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# Acidic ionic liquid as "quasi-homogeneous" catalyst for controllable synthesis of cellulose acetate

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ABSTRACT

In this paper, we demonstrated that acidic ionic liquids (ILs) can be used as "quasi-homogeneous" catalysts for the efficient acetylation of cellulose. Unlike existing techniques that use large amount of ILs as solvent to dissolve and acetylate cellulose, a small amount of acidic ILs was used as catalyst in this study to overcome the low efficiency associated with relatively high viscosity and costs of ILs during homogeneous acetylation. Fully substituted cellulose acetate with a conversion of 88.8% was obtained by using only 9 mol% IL 1-vinyl-3-(3-sulfopropyl) imidazolium hydrogen sulfate as catalyst, which is much higher than that of common commercialized solid acid catalysts. The degree of substitution and solubility of the obtained cellulose acetate can be facilely controlled by varying the concentration of ILs and reaction time. The dual function of swelling and catalyzing of acidic ILs for the acetylation of cellulose is responsible for the excellent catalytic performance.

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## 1. Introduction

There is a growing interest in exploiting and utilization of renewable resources (Liu, Wu, Jiao, Xiong, & Zhou, 2013a; Liu, Zhang, Li, & Zhou, 2013b; Wang, Gurau, & Rogers, 2012). Especially cellulose, the most abundant natural polymer found on earth, is of tremendous economic and environmental importance due to growing public concern over global warming and fossil fuels scarcity (Huber, Bickerton, Müssig, Pang, & Staiger, 2012). Cellulose and its derivatives are extensively used in manufacturing of fibers and functional materials that are extensively used in industries (Cheng, Dowd, Shogren, & Biswas, 2011; Edgar et al., 2001). Particularly, cellulose acetate (CA) has been a well-known cellulose derivative for over 100 years that found many commercial applications in plastics (such as tool handles, face shields, eyeglass frames), tapes, textile fibers, photographic films, and cigarette filters. It is estimated that about 1.5 billion pounds of CA products are manufactured globally every year because of its low cost ($1.80/pound) and biodegradability (Cheng, Dowd, Selling, & Biswas, 2010; Fan et al., 2013).

Traditional methods of manufacturing CA consist of two steps: acetylation of wood pulp cellulose followed by hydrolysis of the cellulose triacetate to expected degree of substitution (DS). Concentrated mineral acids such as sulfuric acid are used in this process (Biswas, Shogren, & Willett, 2005; Dubey et al., 2006). Although sulfuric acid shows good catalytic activity, it drives side reactions and causes considerable corrosion. The traditional methods used in producing CA have some undesirable problems such as serious degradation of cellulose, damage to the environment and high energy-consumption. Therefore, it is necessary to develop efficient and environmentally benign technology for the production of CA.

Over the past decades, much attention has been focused on the development of homogeneous methods to prepare various cellulose derivatives. In spite of advantages of the homogeneous reaction system such as providing opportunities to control the DS values and creating more options to introduce novel functional groups, large quantities of solvents for cellulose are involved. Although solvent systems include N,N-dimethylacetamide/lithium chloride (DMAc/LiCl), dimethylformamide/dinitrogen tetraoxide (DMF/$N_2O_4$), N-methylmorpholine-N-oxide (NMNO), dimethyl sulfoxide/tetrabuthlammonium fluoride trihydrate (DMSO/TBAF), molten salt hydrates and some ionic liquids (ILs) have been proved to be appropriate for the preparation of cellulose esters in lab scale procedure (Barthel & Heinze, 2006; El Seoud, Marson, Ciacco, & Frollini, 2000; FitzPatrick, Champagne, & Cunningham, 2012; Heinze et al., 2000; Marson & El Seoud, 1999; Swatloski, Spear, Holbrey, & Rogers, 2002; Thümmler, Fischer, Peters, Liebert, & Heinze, 2010; Wu et al., 2004; Zhou, Li, Song, Zhang, & Lin, 2010), various shortcomings such as volatility, toxicity, high viscosity and difficult and expensive recycling contradict the large-scale application. Take ILs for example, as the "green" reaction media for the

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homogeneous derivation of cellulose, some ILs have drawn much attention in recent years. The extensive intra- and intermolecular hydrogen bonds in cellulose could be broken and the hydroxyl groups are exposed during the dissolution process, resulting in a high reaction activity of cellulose with anhydrides, aliphatic acids, etc. However, a very dilute solution, typically 4 wt% of cellulose in ILs is required due to the intrinsic high viscosity of ILs (Zhang, Wu, Zhang, & He, 2005; Zhu et al., 2006), leading to a relatively high cost of synthesis and reuse of large amount of ILs for commercial use. Thus, reducing the usage amount of ILs to develop new methods in the synthesis of cellulose derivatives will be of great benefit.

Herein we report a new and environmentally friendly solvent-free method to acetylate cellulose with acetic anhydride using acidic ILs as catalysts. Only a small amount of ILs was used. A novel $SO_3H$-functionalized acidic IL, 1-vinyl-3-(3-sulfopropyl) imidazolium hydrogen sulfate ([VSim]$HSO_4$), was prepared and its catalytic activity for cellulose acetylation as well as its reuse performance were examined. For comparison, two other ILs with similar structures, N-methyl-imidazolium chloride ([Hmim]Cl) and N-methyl-imidazolium bisulfate ([Hmim]$HSO_4$), were also used for the synthesis of CA under the same conditions. Compared with traditional mineral acid catalysts, acidic ILs exhibit many special advantages, such as non-volatility, ease of recovery, less corrosion and especially the capability of swelling cellulose and breaking the inter- and intramolecular hydrogen bonds (Groff et al., 2013), which makes it well-suited for catalyzing cellulose acetylation and opens an avenue to control the DS values at one-step without dissolution of cellulose.

