Influence of Anions of Imidazole Ionic Liquids on Dissolution of Cellulose

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[Bmim]Cl, [Bmim]Br, [Bmim]HSO$_4$, [Bmim]BF$_4$ and [Bmim]PF$_6$ were synthesized to study the influence of anions on the dissolution of cellulose. Experimental studies showed that the dissolution of cellulose was related to the formation of hydrogen bonds between the anions and cellulose, which is attributed to the charge density on the anion. The sequence of solubility of cellulose in six ionic liquids tested was [Bmim]Cl > [Bmim]Br > [Bmim]HSO$_4$ > [Bmim]BF$_4$, [Bmim]PF$_6$. Thermogravimetric method was employed to investigate the stability of ionic liquids. The dissolution process was monitored with polarizing microscope. The results showed that dissolution of cellulose was related to stability of the ionic liquids. For similar ionic liquids, poorer stability led to higher solubility. Both the original and regenerated cellulose samples were characterized with wide-angle X-ray diffraction and FTIR. It was shown that the structures of original cellulose and regenerated cellulose were similar; however, the crystalline structure of cellulose was converted to cellulose II from cellulose I of the original cellulose.

Key Words: Cellulose, Dissolution, Ionic liquid.

INTRODUCTION

Cellulose is one of the most abundant bio-renewable materials, with a long and well-established technological base[1,2]. Products derived from cellulose have many important applications in fiber, paper, film, polymer and paints industries. However, natural cellulose is high crystalloid, with strong inter- and intra-molecular hydrogen bonding caused by the hydroxyl groups and is insoluble in water and common organic solvents. These properties affect the development and utilization of cellulose[3]. Research and development of new fibers that is soluble in green solvent systems, particularly in those solvents which can support homogeneous reactions of cellulose derivatives, is of paramount importance[4,5]. To date, a number of solvent systems, such as inorganic molten salts like LiClO$_4$·3H$_2$O[6], N-methylmorpholine-N-oxide (NMMO)[7], DMAc/LiCl[8], DMF/N$_2$O$_4$[9] and DMSO/TBAF[10] have been found efficient in cellulose dissolution. However, limitations such as toxicity, cost, difficulty in solvent recovery, or instability in processing continue to persist. With increasing governmental regulations restricting the use of current cellulose solvents, the need to replace them is becoming critical. Among potential new solvents, ionic liquids (ILs), which are relatively new types of liquids, have been drawing much attention in the last decade. Their negligible vapor pressure, excellent thermal stabilities, their polar and non-coordinating properties and in particular the provision of a simple and effective method of recovering products and recycling catalysts have made them solvents of choice for green chemistry[11-18]. Based upon these advantages, ionic liquids are gaining greater attention as solvents for cellulose dissolution. Swatloski *et al.*[2], led the research on developing uses of ionic liquids as cellulose solvents. They reported in 2002 that the ionic liquid 1-butyl-3-methyl imidazole chloride ([C$_4$mim]Cl) could be used as a cellulose solvent. In addition, the effects of ionic liquids, with different cations and anions, were investigated on dissolution properties of cellulose. The dissolution experiments were conducted using microwave oven. However, the systematic and in depth comparison of dissolution in ionic liquids that had different anions had not been conducted without using microwave. The behaviour and changes of cellulose in the dissolution process were more extensively studied after Swatloski's first public report that cellulose could be dissolved in ionic liquids.

Recently, more than 20 ionic liquids have shown promise as a class of new solvents which can dissolve cellulose. Cationic types of ionic liquids which have been studied include: alkyl quaternary ammonium cation [NR$_x$H$_{4-x}$]$^+$, alkyl quaternary phosphonium cation [RR$_x$H$_{4-x}$]$^+$, N-alkyl pyridine cation [RPy]$^+$ and N,N-2-alkyl imidazole cation [R$_1$R$_3$im]$^+$, where "im" represents the imidazole structure[19]. As described above, the cations are usually alkylsubstituted imidazoles. Anions such

as BF_4^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $C_3F_7COO^-$, $C_4F_9SO_3^-$, CF_3COO^-, ClO_4^- can be used in combination with these cations to form low melting point liquids[20]. Despite the fact that most of the cations reported are alkyl substituted imidazoles, the possible effects of imidazole ionic liquids with varying anions have seldom been explored on the solubility properties of cellulose.

