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Dissolution of cellulose in 1-allyl-3-methylimizodalium carboxylates at room temperature: A structure–property relationship study

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ABSTRACT

The development of highly efficient cellulose solvents is imperative to the effective utilization of cellulose. In this work, ionic liquids (ILs) with the same 1-allyl-3-methylimidazolium cation ($[Amim]^+$) but different carboxylate anions, such as formate ($[HCOO]^-$), acetate ($[CH_3COO]^-$), propionate ($[CH_3CH_2COO]^-$), butyrate ($[CH_3CH_2CH_2COO]^-$), glycollate ($[HOCH2COO]^-$), lactate ($[CH_3CHOHCOO]^-$) and benzoate ($[C_6H_5COO]^-$) were synthesized, and their thermal properties and viscosities were determined. Then these ILs were used to investigate the effect of anion structure on solubility of cellulose in the ILs. It was shown that the viscosity and cellulose solubility depended strongly on the anion structure of the ILs. For example, at 30 °C solubility of cellulose in $[Amim][CH_3CH_2COO]$ was as high as 19.0%, whereas cellulose was not soluble in $[Amim][HOCH_2COO]$, $[Amim][CH_3CHOHCOO]$ and $[Amim][C_6H_5COO]$. In addition, solvatochromic UV/vis probe and ^{13}C NMR measurements were performed to demonstrate dissolution mechanism of cellulose in the ILs. The results suggested that although cations of the ILs have un-negligible contribution to the highly efficient dissolution of cellulose, hydrogen bonding interactions of anions of the ILs with cellulose is predominant.

1. Introduction

Ever increasing interest in ionic liquids (ILs) is ascribed to their distinguished advantages such as non-flammability, extremely low vapor pressure, wide liquid range, high chemical and thermal stability, and excellent structure and property designability (Dupont, Souza, & Suarez, 2002; Wasserscheid & Keim, 2000). These unique properties have endowed ILs with potential application in various fields such as organic synthesis (Hallett & Welton, 2011; Isambert et al., 2011), biocatalysis (Rantwijk & Sheldon, 2007), carbon dioxide capture (Bara, Camper, Gin, & Noble, 2010; Gurkan et al., 2010), extraction and separation (Cao et al., 2012; Hoogerstraete, Onghena, & Binnemans, 2013), electrochemistry (Kong et al., 2014; Wang, Wang, Tu, Xiong, & Wang, 2013), nanomaterials preparation (Hoang, Park, & Kim, 2011), dye-sensitized solar cells (Xu et al., 2013) and so on.

In addition to the above versatile applications, ILs have been successfully employed to process cellulose in the past decade (Brandt, Gräsvik, Halletta, & Welton, 2013; Wang, Gurau, & Rogers, 2012). In 2002, Swatloski, Spear, John, Holbrey, and Rogers (2002) introduced ILs into the dissolution and processing of cellulose for the first time. It was found that 10 wt% cellulose solubility was obtained in 1-butyl-3-methylimidazolium chloride $[C_4mim]Cl$ at 100 °C, and the solubility could be as high as 25 wt% under microwave heating. This pioneering work opened a new field of cellulose solvent research. Since then, a number of investigations have been carried out to develop ILs in order to increase the solubility of cellulose or to decrease its dissolution temperature. In this context, Zhang, Wu, Zhang, and He (2005) reported that 1-allyl-3-methylimidazolium chloride [Amim]Cl was also a powerful non-derivatizing solvent for cellulose, and a solution containing 14.5 wt% cellulose could be prepared at 80 °C without any pretreatment. Fukaya, Hayashi, Wadab, and Ohno (2008) found that 1-ethyl-3-methylimidazolium alkylphosphates $[C_2mim][(MeO)(R)PO_2]$ displayed superior solubility for cellulose, cellulose solubility in $[C_2mim][(MeO)(H)PO_2]$ was 4 wt% at 30 °C and 10 wt% at 45 °C. To our knowledge, these are the only results reported for the solublization of cellulose at around room temperature. Fukaya, Sugimoto, and Ohno (2006) also reported that 1-ethyl-3-methylimidazolium formate ($[C_2mim][HCOO]$), 1-propyl-3-methylimidazolium formate ($[C_3mim][HCOO]$),

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1-allyl-3-methylimidazolium formate ([Amim][HCOO]) and 1-allyl-3-ethylimidazolium formate ([Aeim][HCOO]) had high cellulose solubility under mild condition. Among these ILs, [Amim][HCOO] was the best cellulose solvent, solubility of cellulose in this IL increased from about 11 wt% at 60 °C to 22 wt% at 85 °C. However, the structure–property relationship is not yet well understood for such cellulose solvent systems.