In addition, waste cotton fabrics (WCF) was chosen as starting material instead of wood pulp cellulose in this study. In China, WCF is a kind of common industrial wastes from cotton textile industry and can be easily obtained just by paying the freight (no more than $30 per ton). Generally, used clothes and leftover materials of textile industry ended in waste stations are landfilled or incinerated (Miranda, Sosa_Blanco, Bustos-Martinez, & Vasile, 2007). Such disposing methods not only create environmental pollution but also lead to a great waste of the valuable resources. In our previous studies, we have developed a series of methods on the recycling of WCF into value-added products (Sun, Lu, Zhang, Tian, & Zhang, 2013; Sun, Lu, Liu, Zhang, & Zhang, 2014). In this paper, in order to make a better recycle of WCF, cellulose in WCF was converted into CA with small amount of acidic ILs as catalysts. The effect of ILs amount as well as ILs structure on the conversion and DS of the obtained CA was studied and the dual function of swelling and catalyzing of ILs during cellulose acetylation was further discussed.

## 2. Experimental

### 2.1. Materials

Waste cotton fabrics (WCF), with high cellulose content (>98%) (Xiong, Zhang, Tian, Zhou, & Lu, 2012), was freely obtained from surplus of textile industries and well loosened before use. [Hmim]Cl and [Hmim]$HSO_4$ were purchased from Chengjie Co., Ltd. (Shanghai, China). 1,3-Butanesultone and 1-vinylimidazole (>98%) were obtained from Aladdin. The structures of the three different ILs are shown in Fig. 1(a). Other chemicals such as acetone, dimethyl sulfoxide (DMSO), acetic anhydride, etc. were supplied by Kelong Chemical Regent Co., Ltd. (Chengdu, China).

### 2.2. Synthesis and characterization of [VSim]$HSO_4$

The synthesis route to [VSim]$HSO_4$ was shown in Fig. 1(b): first, 0.031 mol of 1,3-propanesultone was slowly added to 0.03 mol of 1-vinylimidazole in a 50 mL round-bottom flask in ice/salt bath. The mixture was stirred at 0 °C for about 24 h until it turned into solid. Then the formed solid was washed with ether three times and dried in vacuum at room temperature. The formed solid (87% yield) was dissolved in 2 mL of $H_2O$ in a 50 mL round-bottom flask, and equimolar sulfuric acid was slowly added dropwise into the flask at 0 °C in several minutes. After the addition, the mixture was gradually heated up to 60 °C and stirred for 12 h (Pourjavadi, Hosseini, Doulabi, Fakoorpoor, & Seidi, 2012). Finally, the formed wine-colored liquid was washed with ether followed with ethyl acetate three times. The obtained [VSim]$HSO_4$ was dried in vacuum at 50 °C for 5 h and stored in a desiccator. $^1$H NMR (Bruker AV, 400 MHz, DMSO-$d_6$): $\delta$ 2.13 (t, 2H), 2.44 (t, 2H), 4.34 (t, 2H), 5.40 (d, 1H), 5.95 (d, 1H), 7.29 (dd, 1H), 7.93 (s, 1H), 8.17 (s, 1H), 9.47 (s, 1H) (Fig. 1(c).

### 2.3. UV–vis acidity evaluation of ILs

The acidic scale of these ILs was measured on a UV–visible spectrophotometer (model UV754GD, Shanghai) with 4-nitroaniline as the basic indicator according to the literature reported previously (Thomazeau, Olivier-Bourbigou, Magna, Luts, & Gilbert, 2003). With increasing the acidic scale of the three ILs, the absorbance of the unprotonated form of the basic indicator decreased, whereas, the protonated form of the indicator could not be observed because of its small molar absorptivity and its location. The Hammett acidity functions ($H_o$), which could be regarded as the relative acidity of the ILs, could be calculated by using Eq. (1):

$$H_o = pK_a(I)_{aq} + \log\left(\frac{[I]}{[IH^+]}\right) \quad (1)$$

where $pK_a(I)$ is the $pK_a$ value of the 4-nitroaniline (0.99) indicator in solution, and $[I]$ and $[IH^+]$ are the molar concentrations of the protonated and unprotonated forms of the indicator, respectively. In this study, the ILs and indicator were dissolved in water with concentrations of 50 and 0.1 mmol/L, respectively (Kotadia & Soni, 2013). Then the solutions were homogenized for 2 h with magnetic stirring and then their UV spectra were recorded.

### 2.4. General methods for the synthesis and characterization of CA

The acetylation of cellulose was carried out under atmosphere pressure using [Hmim]Cl, [Hmim]$HSO_4$ and [VSim]$HSO_4$, as catalyst respectively. In a typical reaction, 3.24 g [0.02 mol of anhydroglucose units (AGUs), assuming the sample was pure cellulose] of loosened WCF, 20.4 g (0.2 mol) of acetic anhydride, and 0.03–0.75 molar equivalents of ILs with respect to per mole of AGUs were mixed and heated at 100 °C for 3 h. The reacted mixture was poured into 100 mL of ethanol and stirred for 30 min. The solid consisting of CA and unreacted cellulose was filtered and washed with ethanol three times and then dried in a vacuum oven at 60 °C for 24 h. The recovery of ILs was accomplished by evaporating ethanol and acetic anhydride from the filtrate. In order to extract the CA, the sample was then refluxed for 24 h by the Soxhlet extraction method using DMSO as the solvent. The filtrate was then dried in a vacuum oven at 60 °C for 24 h to obtain the CA product.

The Fourier transform infrared (FTIR) spectra of WCF and CA products were conducted by a Nicolet 560 spectrophotometer (USA). Twenty scans for each sample were taken with a resolution of 2 $cm^{-1}$, ranging from 400 to 4000 $cm^{-1}$. The samples were prepared by using the KBr-disk method.