In this work, 1-butyl-3-methyl imidazole cation [Bmim]$^+$, with different anions, such as Cl$^-$, Br$^-$, HSO_4^-, BF_4^-, PF_6^- and OH$^-$ were synthesized. Systematic comparison of the effects of anions on the dissolution properties of cellulose was investigated.

EXPERIMENTAL

Cotton-ramie pulp obtained from commercial sources was used as the cellulose sample, with a degree of polymerization (DP) of 575.6. All cotton-ramie pulps were cut into small pieces and dried at 100 °C for 12 h without activation treatment before use. All of other chemicals and solvents were of analytical grade and used as received.

The [Bmim]Cl was synthesized using N-methylimidazole and butyl chloride with one step. To N-methylimidazole in a 500 mL glass-lined reactor, approximately 1:1.2 molar ratio of butyl chloride was added dropwise under nitrogen gas atmosphere at room temperature. After completely adding the allyl chloride, the reaction mixture was stirred magnetically with reflux at 70 °C for about 24 h. After removing the residual butyl chloride under reduced pressure, the resulting liquid was repeatedly washed with an excess amount of ethyl acetate to eliminate the residual N-methylimidazole. The obtained ionic liquid was dried in vacuum drier at 40 °C for 24 h. The [Bmim]Br was synthesized according to the above method. [Bmim]HSO_4 was synthesized using [Bmim]Br as substrate. [Bmim]Br was placed in a 500 mL glass-lined reactor in an ice-bath under nitrogen gas atmosphere, approximately 1:1 molar ratio of sulfuric acid was added to it dropwise. After completely adding the sulfuric acid, the reaction mixture was stirred magnetically at room temperature for *ca.* 24 h. Thus [Bmim]HSO_4 was obtained. [Bmim]BF_4 and [Bmim]PF_6 were synthesized by combining [Bmim]Cl with $NaBF_4$ and NH_4PF_6 according to the literature[21].

General procedure: The dissolution of cellulose was processed using Zhao *et al.*[22]. as reference. In the dissolving process, a certain amount of cellulose sample was added into the ionic liquids. The flask was continuously purged with gaseous N_2 and the cellulose solution was stirred continuously in an oil bath at 120 °C. Because of high crystallinity of cellulose, the process of dissolution of cellulose was monitored with a polarizing optical microscope. After the emergence of a blackburst in the cellulose solution, as determined on a polarization microscope, the next level of cellulose sample was added into the dissolved cellulose solution. The above experimental procedure was repeated for several cyclic numbers. The solubility of cellulose corresponding to dissolution times in ionic liquids for each cyclic number was recorded. After the complete dissolution of cellulose in ionic liquids, the solution was cast onto a horizontal glass plate to give a thickness of *ca.* 0.50 mm, the air bubble was removed by placing

another glass plate and then both glass plates were immediately immersed in ethanol repeatedly to eliminate any residual ionic liquids. Subsequently, the transparent regenerated cellulose film was obtained and dried at 50 °C in a vacuum oven for 24 h.

Detection method: X-Ray diffraction (XRD) patterns of the original and regenerated cellulose were obtained using E-1020 diffractometer (Hitachi, Ltd. Japan) with CuK$_\alpha$ at 40 kV and 30 mA. The scattering angle range was from 5-45° with 8 °/min scanning speed and a 2θ step interval of 0.02°. Thermogravimetric analysis (TG/DTA) was employed on TG209 thermal analyzer (NETZSCH Co. Ltd., Germany) to measure the weight loss of ionic liquids. The apparatus was continually flushed with nitrogen. The sample weighed between 7 and 11 mg and the scans were run from room temperature to 600 °C at a rate of 10 °C/min. FTIR spectra of the original and regenerated cellulose were recorded on a FTS-135 spectrometer (BIO-RAD, America) using the KBr wafer technique. The dissolution process of cellulose was monitored by using a polarizing microscope (XP-203, Shanghai Changfang Optical Instrument Co., Ltd., China).