In recent years, a number of studies demonstrated that by using carboxalate (such as [CH_3COO], [C_2H_5COO] and so on) as anion, solubilization capacity of the ILs for cellulose was also significantly enhanced (Chen, Liu, Li, Zhang, & Deng, 2011; Tang, Baker, Ravula, Jonesc, & Zhao, 2012; Xu, Wang, & Wang, 2010; Zhao, Greiner, & Leitner, 2012). Encouraged by these results and the interesting work mentioned above for the dissolution of cellulose in [Amim][HCOO], we decided to study the structure–property relationship of allyl imidazolium carboxalates in room temperature dissolution of cellulose. The contribution of this type of knowledge is undoubtedly helpful for the future design of novel and superior cellulose solvent systems.

For this purpose, a series of 1-allyl-3-methylimidazolium carboxylate ILs: [Amim][HCOO], [Amim][CH_3COO], [Amim][CH_3CH_2COO], [Amim][$CH_3CH_2CH_2COO$], [Amim][$HOCH_2COO$], [Amim][$CH_3CHOHCOO$] and [Amim][C_6H_5COO] were synthesized and characterized in this work. Thermal properties and viscosities of these ILs were determined, and solubility of cellulose in the resulting ILs was investigated as a function of temperature. The effects of anionic structure of the ILs on the viscosities, thermal properties and cellulose solubilities were evaluated. In order to understand the high solubility of cellulose in these ILs, solvatochromic UV/vis probe technique was used to study hydrogen bond accepting ability of the ILs toward protons of the hydroxyl groups of cellulose. Meanwhile, [Amim][CH_3COO] was chosen as a representative IL to investigate the interactions of the ILs with cellulose in the mixture of cellulose + [Amim][CH_3COO] by ^{13}C NMR measurements. Some important information was provided for the rational design of novel IL solvents of cellulose.

2. Experimental

2.1. Materials

1-Methylimidazole (>99%) was purchased from Shanghai Chem. Co. Ltd. Anion exchange resin (Ambersep 900-OH) and 4-nitroaniline (98.0%) were purchased from Alfa Aesar. *N*,*N*-Diethyl-4-nitroaniline (97.0%) was obtained from Beijing Chem. Co. Allyl chloride (>98%), butyric acid (>98%), benzoic acid (>99.5%) and glycollic acid (>98%) were the products of Aladdin Chem. Co. Ltd. Formic acid (>88.0%), acetic acid (>99.5%), propanoic acid (>99%) and lactic acid (85.0–90.0%) were purchased from Tianjin Kermel Chem. Co. Ltd. Sodium dicyanamide (>98%) and methanol (>99.8%) were obtained from Nanjing Chemlin Chem. Co. Ltd. and Sinopharm Chem. Co. Ltd., respectively. Deuterated dimethyl sulfoxide (DMSO-d_6) was purchased from Qingdao Weibo Tenglong Technol. Co. Ltd. These reagents were used without further purification.

Microcrystalline cellulose (MCC) with a viscosity-average degree of polymerization (DP) of 229 was purchased from Alfa Aesar, and used directly after being dried at 60 °C under vacuum for 10 h. The degree of polymerization of cellulose was determined by using an Ubbelohde viscometer in cupriethylenediamine hydroxide solutions (Xu et al., 2010).

2.2. Synthesis of the ILs

1-Allyl-3-methylimidazolium chloride ([Amim]Cl) was prepared and purified by using the procedure reported in literature (Zhang et al., 2005). Briefly, 1-methylimidazole and allyl chloride were added, at a molar ratio of 1:1.25, into a round-bottomed flask fitted with a reflux condenser, and the reaction was continued for 8 h at 55 °C with stirring. The product [Amim]Cl was obtained by removing un-reacted allyl chloride via distillation at reduced pressure. Then, in order to obtain [Amim][OH], an aqueous solution of [Amim]Cl was allowed to pass through a column filled with anion exchange resin (Ambersep IRA 900-OH) (Fukaya et al., 2006; Xu et al., 2010). Finally, the [Amim][OH] aqueous solution was neutralized with an equimolar quantity of formic acid. After removing water by evaporation under reduced pressure, the viscous liquid [Amim][HCOO] was thoroughly washed with diethyl ether, and dried under vacuum for 48 h at 70 °C in the presence of P_2O_5. The other ILs were prepared by a similar process as described for the preparation of [Amim][HCOO].