The DS value of CA was determined by titration with aqueous sodium hydroxide solution (Biswas et al., 2007) and further confirmed by $^1$H NMR spectroscopy. The sample was dissolved in

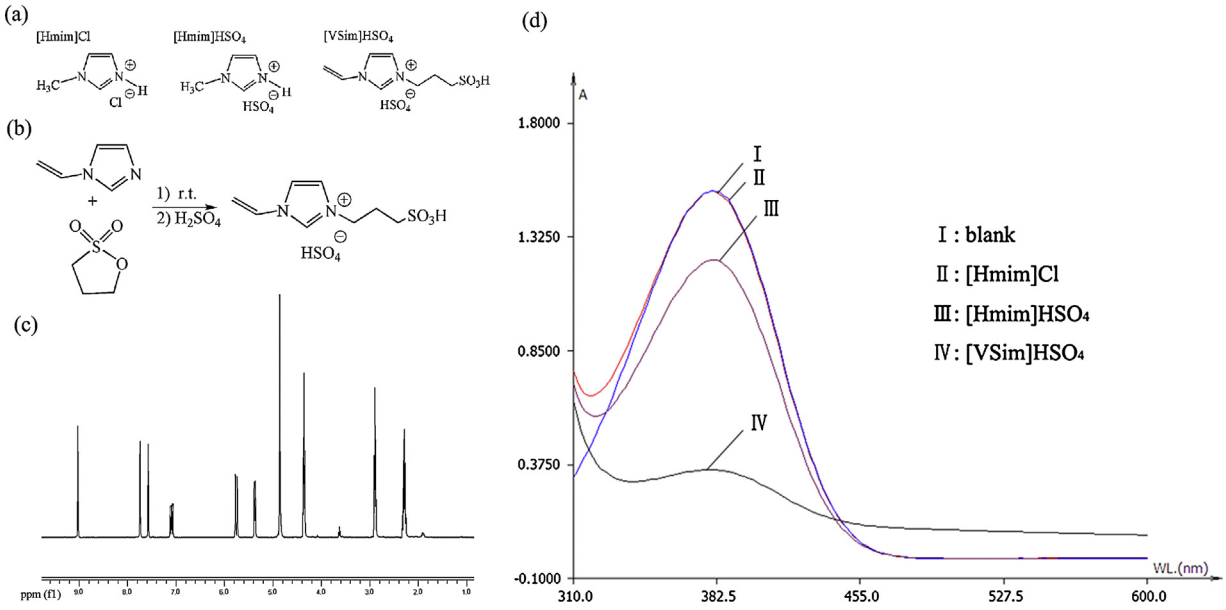


**Fig. 1.** (a) Structures of the ILs used in this study, (b) synthetic route to $[VSim]HSO_4$, (c) $^1H$ NMR of $[VSim]HSO_4$, (d) absorbance spectra of 4-nitroaniline for [Hmim]Cl, $[Hmim]HSO_4$ and $[VSim]HSO_4$ in water.

DMSO-$d_6$ containing a drop of deuterated trifluoroacetic acid, and the DS value of CA was calculated by Eq. (2):

$$DS = \frac{7 \times I_{acetyl}}{3 \times I_{H,AGU}} \quad (2)$$

where $I_{acetyl}$ is the peak integral of methyl protons of acetyl moiety, and $I_{H,AGU}$ is the peak integral of all protons of AGUs (Goodlett, Dougherty, & Patton, 1971).

X-ray diffraction (XRD) patterns of unreacted WCF and CA products were collected on a Philips Analytical X'Pert X-diffractometer (Philips Co., Netherlands), using Cu-Ka radiation ($k = 0.1540$ nm) atanaccelerating voltage of 40 kV and the current of 40 mA. The data was collected from $2\theta = 5–60^\circ$ with a step interval of 0.03°.

### 2.5. Characterization of interactions between WCF and ILs

0.5 g of WCF sample was suspended in the three ILs (10 g) respectively and heated to 100 °C with stirring for 3 h, then 50 mL of water was added and the suspension was agitated, and centrifuged at 4000 rpm for 5 min. The supernatant was decanted and the ILs-treated WCF was exhaustively washed with water five times to remove any residual ILs and then freeze-dried.

The XRD pattern of the ILs-treated WCF was recorded following the same operating procedure as that of CA. Particularly, the degree of crystallinity could be relatively expressed by the percentage crystallinity index (% CrI). The CrI was calculated by Eq. (3) (Segal, Creely, Martin, & Conrad, 1959):

$$CrI(\%) = \left[\frac{(I_{002} - I_{am})}{I_{002}}\right] \times 100 \quad (3)$$

where $I_{002}$ is the maximum intensity of $2\theta$ close to 22° and $I_{am}$ corresponds to the minimum intensity of $2\theta$ close to 18°. The average crystal size $\tau$ was determined by the Scherrer equation (French & Cintrón, 2013):

$$\tau = \frac{K\lambda}{(\beta \cos\theta)} \quad (4)$$

where $K$ is a constant that depends on the crystal shape (1.0 in this case), $\lambda$ is the wavelength of the incident beam in the diffraction experiment, $\beta$ is the full width at half maximum in radians and $\theta$ is the position of the peak (half of the plotted $2\theta$ value).

The average degree of polymerization (DP) of WCF and ILs-treated samples was determined by viscosity (25 °C) of cellulose solution in cupric ethylenediamine solution using Ubbelohde viscometer according to the previous reports (Xiong et al., 2012).