RESULTS AND DISCUSSION

Solubility of cellulose: The solubility of cellulose in different imidazole-base ionic liquids is summarized in Table-1. It is seen that there are significant differences in the solubility of cellulose in ionic liquids. Cellulose sample dissolves quickly in [Bmim]Cl at 120 °C, the solubility being 10 % in 0.5 h, while it dissolves slowly in ionic liquids which contained anions Br$^-$, HSO_4^-. It was insoluble in other two ionic liquids of [Bmim]BF_4, [Bmim]PF_6 even after 48 h. As has been recognized, the dissolution mechanism of cellulose in ionic liquids[23] involves oxygen and hydrogen atoms of the hydroxy group of cellulose-OH in the formation of electron donor-electron acceptor (EDA) complexes that interact with the ionic liquid. Correspondingly, the cations in ionic liquid solvents act as the electron acceptor center while anions act as electron-donor center. The two centers must be located close enough spatially to permit the interactions and to permit the EDA complexes to form. Upon interaction of the cellulose-OH and the ionic liquid, the oxygen and hydrogen atoms from hydroxyl groups are separated, resulting in opening of the hydrogen bonds between molecular chains of the cellulose, resulting eventually in dissolution of the cellulose. When the cation in all ionic liquids is same, the electronegativity and charge density of anion would affect the interaction between anion of ionic liquids and the hydrogen atoms from hydroxyl groups. The larger the electronegativity and charge density on the anion, the greater would be the strength of binding between the anions and hydrogen atoms. The significantly different solubilities of cellulose seen in Table-1 confirm this hypothesis. For single anions, the electronegativity and charge density of Cl$^-$ are greater than that of Br$^-$. According to the theory of hydrogen bonding, the ion with large electronegativity and charge density would form stronger hydrogen bonding. The hydrogen bonding formed by Cl$^-$ and hydroxyl of cellulose (cellulose -O-H---Cl$^-$) is stronger than that formed by Br$^-$ and hydroxyl of cellulose (cellulose -O-H---Br$^-$). Therefore, solubility of cellulose in [Bmim]Cl is

TABLE-1
SOLUBILITY OF CELLULOSE IN IMIDAZOLE IONIC LIQUIDS

Ionic liquids	Dissolution conditions	Solubility (wt %)
[Bmim]Cl	120 °C, 0.5 h	10
[Bmim]Br	120 °C, 48 h	2
[Bmim]HSO$_4$	120 °C, 48 h	1
[Bmim]BF$_4$	120 °C, 48 h	–
[Bmim]PF$_6$	120 °C, 48 h	–

Fig. 1. TG curves of ionic liquid: (a) [Bmim]Cl; (b) [Bmim]Br; (c) [Bmim]HSO$_4$

larger than that in [Bmim]Br. It is difficult to quantify the electronegativity of atoms in multi-atom ions but the ability to form hydrogen bonding can be compared qualitatively according to the charge density on the ion. Since the charge density of multi-atomic ion is smaller than that of single ion, the solubilities in [Bmim]HSO$_4$, [Bmim]BF$_4$ and [Bmim]PF$_6$ are expected to be smaller than those of [Bmim]Cl and [Bmim]Br. Through the H atom, [Bmim]HSO$_4$ can form hydrogen bonding with the oxygen atom of cellulose, *e.g.*, cellulose -O···H-O-SO$_4$-; however, the strength of hydrogen bonding is affected by the polarity of H. The polarity is stronger for the H of HSO$_4^-$, resulting in larger solubility of cellulose in [Bmim]HSO$_4$. In case of BF$_4^-$, PF$_6^-$, although the electronegativity of fluorine is higher than that of chlorine, the charge density of fluorine is smaller than that of Cl$^-$ and Br$^-$. Table-1 suggests that in spite of differences in the electronegativity, it is reasonable to deduce the sequence of influence of anions on the solubility of cellulose as: Cl$^-$ > Br$^-$ > HSO$_4^-$ > BF$_4^-$, PF$_6^-$.