2.3. Measurements of ^1H NMR and impurity content of the ILs

^1H NMR spectra of the ILs were collected at room temperature from a Bruker Avance-400 NMR spectrometer operating at 400.13 MHz. The solutions used for the ^1H NMR experiments were prepared by adding a given amount of IL into a 5 mm NMR tube, and the internal DMSO-d_6 was then added to allow the IL to be completely dissolved at room temperature. ^1H NMR data of these ILs were reported in the supporting information.

Since impurities existing in the ILs, such as water and Cl^-, would greatly affect their physicochemical properties (Jacquemin, Husson, Padua, & Majer, 2006; Seddon, Stark, & Torres, 2000), the water and Cl^- contents in the investigated ILs were determined, respectively, by Karl–Fischer titration using a 851 moisture titrator (Metrohm, Switzerland) and by potential titration using a PCl-1 chloride-selective electrode (Shanghai Precision & Scientific Instrument Co., Ltd). It was found that 329–558 ppm of water and 291–532 ppm of chloride were remained in the ILs reported here. Zhao et al. (2012) reported that for the dissolution of cellulose in [C_2mim][CH_3COO], water content of lower than 2500 ppm and chloride content of lower than 1192 ppm did not affect cellulose solubility. This suggests that the ILs prepared in this work are qualified for the cellulose solubility measurements.

2.4. Determination of thermal properties and viscosities of the ILs

Glass transition temperatures of the ILs were determined on a differential scanning calorimeter (Netzsch DSC 204 F1). Each IL sample was sealed in aluminum pans and heated at a rate of 5 °C min^{-1} under N_2 atmosphere in the temperature range from −130 °C to 30 °C. Thermogravimetric analysis (TGA) was recorded on a thermal analyzer (Netzsch STA 449C) using alumina crucibles with 10 wt% mass loss at a heating rate of 10 °C min^{-1} under N_2 atmosphere, and all the IL samples were heated from room temperature to 600 °C.

Viscosities of the ILs were measured by a suspended level Ubbelohde viscometer, which was placed in a water thermostat (Schott, Germany) at 25 °C. The temperature of the water thermostat was controlled by circulating water from a constant-temperature bath (Schott, Germany), and the temperature uncertainty was ±0.01 K. The viscometer was calibrated with known viscosities of pure water. Viscosities for water at different temperatures were taken from literature (James, Mulcahy, & Steel, 1984). Flow time measurements were performed by a Schott AVS310 photoelectric time unit with a resolution of 0.01 s. The estimated uncertainty of the experimental viscosity was lower than ±2.0%. Viscosities of the ILs were given by the following equation

$$\frac{\eta}{\rho} = \frac{Ct - K}{t} \qquad (2.1)$$

Table 1
Glass transition temperature T_g, thermal decomposition temperature T_d, viscosity η and density ρ for the ILs investigated at 25 °C.

IL	T_g (°C)	T_d (°C)	η (mPa s)	ρ (g cm^{-3})
[Amim][HCOO]	−82	202	32.66	1.130
[Amim][CH_3COO]	−71	217	88.93	1.111
[Amim][CH_3CH_2COO]	−76	214	122.6	1.086
[Amim][$CH_3CH_2CH_2COO$]	−74	217	212.7	1.062
[Amim][C_6H_5COO]	−50	231	689.4	1.149
[Amim][$HOCH_2COO$]	−58	248	277.3	1.189
[Amim][$CH_3CHOHCOO$]	−51	245	312.7	1.148

where C and K are the cell constants, t is the flow time, and ρ is the density of the ILs. The latter was determined by using a vibrating-tube digital densimeter (model DMA 60/602, Anton Paar Austria) at 25 °C as described in the literature (Xu, Wang, Zhang, & Chen, 2012). The density values of these ILs are also given in Table 1.

