.

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- 28 M. A. Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N. H. Hassan, J. P. Hallett, P. A. Hunt, H. Niedermeyer, J. M. Perez-Arlandis, M. Schrems, T. Welton and R. Wilding, *Phys. Chem. Chem. Phys.*, 2011, 13, 16831–16840.
- 29 L. Crowhurst, P. R. Mawdsley, J. M. Perez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, 5, 2790-2794.
- 30 A. Oehlke, K. Hofmann and S. Spange, New J. Chem., 2006, 30, 533-536.
- 31 C. Chiappe and D. J. Pieraccini, J. Phys. Org. Chem., 2005, 18, 275-297.
- 32 J. G. Huddlestone, G. A. Broker, H. D. Willauer and R. D. Rogers, ACS Symp. Ser., 2002, 818, 270-288.
- 33 H. Zhao, G. A. Baker, Z. Song, O. Olubajo, T. Crittle and D. Peters, *Green Chem.*, 2008, 10, 696-705.
- 34 Y. Fukaya, K. Hayashi, S. S. Kim and H. Ohno, ACS Symp. Ser., 2010, 1033, 55-66.
- 35 B. Hinterstoisser, M. Åkerholm and L. Salmén, *Biomacromolecules*, 2003, 4, 1232-1237.
- 36 A. S. Gross and J. W. Chu, J. Phys. Chem. B, 2010, 114, 13333-13341.
- Y. Nishiyama, J. Sugiyama, H. Chanzy and P. Langan, J. Am. Chem. Soc., 2003, 125, 14300-14306.
- 38 A. S. Gross, A. T. Bell and J. W. Chu, J. Phys. Chem. B, 2011, 115, 13433-13440.
- 39 H. M. Cho, A. S. Gross and J. W. Chu, J. Am. Chem. Soc., 2011, 133, 14033-14041.

- 40 S. H. Yeon, K. S. Kima, S. Choi, H. Lee, H. S. Kimb and H. Kimc, *Electrochim.* Aeta, 20195; 350;1733F 5399-5407.
- 41 Y. Y. Wang, D. Jiang and L. y. Dai, Catal. Commun., 2008, 9, 2475-2480.
- 42 S. M. Zhang, Y. W. Hou, W. G. Huang and Y. k. Shan, *Electrochim. Acta*, 2005, **50**, 4097-4103.
- 43 A. Stark, P. Behrend, O. Braun, A. Müller, J. Ranke, B. Ondruschka and B. Jastorff, *Green Chem.*, 2008, 10, 1152–1161.
- 44 Y. Fukaya, K. Hayashi, M. Wada and H. Ohno, Green Chem., 2008, 10, 44-46.

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Entres	Solubility (g/mol)									
Entry	IL	40°C	50°C	60°C	70°C	80°C	90°C	100°C	110°C	120°C
1	[C ₄ mim][CH ₃ COO]	23	25	26	31	36	49	54	56	58
2	[C ₁ OC ₂ mim][CH ₃ COO]	8	17	21	23	29	39	44	49	56
3	[C ₂ OHmim][CH ₃ COO]	a	1	18	22	26	30	33	34	34
4	[C ₄ dmim][CH ₃ COO]	a	5	18	24	27	29	32	35	37
5	[phC ₁ mim][CH ₃ COO]	a	1	14	17	20	22	24	30	34
6	[C ₂ mmor][CH ₃ COO]	a	a	1	3	6	18	21	28	31
7	[C=C ₂ mmor][CH ₃ COO]	a	1	2	4	12	17	21	24	28
8	[C=C ₂ mpip][CH ₃ COO]	a	a	a	а	а	10	14	16	19
9	[C ₄ mpip][CH ₃ COO]	а	а	а	а	1	2	3	4	7
10	[C ₄ mpyr][CH ₃ COO]	a	а	a	а	а	a	1	2	3
11	[C ₄ ebim][CH ₃ COO]	a	a	a	а	а	a	а	а	<1
12	[C ₂ ebim][CH ₃ COO]	а	а	а	а	a	a	а	а	<1
13	[C ₄ ebt][CH ₃ COO]	a	а	a	а	а	a	а	а	<1
а	Insoluble at given temperature.									