Thermogravimetric analysis (TG): The TG curves of ionic liquids are shown in Fig. 1. During their thermal degradation process, the starting decomposition temperatures of the [Bmim]Cl and [Bmim]Br ionic liquids occur approximately at 213 and 220 °C, respectively. When placed in a N$_2$ atmosphere at temperatures ranging from 30 to 220 °C, the weight losses of [Bmim]Cl and [Bmim]Br were 21.76 and 3.92 %, respectively, presumably due to elimination of smaller residual molecules. The greatest decomposition temperature (T$_d$) of these ionic liquids varied from 274.3 to 283.1 °C. All the information indicates the relatively poor thermal stability of [Bmim]Cl as compared to [Bmim]Br. For [Bmim]HSO$_4$, the starting decomposition temperature occurred at *ca.* 220 °C, which is relatively lower than that of 300-400 °C observed for the ionic liquids [Bmim]PF$_6$, [Bmim]BF$_4$[23]. Based on the above data, it can be conjectured that the solubility of cellulose is related to the stability of ionic liquid. The poorer stability of ionic liquid leads to higher solubility of cellulose. It must be noted that this correlation is applicable to ionic liquids with single anion or multi-atomic anion. For example, the solubility of cellulose in [Bmim]Cl is relatively larger than in [Bmim]Br. However, the stability of these two ionic liquids is the reverse. The same conclusion can be obtained for the [Bmim]HSO$_4$, [Bmim]BF$_4$ and [Bmim]PF$_6$. The dissolution process of cellulose in ionic liquid relates to the interaction between the cellulose-OH and the ionic liquid. The cation and anion in ionic liquid solvents must be separated to provide the electron acceptor center and electron-donor center. The high stability of ionic liquids acts against this separation of charges, resulting in weakened interaction between the ionic liquid and the hydrogen bonds between molecular chains of the cellulose, thus leading to poor solubility.
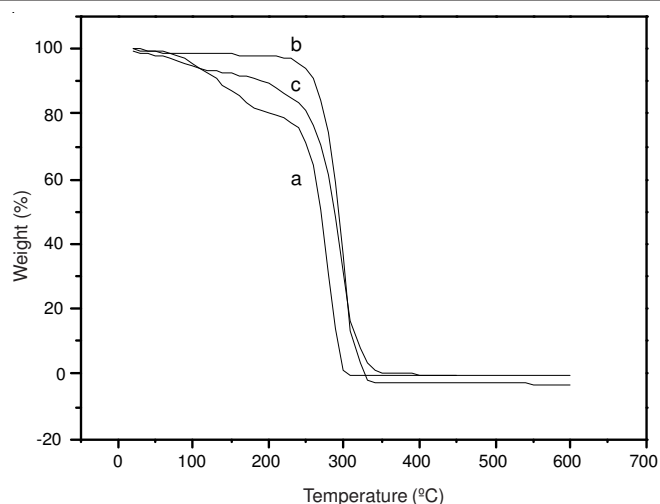
The interactive force between the anion and cation of [Bmim]Cl, with strong polarity resulting from the large charge density of Cl$^-$, is electrostatic in nature; therefore, like traditional ion crystals, its stability is poor. For the [Bmim]Br which has large deformability because of the big volume of Br$^-$, the interactive force is largely covalent, which results in stronger stability. This is consistent with our results. The same reasoning can be applied to [Bmim]HSO$_4$, [Bmim]BF$_4$ and [Bmim]PF$_6$.