2.5. Measurements of the β parameters of the ILs

The β parameter values of the ILs were determined based on the procedures reported by Fukaya et al. (2008). Briefly, two different dyes, 4-nitroaniline (NA) and *N*,*N*-diethyl-4-nitroaniline (DENA), were respectively dissolved in dry methanol to obtain a concentrated methanol solution of NA or DENA. In a dry box, a given amount of the IL and the concentrated solution of NA or DENA were added into a vial and mixed homogeneously. The methanol was then carefully removed by drying under vacuum for 2 h at 40 °C. The IL containing NA or DENA was added into a quartz cell in a dry box and the cell was capped and sealed. The visible spectra of the IL solutions were recorded on a TU-1810 ultraviolet-visible spectrophotometer at 25.0 ± 0.1 °C. The wavelength at the maximum absorption ($\lambda_{\max}$) was determined and then used to calculate the β values by the following equations (Fukaya et al., 2008):

$$\beta = \frac{(1.035\nu_{(DENA)} + 2.64 - \nu_{(NA)})}{2.80} \tag{2.2}$$

where

$$\nu_{(DENA)} = \frac{1}{(\lambda_{\max(DENA)} \times 10^{-4})} \tag{2.3}$$

and

$$\nu_{(NA)} = \frac{1}{(\lambda_{\max(NA)} \times 10^{-4})} \tag{2.4}$$

2.6. Measurements of solubility and ^{13}C NMR spectra

0.01 g of dried microcrystalline cellulose sample was added into a 20 mL colorimetric tube containing 2.0 g of the dried IL, and the tube was sealed with parafilm. The tube was then immersed in an oil bath (DF-101S, Gongyi Yingyu Instrument Factory), and instability of the bath temperature was estimated to be ±0.5 °C. The mixture was heated at a given temperature and stirred under argon atmosphere. After the solution became optically clear under a polarization microscope (Nanjing Jiangnan Novel Optics Co. Ltd.), additional cellulose was added. When cellulose solution became saturated, judged by the fact that cellulose could not be dissolved further within 1 h, its solubility at the given temperature could be calculated from the amount of the solvent and cellulose added. For each IL, the solubility values of cellulose were measured at different temperatures with 10 °C interval. Measurements of ^{13}C NMR spectra for [Amim][CH_3COO] in the pure liquid and in the solution of [Amim][CH_3COO] + cellulose (10.0 wt%) were performed on a Bruker DMX 300 spectrometer at 90 °C. Chemical shifts were given in ppm downfield from TMS.

3. Results and discussion

3.1. Effects of anionic structure on thermal properties and viscosities of the ILs

Thermal properties determined for the ILs were shown in Table 1. It can be seen that these ILs have only low glass transition temperatures (T_g) from −50 to −82 °C, which suggests that all of the ILs have very low "melting point" and they are really room temperature ILs. The T_g values were correlated with anionic structure of the ILs. Generally, it was found that replacement of H in the anions by an alkyl chain (such as CH_3, CH_3CH_2 and $CH_3CH_3CH_2$), hydroxyl group or benzene ring unit led to an increase in the glass transition temperature. Therefore, the glass transition temperature (−82 °C) for [Amim][HCOO] was lower than those (from −76 °C to −50 °C) for the other ILs investigated. This indicated that smaller size and shorter alkyl chain resulted in the lower T_g values, which was in agreement with the results reported in the literature (Zhou, Matsumoto, & Tatsumi, 2004, 2005). In addition, it was found that thermal decomposition temperature of the ILs was higher than 202 °C, and also influenced by the anionic structures in a similar way observed for their glass transition temperature. A similar trend was reported in previous investigations (Crosthwaite, Muldoon, Dixon, Anderson, & Brennecke, 2005; Zhou, Matsumoto, & Tatsumi, 2005).

Viscosities of the ILs determined at 25 °C were also given in Table 1. It is evident that [Amim][HCOO] (33.79 mPa s), [Amim][CH_3COO] (88.93 mPa s), [Amim][CH_3CH_2COO] (122.6 mPa s) and [Amim][$CH_3CH_2CH_2COO$] (212.7 mPa s) showed a considerably lower viscosity at 25 °C, while [Amim]Cl displayed a viscosity of 685 mPa s at 30 °C (Zhang et al., 2005), and [C_4mim][HCOO], [C_4mim][CH_3COO], [C_4mim][CH_3CH_2COO] and [C_4mim][$CH_3(CH_2)_2COO$] had a viscosity of 188.8, 420.3, 468.0 and 521.2 mPa s, respectively. At the same time, viscosities of the ILs were found to increase in the order: [Amim][HCOO] < [Amim][CH_3COO] < [Amim][CH_3CH_2COO] < [Amim][$CH_3CH_2CH_2COO$]. This suggests that viscosities of the ILs increase with increasing alkyl chain length in carboxylate anions because of the increased van der Waals interactions (Ghatee, Zare, Moosavi, & Zolghadr, 2010; Gómez, González, Domínguez, Tojo, & Tojo, 2006; Greaves, Weerawardena, Fong, Krodkiewska, & Drummond, 2006). Moreover, it was found that viscosity significantly increased owing to the substitution of H in the anions by a hydroxyl group. For example, the viscosity of [Amim][$HOCH_2COO$] (277.3 mPa s) was much higher than that of [Amim][CH_3COO] (88.93 mPa s). This could be attributed to the increased interactions between cation and anion of the ILs in the presence of hydroxyls in the side chain of anions. A similar trend has been reported for ethanolammonium fomate/acetate with hydroxyl group in cations, ethylammonium glycolate/lactate with hydroxyl group in anions, and ethanolammonium glycolate/lactate with hydroxyl groups in both cations and anions (Hirao, Sugimoto, & Ohno, 2000). Compared with alkyl group substitution in carboxylate anion, hydroxyl group substitution was found to have a more pronounced influence on viscosity of the ILs. For example, the viscosity of [Amim][$HOCH_2COO$] was 3.1 time that of [Amim][CH_3COO], whereas the viscosity of [Amim][CH_3CH_2COO] was only 1.4 time that of [Amim][CH_3COO].