## 3. Results and discussion

### 3.1. Determination of $H_o$ values of the ILs

As the acetylation of cellulose is closely associated with the acidity of the catalyst (Shimizu, Furukawa, Kobayashi, Itaya, & Satsuma, 2009), Hammett acidity function of the different ILs was investigated in water solution based on the protocol given by Thomazeau et al. (2003), which is a relatively new way in determination of the acidity of ILs. In this experiment, water was chosen as solvent because it has considerable solubility for all tested ILs. As shown in Fig. 1(d), the maximum absorbance of the unprotonated form of the indicator was observed at 380 nm in water. No absorbance change could be observed when [Hmim]Cl was added, indicating [Hmim]Cl hardly ionized $H^+$. On the contrary, there was a noticeable decrease in the absorption curve of 4-nitroaniline upon the addition of $[Hmim]HSO_4$ and $[VSim]HSO_4$. The absorbance of the unprotonated form of the indicator decreased as follows: [Hmim]Cl > $[Hmim]HSO_4$ > $[VSim]HSO_4$. Based on the UV spectra, the quantitative data of $H_o$ values were obtained according to Eq. (1). The corresponding $H_o$ values of [Hmim]Cl, $[Hmim]HSO_4$ and $[VSim]HSO_4$, are 4.51, 1.62, and 0.47, respectively. The results indicate that the acidity of $[VSim]HSO_4$ is the strongest among the three ILs, followed by $[Hmim]HSO_4$ and [Hmim]Cl. It also can be seen that the acidities of the ILs depend both on the characteristics of the cations and anions. The acidity of [Hmim]Cl with the conjugate base of $Cl^-$ is weaker than that of $[Hmim]HSO_4$ with the conjugate base of $HSO_4^-$. On the other hand, the acidity of $[VSim]HSO_4$ was also significantly enhanced by introducing $-SO_3H$ groups on the vinyl imidazole cations compared with that of $[Hmim]HSO_4$, which has the same anion as $[VSim]HSO_4$.

**Table 1**
Effect of different ILs on the conversion, DS and solubility of CA produced from WCF.

| Entry | mol% | Conversion (%)[a] | DS | Solubility[b] | | |
|---|---|---|---|---|---|---|
| | | | | Water | Acetone | DMSO |
| 0 | 0[c] | ○[d] | 0.03 | – | – | – |
| [Hmim]Cl | | | | | | |
| 1a | 15 | ○ | 0.16 | – | – | – |
| 1b | 30 | ○ | 0.17 | – | – | – |
| 1c | 45 | ○ | 0.21 | – | – | – |
| 1d | 60 | ○ | 0.23 | – | – | + |
| 1e | 75 | ○ | 0.25 | – | – | + |
| [Hmim]$HSO_4$ | | | | | | |
| 2a | 15 | 88.6 | 1.13 | ++ | – | ++ |
| 2b | 30 | 84.0 | 1.92 | + | ++ | ++ |
| 2c | 45 | 96.4 | 2.13 | + | ++ | ++ |
| 2d | 60 | 95.2 | 2.68 | – | ++ | ++ |
| 2e | 75 | 82.4 | 2.98 | – | – | ++ |
| [VSim]$HSO_4$ | | | | | | |
| 3a | 3 | 97.3 | 1.75 | + | + | ++ |
| 3b | 6 | 99.6 | 2.17 | – | ++ | ++ |
| 3c | 9 | 88.8 | 2.92 | – | – | ++ |
| 3d | 12 | 86.5 | 3.03 | – | – | ++ |
| 3e | 15 | 84.3 | 2.95 | – | – | ++ |

[a] The conversion of CA (extracted with DMSO) was calculated based on the DS value.
[b] – Insoluble, + swelling, ++ soluble.
[c] Without IL.
[d] ○ close to 0 and the reacted cellulose was only surface-acetylated, thus the DS of such acetylated cellulose was obtained by titration and calculation method.

### 3.2. Catalytic performance of ILs for the acetylation of WCF

One of the main aims of the present work was to study the possibility of using acidic ILs as catalysts for WCF acetylation with controllable DS and to elucidate the effect of the molecular structure and acidity of ILs on the catalytic performance. Table 1 clearly shows that acetic anhydride is almost unable to acetylate cellulose without IL. Furthermore, different amount of the three ILs resulted in different conversions and DS values of CA. In the presence of [Hmim]Cl, the outward appearance of WCF was not changed even at the amount of 75 mol%. Strictly speaking, such cellulose products were only surface-acetylated and could not be called CA, and it was difficult to obtain the accurate DS values by $^1$H NMR spectroscopy because it is insoluble in DMSO-$d_6$. Therefore, the conversions of the CA were deemed to be 0%. Kamide, Okajima, Kowsaka, and Matsui (1987) have demonstrated that CA with a DS value higher than 0.38 could be dissolved well in DMSO. From their report, we deduced that the DS values of such acetylated cellulose products were rather low. Thus the DS value of the surface-acetylated cellulose was calculated from titration method (Kim, Nishiyama, & Kuga, 2002). A typical sample (entry-1e) showed no obvious weight gain, corresponding to a DS of 0.25, indicating that [Hmim]Cl had limited catalytic capability. The insolubility of such samples with low DS values agreed with the experimental data reported before (Kamide et al., 1987). On the contrary, all of the acetylated products catalyzed by [Hmim]$HSO_4$ and [VSim]$HSO_4$ were soluble well in DMSO without purification, indicating relatively higher DS. Using [Hmim]$HSO_4$ as catalyst, with only 15 mol% amount, a water-soluble CA product with a DS of 1.13 was achieved and the DS of CA increased with the increase of [Hmim]$HSO_4$ amount. A similar phenomenon also occurred in the presence of [VSim]$HSO_4$, which showed more remarkable catalytic capability. A lower amount of 9 mol% [VSim]$HSO_4$ was used but resulted in higher DS value of 2.92, revealing that the esterification of the hydroxyls on cellulose was almost complete. It is worth noting that with the DS of 2.17 (entry-3b), the conversion of WCF into CA was 99.6%, which coincides well with the theoretical value (100%). However, when the usage amount of [VSim]$HSO_4$ further increased, the conversion decreased. This might be ascribed to the hydrolysis of cellulose in the presence of acidic ILs (Li, Wang, & Zhao, 2008).