Dissolution process of cellulose: The dissolution process of cellulose in [Bmim]Cl was studied as an example. The polarizing microscope was employed to monitor the variation of cellulose during the dissolution. The results are shown in Fig. 2. It may be seen that at the beginning of dissolution, there was plenty of bright cellulose fibrils (Fig. 2a) under the polarizing microscope, presumably due to the presence of extensive crystalline structure in original cellulose. As the dissolution progressed, native cellulose fibers started to swell in isolated points along the fiber. Thus the cellulose became swollen and shortened, the eyeshot of the microscope became diffused. At 10 min, cellulose was completely dissolved and the eyeshot of the polarizing microscope became black, as shown in Fig. 2f. Similar results were obtained for [Bmim]Br and [Bmim]HSO$_4$, indicating similar dissolution mechanism.
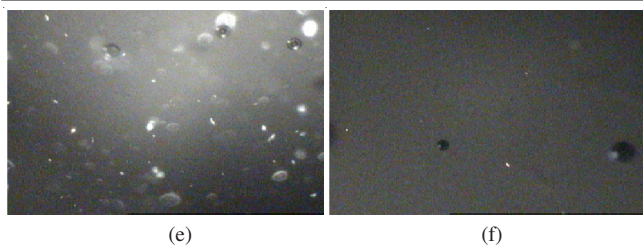

(a)

(b)

(c)

(d)
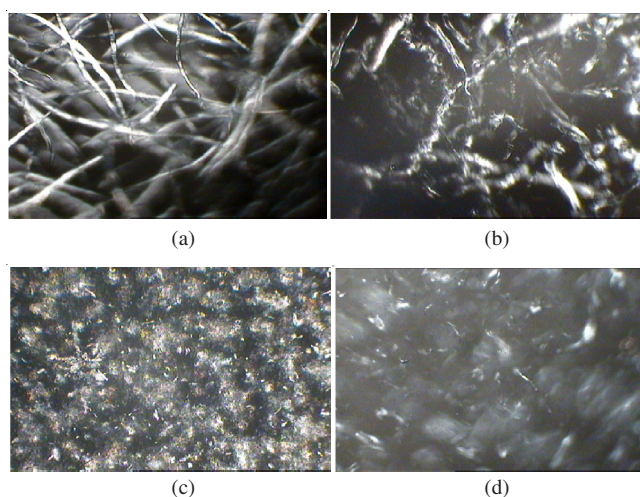
Fig. 2.   Optical microscope photos of cellulose dissolution at different time: (a) 0 min; (b) 2 min; (c) 4 min; (d) 6 min; (e) 8 min; (f) 10 min. Dissolution condition: 120 ℃, cotton-ramie pulp was dissolved in [Bmim]Cl

FT-IR: Common methods for the characterization of cellulose structure are based on X-ray, infrared absorption and NMR. FT-IR and NMR spectroscopy show some useful information related to changes in hydrogen bonding during crystal transformation[24,25]. The present study used FT-IR to measure changes in the structure of the regenerated cellulose samples after dissolution in ionic liquids. FT-IR spectra of original cellulose and regenerated cellulose are illustrated in Fig. 3. It shows that the bands in the two spectra are similar, indicating similar structure of original cellulose and regenerated cellulose. In addition, spectra of regenerated cellulose shows a shift of the peaks of O-H stretching vibrations from 3413-3400 cm^{-1}, indicating that the degree of free hydroxyl groups, *i.e.*, not cross-linked to form hydrogen bonds, increased in regenerated cellulose. The peak of the CH$_2$ bending shifted from 1429 cm^{-1} in spectrum (a) to 1423 cm^{-1} in spectrum (b), which, to some extent, is an indication of the cleavage of hydrogen bond in C$_6$-OH[26].
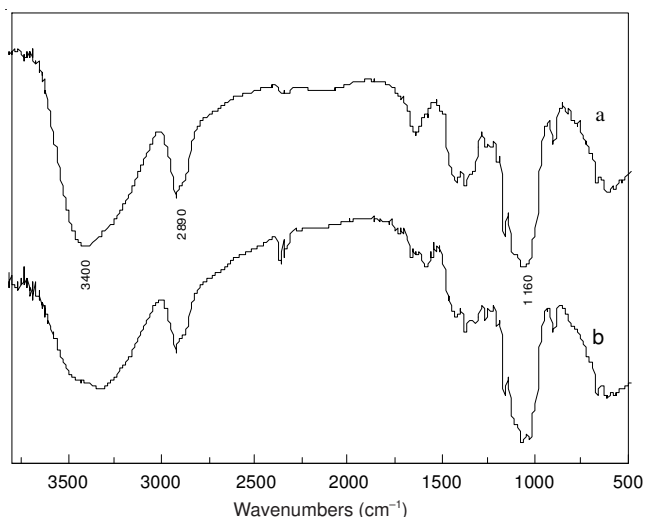