In the case of [Amim][C_6H_5COO] (689.4 mPa s), the presence of benzene ring unit in the anion resulted in strong ion-ion interactions through stocking benzene rings (Greaves & Drummond, 2008), and thus in considerably high viscosity. However, incorporating allyl group in the imidazolium cation greatly reduced viscosity of the ILs. For instance, although [Amim][HCOO] and [C_3mim][HCOO] have the same carbon atom number (three) in the side chain of the imidazolium cations, viscosity of the latter

Table 2
Solubility of microcrystalline cellulose in the ILs as a function of temperature.

IL	Solubility (g per 100 g of IL)						
	25 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C
[Amim][HCOO]	<0.5	6.0	*8.5*	*10.0*	**12.0**	17.0	18.5
[Amim][CH_3COO]	<0.5	14.0	*16.0*	*16.5*	**18.0**	21.0	22.0
[Amim][CH_3CH_2COO]	<0.5	19.0	*21.0*	*22.0*	**22.5**	22.5	23.0
[Amim][$CH_3CH_2CH_2COO$]	<0.5	12.5	*15.5*	*16.0*	**16.5**	17.5	18.5
[Amim][C_6H_5COO]	<0.5	<0.5	*0.5*	*10.5*	**15.0**	17.0	18.0
[Amim][$HOCH_2COO$]	<0.5	<0.5	*9.0*	*13.0*	**14.0**	15.0	15.0
[Amim][$CH_3CHOHCOO$]	<0.5	<0.5	*<0.5*	*8.0*	**10.5**	11.5	11.5

(117 mPa s) (Fukaya et al., 2006) was about 3.5 times that of the former (33.79 mPa s) at 25 °C. Therefore, it is strongly suggested that for the rational design of a low viscosity IL, an allyl group rather than an alkyl, hydroxyl or phenyl unit would be incorporated in the side chain of their cations and/or anions.

3.2. Effects of anionic structure on dissolution performance of the ILs for cellulose

The solubility values of microcrystalline cellulose in the studied ILs were summarized in Table 2 as a function of temperature. It can be seen that all of the ILs are excellent solvents for the dissolution of cellulose as the temperature was equal to or higher than 50 °C. Even at 30 °C, the ILs with $[HCOO]^-$, $[CH_3COO]^-$, $[CH_3CH_2CH_2COO]^-$ and $[CH_3CH_2COO]^-$ as the anions could dissolve considerable amounts of cellulose (say 19% in [Amim][CH_3CH_2COO]). However, it was found that [Amim][C_6H_5COO], [Amim][$HOCH_2COO$] and [Amim][$CH_3CHOHCOO$] could only dissolve less than 0.5% of cellulose at 30 °C. This indicates that the solubility of cellulose strongly depends on the anionic structure of the ILs. Our previous studies (Xu et al., 2010) revealed that replacement of H in CH_3COO^- anion of [C_4mim][CH_3COO] by electron-withdrawing groups such as OH, SH, NH_2 and CH_3OH led to the decrease in cellulose solubility. In the present work, it is interesting to find that replacement of H in $HCOO^-$ anion of [Amim][HCOO] by the electron-donating groups such as CH_2 and CH_2CH_3 caused an increased solubility of cellulose. This can be explained by the fact that replacement of H in CH_3COO^- anion by an electron-withdrawing group (X) would result in a decrease in the hydrogen bond formation ability of CH_2XCOO^- with the hydroxyl protons of cellulose, whereas replacement of H in $HCOO^-$ anion by an electron-donating group would lead to an increase in the hydrogen bond formation ability of $XCOO^-$ with the hydroxyl protons of cellulose. From this point, we can conclude that to design ILs with strong hydrogen bond formation ability, it is exactly electron-donating not electron-withdrawing groups that should be incorporated into the anions. In addition, solubility of cellulose in the ILs was enhanced with increasing temperature. In the case of [Amim][CH_3COO], the solubility of cellulose at 70 °C (21.0%) was higher than that at 30 °C (14.0%) by about 50%. This is an indication that hydrogen bonds of cellulose were also partially disrupted by the rise of temperature.