### 3.3. FTIR analysis

The structure change of WCF before and after acetylation catalyzed by three different ILs with the same content (15 mol%) was further evaluated using FTIR spectra. As shown in Fig. 2(a), the absorption band around 1060 $cm^{-1}$ which could be ascribed to —C—O— stretching vibration are found in all samples. It is the symbol of glucose ring. The intensity of this peak was not changed after reaction. Compared with the spectrum of unreacted WCF, the strong absorption peaks at 1752 $cm^{-1}$ (C=O ester) and 1237 $cm^{-1}$ (—CO— stretching of acetyl group) were observed in all the three CA products, which confirmed the successful acetylation of WCF (Sun et al., 2013; Zhang, Zhang, Tian, Zhou, & Lu, 2013). Furthermore, with the increasing DS of the CA products there was a reduced intensity of the band at 3412 $cm^{-1}$ (stretching of the hydroxyl groups), which further confirmed the conversion of hydroxyl groups into carbonyl groups during acetylation of cellulose. The spectra provide an evidence that the catalytic capability of the ILs is as follows: [Hmim]Cl < [Hmim]$HSO_4$ < [VSim]$HSO_4$, which is consistent with the sequence of acidity confirmed by UV–vis spectra.

According to the aforementioned analysis, it could be concluded that the catalytic activity of ILs was strongly affected by the structure of ILs. Although some imidazolium ILs with $Cl^-$ anions have been proved to be efficient in swelling and dissolving cellulose (Brandt, Hallett, Leak, Murphy, & Welton, 2010; Zhang et al., 2005), increasing the amount of [Hmim]Cl caused little change in the conversion and DS of the obtained CA. On the contrary, enhancement of the acidity of ILs by introducing $HSO_4^-$ anions or —$SO_3H$ groups on the vinyl imidazole cations which made no contribution to the swelling of WCF, showed a remarkable performance in the catalyzation of WCF acetylation. And further increasing the amount of [Hmim]$HSO_4$ or [VSim]$HSO_4$ ILs resulted in a higher DS of CA. These results clearly suggest that the structure and acidity of ILs played a key role on their catalytic activity, which provided reference for the design and synthesis of acidic ILs used as catalysts for cellulose esterification.

### 3.4. XRD analysis

The crystalline structure of WCF and CA products with various DS values are shown in Fig. 2(b) on the basis of XRD patterns. WCF diffraction patterns exhibit typical diffraction cellulose Iβ angles ($2\theta$) around at 14.6°, 16.5° and 22.7°, which are assigned to the diffraction planes of (1 $\bar{1}$ 0), (1 1 0) and (2 0 0), respectively (Nishiyama, Langan, & Chanzy, 2002). It can be seen that the identical characteristic peaks of cellulose still appear in the patterns of CA sample catalyzed by [Hmim]Cl (entry-1a) with only little decrease in the intensity, showing that the cellulose structure barely changed. However, the patterns of the obtained CA catalyzed by [Hmim]$HSO_4$ (entry-2a) and [VSim]$HSO_4$ (entry-3d) show a decrease and broadening in the intensities of the peaks at around 14.5°, 16.0°, and 22.5°, while the intensity of the corresponding peak of 33.5° is disappeared. In addition, new peaks ranging from 15° to 20° which are ascribed to cellulose triacetate are observed (entry-3d), demonstrating the hydroxyl groups of cellulose were almost fully substituted during the acetylation.

### 3.5. $^1$H NMR analysis

$^1$H NMR analysis was used to determine not only the DS values of CA but also the distribution of acetyl moieties among the three —OH