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

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IL		α, β and π^*							
		25°C	35°C	45°C	55°C	65°C	90°C ^a		
	α	0.61	0.61	0.61	0.60	0.60	0.59		
[C ₄ mim][CH ₃ COO]	β	1.14	1.14	1.14	1.14	1.14	1.14		
	π^*	1.02	1.02	1.02	1.02	1.02	1.02		
	α	0.51	0.50	0.50	0.50	0.49	0.48		
[C ₁ OC ₂ mim][CH ₃ COO]	β	1.10	1.10	1.10	1.106	1.10	1.10		
	π^*	1.06	1.06	1.06	1.06	1.06	1.06		
	α	0.44	0.43	0.42	0.41	0.41	0.39		
[phC ₁ mim][CH ₃ COO]	β	1.05	1.05	1.05	1.05	1.05	1.05		
	π^*	1.09	1.09	1.09	1.09	1.09	1.09		
	α	0.36	0.35	0.35	0.35	0.34	0.34		
[C ₂ mmor][CH ₃ COO]	β	1.10	1.10	1.10	1.10	1.10	1.10		
	π^*	1.17	1.17	1.17	1.17	1.17	1.17		
	α	0.25	0.25	0.25	0.24	0.24	0.23		
[C=C ₂ mmor][CH ₃ COO]	β	1.12	1.12	1.12	1.12	1.12	1.12		
	π^*	1.15	1.15	1.15	1.15	1.15	1.15		
	α	b	b	b	b	0.54	0.54 ^c		
[C ₂ OHmim][CH ₃ COO]	β	b	b	b	b	0.97	0.97^{c}		
	π^*	b	b	b	b	1.06	1.06 ^c		
^a Extrapolated to 90°C; ^b can't be measured; ^c data determined at 65°C.									

Table 2 Values of α , β and π^* parameters for the ILs at different temperatures

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Table 3 The ¹³C NMR chemical shifts (δ /ppm relative to DMSO) of [phC₁mim][CH₃COO] in the solution of [phC₁mim][CH₃COO] + cellulose at 90°C

wt 9/ MCC	δ/ppm										
wt % MCC	C2	C4	C5	C6	C7	C8	C9,13	C10,11,12	C14	C15	
0	138.059	122.264	123.825	35.201	51.632	134.969	128.146	128.417	25.412	174.670	
5	137.958	122.258	123.842	35.245	51.686	134.922	128.167	128.454	25.351	174.847	
8	137.821	122.225	123.861	35.296	51.780	134.826	128.195	128.506	25.240	175.069	

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Table 4 The ¹³C NMR chemical shifts (δ /ppm relative to DMSO) of cellulose in the solution of [phC₁mim][CH₃COO] + cellulose at 90°C

ut 9/ MCC	δ/ppm									
wt % WICC	C1	C2	C3	C4	C5	C6				
5	102.662	73.839	75.167	79.131	75.845	60.767				
8	102.725	74.029	75.124	79.122	75.870	60.421				
$\Delta\delta$	0.063	0.190	-0.043	-0.009	0.025	-0.346				



Scheme 1 Schematic structures of cations and anion of the ILs studied in the present work.



Fig. 1 The linear correlation between solubility of cellulose and α parameter of the ILs at 90°C.

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Fig. 2 The schematic structure and numbering of [phC₁mim][CH₃COO].

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Fig. 3 The schematic structure and numbering of cellulose.

Cation does matter: How cationic structure affects the dissolution of cellulose in ionic liquids

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It's found that cations of ILs significantly affect cellulose solubility by their acidic protons, steric hindrance and interaction with anions.