Compared with other ILs solvents for cellulose, the ILs reported in this work exhibited low viscosity, low dissolution temperature, and high solubility of cellulose. For example, at 30 °C [Amim][CH_3CH_2COO] gave the solubility of 19.0%, but only 4.0% cellulose could be dissolved in [C_2mim][(MeO)(H)PO_2] (Fukaya et al., 2008) which was the only IL reported to have the capacity of dissolving cellulose at around 30 °C up to now. Therefore, the ILs reported in this work are highly efficient solvents for the dissolution of cellulose at room temperature.

3.3. Interactions between ILs and cellulose and the possible dissolution mechanism

It has been reported that Kamlet–Taft β parameter can be used to measure hydrogen bond accepting ability of ILs (Chiappe & Pieraccini, 2005; Huddleston, Broker, Willauer, & Rogers, 2002; Oehlke, Hofmann, & Spange, 2006). Therefore, we determined these parameters in the temperature range from 25 to 60 °C and the results were given in Table 3. It was noted that the β parameter values keep unchanged with the increase of temperature. This is the reason why β parameter at 25 °C was often used to correlate the solubility data at other temperatures (Xu et al., 2010). However, these parameters do vary with the change in anionic structures. Additionally, we found that the reported ILs displayed quite high β values (from 0.942 to 1.141) in the temperature range investigated, suggesting that these ILs have strong hydrogen bond basicity and they are excellent solvents for biomacromolecules such as cellulose.

As an example, the relationship between cellulose solubility and the β parameter values of the ILs at 70 °C was shown in Fig. 1. It was clearly indicated that solubility of cellulose increased with increasing β parameter. Considering the fact that these ILs have the same cation but different anions, this verifies that solubility of cellulose strongly depends on the hydrogen bond accepting ability of anions of the ILs, and nature of anions is crucial to the dissolution of cellulose. Meanwhile, it was suggested that dissolution of cellulose was determined by the formation of hydrogen bonds of the ILs anions with protons of the hydroxyl groups of cellulose and thus by the breaking of the inter- and intra-chain hydrogen bonds of cellulose.

Table 3
Kamlet–Taft β parameters of the ILs at different temperatures.

IL	β parameter						
	25 °C	30 °C	40 °C	50 °C	60 °C	70 °C[a]	80 °C[a]
[Amim][HCOO]	0.990	0.991	0.990	0.990	0.990	0.990	0.990
[Amim][CH_3COO]	1.118	1.118	1.119	1.118	1.119	1.118	1.118
[Amim][CH_3CH_2COO]	1.141	1.140	1.140	1.140	1.141	1.140	1.140
[Amim][$CH_3CH_2CH_2COO$]	1.117	1.118	1.117	1.118	1.118	1.118	1.118
[Amim][C_6H_5COO]	1.032	1.043	1.043	1.053	1.054	1.055	1.056
[Amim][$HOCH_2COO$]	0.989	0.989	0.989	0.989	0.988	0.988	0.988
[Amim][$CH_3CHOHCOO$]	0.945	0.945	0.944	0.944	0.943	0.942	0.942

[a] The extrapolated values.

Table 4
^{13}C NMR chemical shifts (δ/ppm relative to TMS) of [Amim][CH_3COO] in pure liquid and in the mixture of [Amim][CH_3COO] + cellulose (10.0 wt%) at 90 °C.