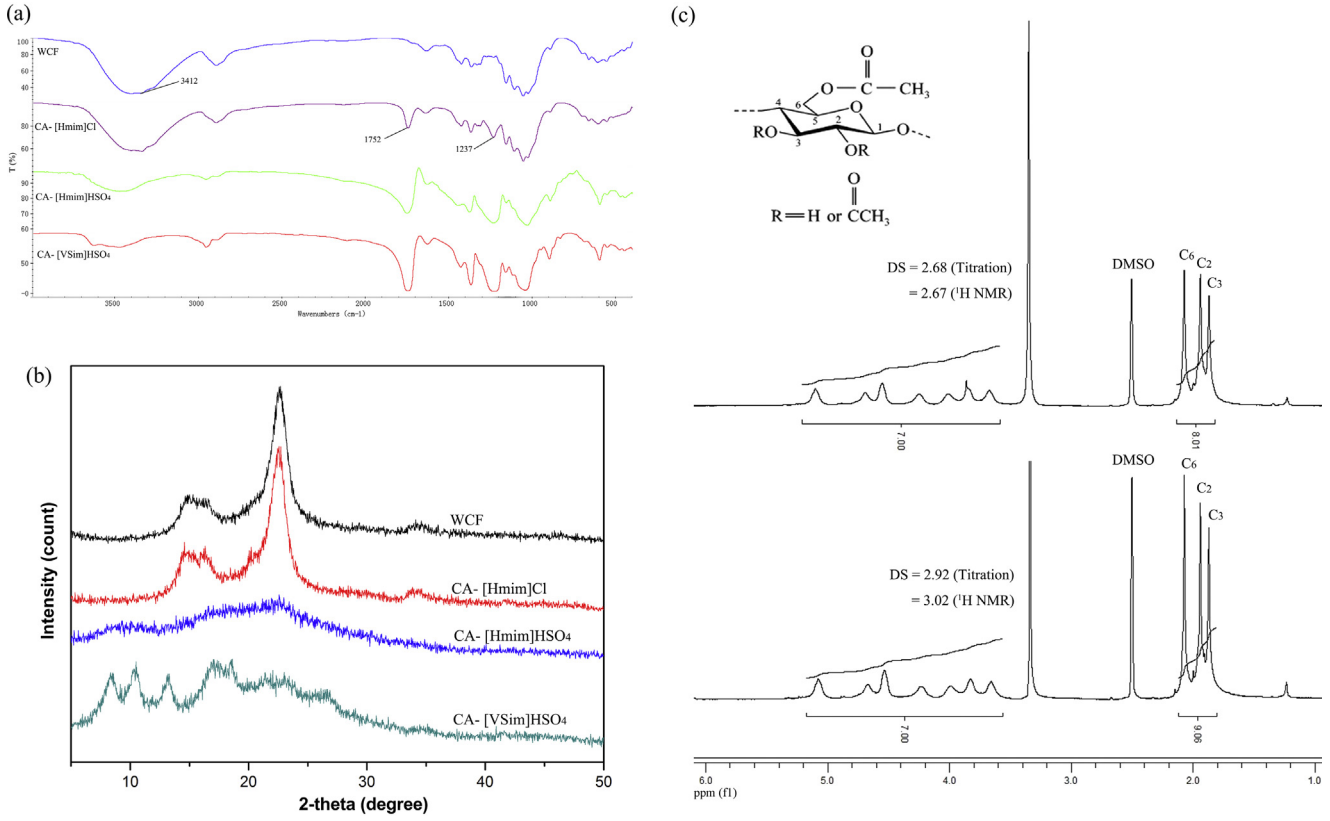


**Fig. 2.** (a) FTIR spectra of WCF and the obtained CA produced using different ILs (with the same amount, 15 mol%), (b) XRD patterns of WCF and the obtained CA produced using different ILs (with the same amount, 15 mol%), (c) $^1$H NMR spectra of the CA samples with a DS value of 2.67 (entry-2d) and 3.02 (entry-3c).

groups of the AGU. Fig. 2(c) shows two typical $^1$H NMR spectra of the CA samples with a DS of 2.67 (entry-2d) and 3.02 (entry-3c), which consisted well with the value obtained by titration method. The three hydroxyl groups at $C_2$, $C_3$, and $C_6$ positions exhibit different reaction activities with an order $C_6$—OH > $C_2$—OH > $C_3$—OH, which is similar to that observed in most homogeneous cellulose acetylation system but quite different from that of CA samples industrially synthesized through acetylation-hydrolysis process, whose reactivity order is $C_3$—OH > $C_2$—OH > $C_6$—OH (Buchanan, Edgar, & Wilson, 1991; Roy, Semsarilar, Guthrie, & Perrier, 2009; Wu et al., 2004). Moreover, in our previous communication (Zhang et al., 2013), the DS of CA increases with the reaction time in the presence of different amounts of [Hmim]$HSO_4$, showing a typical characteristic of homogeneous acetylation. Thus one-step synthesis of partially substituted CA could be realized in the current reaction system by changing the acidic ILs amount or reaction time. The possible reason is that the acidic ILs could swell cellulose from WCF and break the inter- and intramolecular hydrogen bonds in cellulose. As a result, a "quasi-homogeneous" state was produced. The hydroxyl groups of cellulose were gradually exposed and the interval of macromolecular chain of cellulose increased. Therefore, small molecules of acetic anhydride could enter in and finally substitute the hydroxyl groups homogeneously (Brandt et al., 2010; Zhang, Brendler, Geissler, & Fischer, 2011; Zhang, Su, Luo, & Wei, 2012).

### 3.6. Interaction between WCF and ILs

To investigate the effect of ILs on the cellulose structure and the resulted crystallinity, XRD analysis was carried out. The changes in the crystalline structure of WCF before and after acidic ILs treatment are shown in Fig. 3(a). In order to reach better analysis, all the experimental data were scaled so that the maximum height of all patterns was the same. The main peak at $2\theta = 22.7^\circ$ observed for untreated WCF broadens and shifts to lower angles for all of the WCF treated by the three ILs, together with the lower shifts of the peak observed at around $2\theta = 16.0^\circ$. In general, the XRD pattern of regenerated cellulose would change from cellulose I to cellulose II after dissolution and regeneration in ILs. In this study, all of the diffraction patterns exhibit typical diffraction cellulose I angles, suggesting that the three ILs cannot dissolve cellulose effectively (Wang et al., 2012; Zhang et al., 2005). The CrI of untreated WCF obtained by the Segal method was 81.62%, and decreased to 70.78%, 68.91%, 54.18% after [Hmim]Cl, [Hmim]$HSO_4$ and [VSim]$HSO_4$ treatment, respectively (Table 2). In Table 2, it also can be seen that the DP of WCF decreased after the IL treatment at 100 °C, which is in line with previous report (Zhang et al., 2005). In cellulose I, parallel cellulose chains are aligned side-by-side and stacked in flat sheets by hydrogen bonds and van der Waals interactions (Nishiyama et al., 2002). The shift in the main peak to lower values of $2\theta$ indicates an increase in the space between the stacked sheets of cellulose molecules and the wider peak width is an indicative of smaller crystallites. The results indicate that ILs could swell cellulose and disrupt the van der Waals and hydrogen bonds between cellulose chains, which can significantly improve the accessibility of hydroxyl groups on cellulose during acetylation.