Fig. 3. FTIR spectra of original cellulose (a) and regenerated cellulose (b)

XRD: XRD has been used extensively for the investigation of the super molecular order (crystalline) of cellulose and their derivatives. Fig. 4 illustrates the wide-angle X-ray diffraction curves of original cellulose (spectrum a) and regenerated cellulose (spectrum b). The diffraction curve of original cellulose is typical of cellulose I structure. It has strong crystalline peaks at 14.26, 16.77 and 22.58°, corresponding to
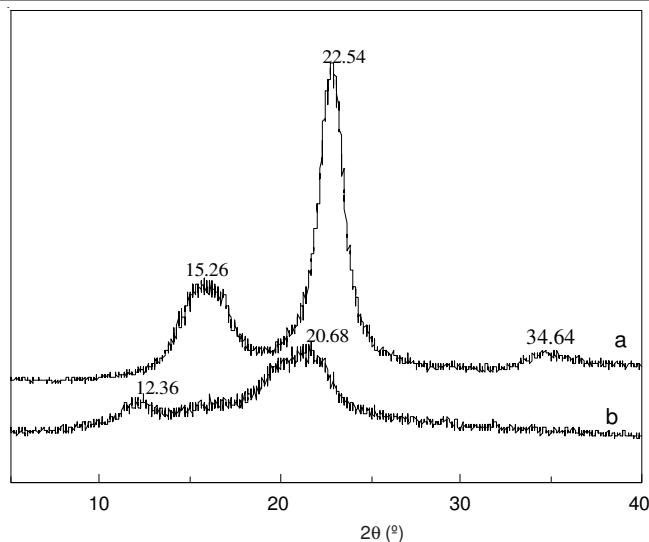

Fig. 4. XRD patterns (a) original cellulose; (b) regenerated cellulose

the (1 1 0), (1 1 0) and (0 0 2) planes of crystals, respectively and weak crystalline peaks at 34.64° corresponding to the (0 0 4) plane[24]. After dissolution and regeneration, the diffraction curve of regenerated cellulose film is typical of the diffraction patterns of cellulose II, as illustrated by the presence of the broad crystalline peak at around 12.5 and 20.0°[27]. These results show that cellulose is changed from cellulose I to cellulose II during dissolution and regeneration.

Compared to original cellulose, the intensity of diffraction peaks of regenerated cellulose is reduced significantly. In other words, the crystallinity of regenerated cellulose is lower than the original cellulose. This phenomenon means that during the dissolution process, ionic liquid rapidly breaks intermolecular and intramolecular H-bonds and destroys the original crystalline form. Moreover, the coagulation process is so transitory as to be unfavorable to the cellulose crystallization.

Conclusion

The dissolution of cellulose in different anion imidazole ionic liquids is related to the formation of hydrogen bonds between the anions and cellulose, which is attributed to the charge density on the anion. The stronger the hydrogen bonding, the higher the solubility of cellulose is. The solubility of cellulose is influenced by anions according to the sequence: Cl$^-$ > Br$^-$ > HSO$_4^-$ > BF$_4^-$, PF$_6^-$. In addition, the stability of ionic liquids affects the dissolution of cellulose. For similar ionic liquids, the poorer stability of ionic liquid leads to higher solubility of cellulose. After dissolution and regeneration in ionic liquid, the crystalline structure of cellulose was converted from cellulose I to cellulose II. FTIR and X-ray diffraction analyses indicated that the regenerated cellulose was a mixture of amorphous cellulose and cellulose II.

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