Concentration of cellulose	δ (ppm)								
	C2	C4	C5	C6	C7	C8	C9	C10	C11
0	140.49	124.62	125.97	37.20	52.33	134.20	121.18	27.41	176.15
10%	140.03	124.42	125.82	37.24	52.35	133.93	121.37	27.05	176.54
$\Delta\delta$	−0.46	−0.20	−0.15	0.04	0.02	−0.27	0.19	−0.36	0.39

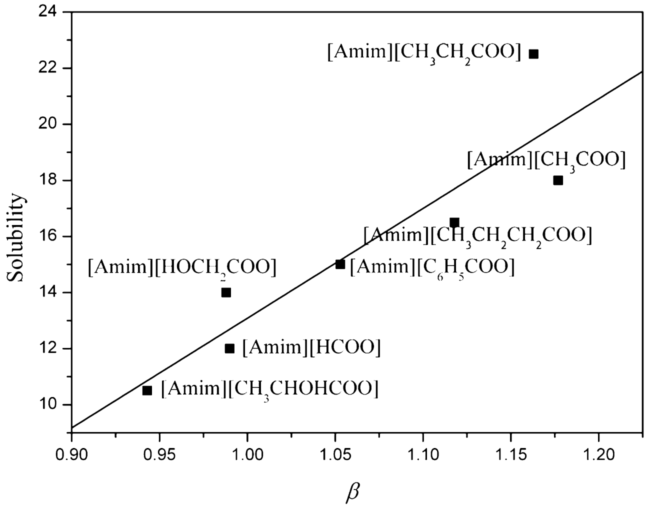

Fig. 1. Linear relationship between solubility of cellulose in the ILs and the β parameter of the ILs at 70 °C.

In order to have a further understanding for the interactions of the ILs with cellulose, [Amim][CH_3COO] was chosen as a model IL, and the ^{13}C NMR spectra of the pure IL and the IL in the mixture of [Amim][CH_3COO] + cellulose (10.0 wt%) were determined at 90 °C. These NMR spectra were shown in Figs. 2 and 3, and the NMR data were given in Table 4. For the sake of easy understanding, the chemical structure and numbering of C atoms in [Amim][CH_3COO] were shown in Fig. 4. It can be seen from Table 4 that the dissolution of cellulose in [Amim][CH_3COO] produced a greater downfield shift (an increase of chemical shift) for C9 and C11 atoms, but greater upfield shifts (decrease of chemical shift) for C2, C4, C5, C8, and C10 atoms. The larger downfield shift for C11 atom may be an indicative of the strong hydrogen bonding interaction of the proton on the hydroxyl groups of cellulose with the oxygen on the carboxyl group of [CH_3COO]$^-$, which led to a significant decrease of electron cloud density around the C11 atom and thus a larger downfield shift of its ^{13}C NMR signal. At the same time, this hydrogen bonding interaction impaired the electron-withdrawing capacity of COO$^-$ toward CH_3 in the [CH_3COO]$^-$ anion, thus the signal of C10 moved upfield.

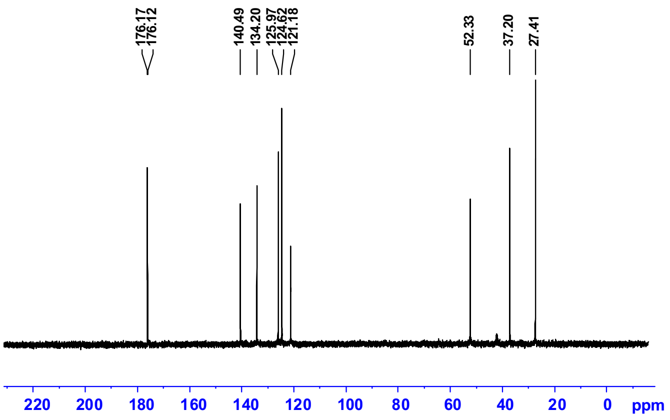

Fig. 2. ^{13}C NMR spectra of [Amim][CH_3COO] at 90 °C.

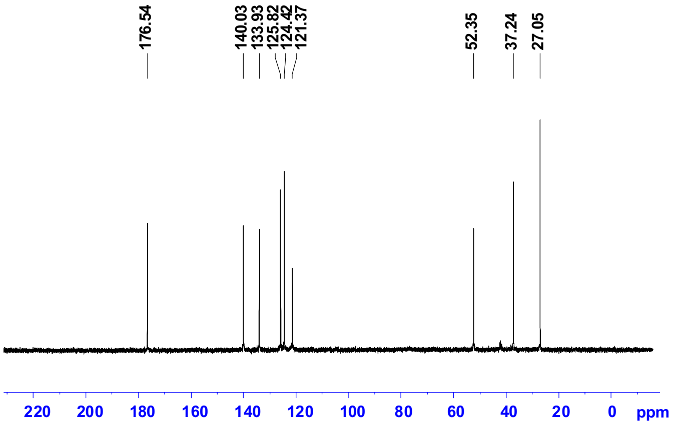

Fig. 3. ^{13}C NMR spectra of [Amim][CH_3COO] in the mixture of [Amim][CH_3COO] + cellulose (10.0 wt%) at 90 °C.