**Table 2**
Segal CrI, crystal size and DP of WCF before and after ILs treatment.

| Sample | CrI (%) | Crystal size (nm) | DP |
|---|---|---|---|
| WCF | 81.62 | 4.63 | 900 |
| WCF-[Hmim]Cl | 70.78 | 3.35 | 750 |
| WCF-[Hmim]$HSO_4$ | 68.91 | 3.34 | 712 |
| WCF-[VSim]$HSO_4$ | 54.18 | 1.67 | 563 |

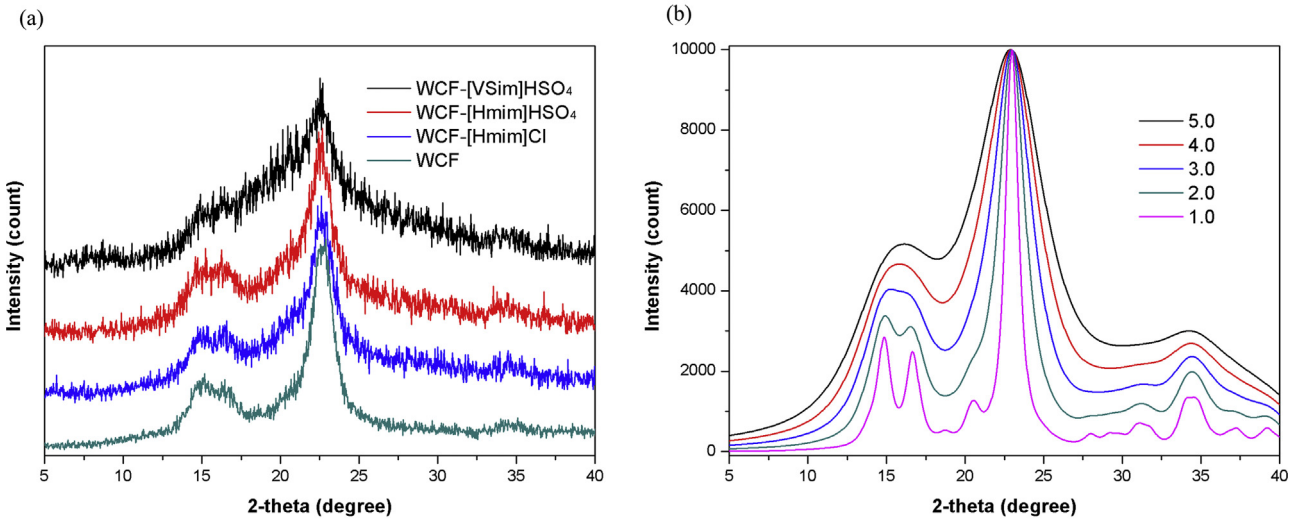


**Fig. 3.** (a) XRD patterns of WCF before and after ILs treatment, (b) theoretical diffraction patterns for cellulose Iβ calculated for peak widths at half maximum from 1° to 5°.

French and Cintrón (2013) pointed out that the Segal method to determinate the CrI of cellulose is an empirical method simply based on that there are only crystalline and non-crystalline materials in cellulose, and there has some limitation in determination of CrI with different crystallite sizes. To get a better understanding in this part, some theoretical diffraction patterns which are only based on crystalline material were created using Mercury program according to the previous reports (French & Cintrón, 2013; French, 2013), and compared with XRD patterns of WCF before and after ILs treatment. As shown in Fig. 3(b), as the input peak widths at half of the maximum peak intensity (pwhm) changes from 1° to 5° (the pwhm of the main (200) peak of WCF before and after ILs treatment), a series of values of the Segal CI and crystal size for the different pwhm values were obtained. In fact, French and Cintrón (2013) reported that there was a nonlinear relationship between the Segal CI and the crystal size. The values of Segal CrI and crystal size of WCF before and after ILs treatment obtained in this work are in agreement with their calculations (Table 2). Thus it can be concluded from the aforementioned analysis that acidic ILs could decrease the CrI and crystal size without transformation of crystal type, demonstrating that WCF was swollen in the ILs and the "quasi-homogeneous" state was achieved during cellulose acetylation.

### 3.7. Plausible mechanism for the dual function of swelling and catalyzing of acidic ILs

According to the analysis above, we try to explain the general reaction mechanism for the one-step synthesis of CA with controllable DS catalyzed by acidic ILs. As shown in Fig. 4, at first, acidic ILs swelled cellulose, destroying the hydrogen bonds and increasing the space between the stacked sheets of cellulose molecules and thus the acetic anhydride could diffuse in (Olsson, Idström, Nordstierna, & Westman, 2014; Torr et al., 2012). Then the CrI and crystal size of cellulose decreased and the hydroxyl groups were exposed, leading to a "quasi-homogeneous" reaction system. Meanwhile, $H^+$ was ionized by ILs and activated the carbonyl group of acetic anhydride, drawing electrons away from the carbonyl carbon of cellulose and making it more positively charged and thus more reactive with acetic anhydride (Biswas et al., 2005). This putative mechanism was in accordance with the results in Table 1 that the acetylation of cellulose started with heterogeneously dispersed cellulose but ended with a homogeneous "paste-like" state (Zhang et al., 2011, 2012). The dual-function (swelling and catalyzing) of acidic ILs resulted in the one-step synthesis of CA with controllable DS, just like that in the homogeneous reaction system. As seen in Fig. 4, two kinds of most widely used CA products,

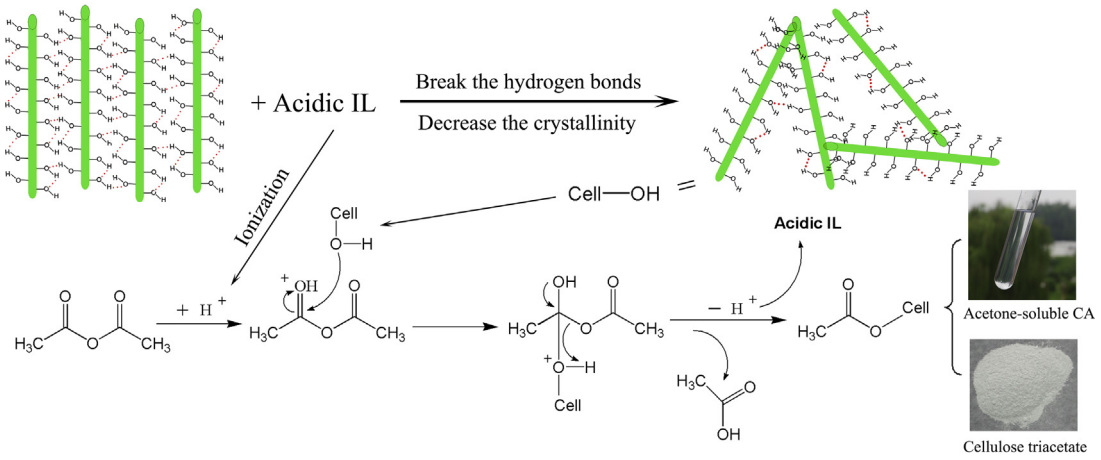


**Fig. 4.** Plausible mechanism for acetylation of WCF with controllable DS using acidic ILs as catalyst.

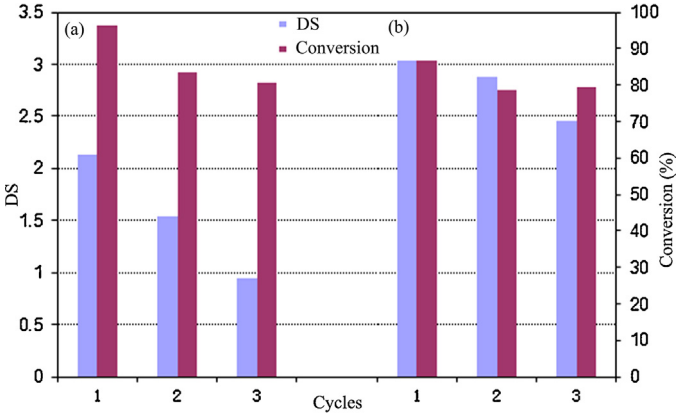


**Fig. 5.** Reusability of (a) [Hmim]$HSO_4$ at the amount of 45 mol% (entry-2c) and (b) [VSim]$HSO_4$ at the amount of 12 mol% (entry-3d).

acetone-soluble CA with a DS of 2.17 (entry-3b) and cellulose triacetate with a DS of 2.92 (entry-3c) were obtained by adjusting the amount of [VSim]$HSO_4$. However, for [Hmim]Cl, although it can swell cellulose as that of [Hmim]$HSO_4$ (Table 2), the catalytic capacity of [Hmim]Cl was much lower due to its limited acidity. Thus acidic ILs which had dual-function of swelling and catalyzing, tend to exhibit outstanding performance in acetylation of cellulose with controllable DS values.

### 3.8. Reusability of the IL catalysts

In modern green chemistry, the recycling of catalysts is very important. Consequently, we investigated the catalytic activity of the recycled [Hmim]$HSO_4$ (entry-2c) and [VSim]$HSO_4$ (entry-3d). The acidic ILs were recycled by vacuum distillation and the experiments were carried out for three runs under the same conditions. As shown in Fig. 5, [Hmim]$HSO_4$ suffered an obvious loss of catalytic activity even in the second run while [VSim]$HSO_4$ exhibited higher stability during the reaction process and the conversion and DS decreased a little after 3 recycling instances. The possible reason is that $-SO_3H$ groups on the cation made a great contribution in IL acidity and perhaps were more stable than $HSO_4^-$. These results indicate that the [VSim]$HSO_4$ is a high efficient and recyclable catalyst in cellulose acetylation.

### 3.9. A comparison study with commercialized solid acid catalysts

Solid acid catalysts were widely studied in cellulose hydrolysis owing to some obvious advantages such as ease of recovery, less corrosion and milder reaction conditions. In this part, the performance of [VSim]$HSO_4$ and several commercialized solid acid catalysts for the cellulose acetylation are summarized in Table 3. The results indicate that [VSim]$HSO_4$ has the highest activity among all the catalyst at the same dosage. The sulfonated polystyrene resins, Amberlyst® 15 and Amberlite 732, showed very low catalytic capacity due to their limited surface area. Zeolite H-ZSM-5 produced CA with a conversion of 50.0% and DS of 0.90, leaving half of the cellulose unreacted, showing a typical characteristic of heterogeneous reaction. The relatively small pore size (0.55 nm) in H-ZSM-5 increased its active sites but it was too small to be accessed by cellulose without swelling or dissolution (Deng, Liu, Zhang, Tan, & Wang, 2010; Rinaldi, Palkovits, & Schüth, 2008). Based on the experimental data, there are some obstacles in the application of the solid acid catalysts, such as low efficiency and non-uniform products in the cellulose acetylation. Because of high efficiency and DS controllable, [VSim]$HSO_4$ showed a potential use in the cellulose esters industry.

**Table 3**
Catalytic performance of [VSim]$HSO_4$ compared with commercialized solid acid catalysts.

| Catalyst | Conversion (%) | DS |
|---|---|---|
| [VSim]$HSO_4$ | 88.8 | 2.92 |
| H-ZSM-5 | 50.0 | 0.90 |
| Amberlite 732 | ○ | 0.22 |
| Amberlyst® 15 | ○ | 0.13 |

Cellulose: 1.62 g, catalyst: 0.28 g, ○ close to 0.

## 4. Conclusions

The present work showed the possibility of the conversion of cellulose into CA with controllable DS values using very small amount (only 3–9 mol% for [VSim]$HSO_4$) of acidic ILs as catalysts. CA with different DS values ranging from 1.13 to 2.95 could be obtained by controlling the reaction time and the amount of ILs. The dual-function of swelling and catalyzing of acidic ILs played an important role in producing "quasi-homogeneous" acetylation system and controlling the DS of CA. Based on the fact that the acidic ILs [VSim]$HSO_4$ could be reused effectively and its efficiency was much higher than that of the commercialized solid acid catalysts, it provided a technically feasible and environmentally friendly one-step method to prepare CA products with expected DS using industrial waste WCF as cellulose resource. Furthermore, it opened an avenue in controllable synthesis of other cellulose esters or ethers under "quasi-homogeneous" conditions.

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