For the upfield shifts of the C2, C4 and C5 atoms in imidazolium ring of the cation, the possible explanation is that in the dissolution process, the hydroxyl oxygen in cellulose interacts with the protons around these C atoms. Therefore, the electron cloud density increased around the C2, C4 and C5 atoms, leading to the decrease of their ^{13}C NMR signals. The greater shift of the C2 atom could be ascribed to the stronger acidity of the C2 proton (Rantwijk & Sheldon, 2007). More interestingly, it was found that the signal of C8 on allyl chain of the cation also moved upfield, suggesting that the hydroxyl oxygen in cellulose did interact with the proton of the C8 atom. However, interactions of the protons on alkyl chain of the imidazolium cation with the hydroxyl oxygen in cellulose were generally absent (Zhang et al., 2010). This is one of the reasons why 1-allyl-3-methylimizodalium carboxylate ILs exhibited higher solubility for cellulose. The downfield shift of C9 atom could also be explained from the weak hydrogen bonding interaction between the hydroxyl oxygen in cellulose and the proton of the C8 atom, which enhanced the electron-withdrawing capacity of C8 toward CH_2 on allyl chain of the cation. In addition, the nearly invariable signals of C6 and C7 indicated that the CH_3 and CH_2 linked on N atoms of the imidazolium ring had a very weak interaction with the hydroxyl groups of cellulose, resulting in a quite small contribution to the dissolution of cellulose.

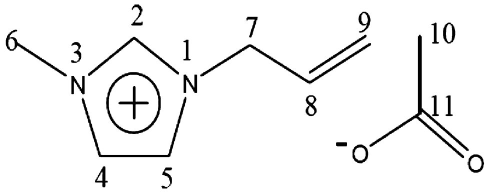

Fig. 4. Schematic structure and carbon numbering of [Amim][CH_3COO].

From the discussion of the above Kamlet–Taft β parameters and ^{13}C NMR chemical shifts, it is clear that not only the $[CH_3COO]^-$ anion but also the $[Amim]^+$ cation played role in the dissolution of cellulose by disrupting the inter- and intra-chain hydrogen bonds in cellulose. However, the hydrogen bonding interactions of the hydroxyl protons of cellulose with anion of the IL would be much stronger than those of the hydroxyl oxygens of cellulose with protons of cation of the IL. Therefore, it is appropriate to state that although the contribution from cation of the ILs cannot be neglected, the role of anion is predominant in the cellulose dissolution process.

4. Conclusions

In the present work, the 1-allyl-3-methylimizodalium carboxylate ILs of [Amim][HCOO], $[Amim][CH_3COO]$, $[Amim][CH_3CH_2COO]$, $[Amim][CH_3CH_2CH_2COO]$, $[Amim][C_6H_5COO]$, $[Amim][HOCH_2COO]$ and $[Amim][CH_3CHOHCOO]$ were synthesized, characterized, and used to dissolve cellulose at different temperatures. It was found that these ILs have outstanding advantages of low viscosity, low dissolution temperature and high cellulose solubility. They are highly efficient cellulose solvents at around room temperature due to their strong hydrogen bond basicity characterized by high β parameter values. [Amim][HCOO], $[Amim][CH_3COO]$, $[Amim][CH_3CH_2COO]$ and $[Amim][CH_3CH_2CH_2COO]$ were found to solubilize cellulose with high concentrations at 30 °C, and all these ILs were highly efficient solvents for the dissolution of cellulose at 50 °C. Combined with the ^{13}C NMR analysis, it seems likely that the hydrogen bonding interactions of the hydroxyl protons of cellulose with the oxygen on the carboxyl group of anions of the ILs and those of the hydroxyl oxygen of cellulose with some protons of cations of the ILs were all involved in the dissolution process of cellulose. However, the hydrogen bonding interactions between cellulose and anion is much stronger than those between cellulose and cation. Therefore, it is reasonable to conclude that although both the anion and the $[Amim]^+$ cation played roles in the dissolution of cellulose possibly by the disruption of the inter- and intra-chain hydrogen bonds of cellulose, the role of anion of the ILs is predominant. In addition, it was interesting to note that for the design of the ILs with strong hydrogen bond accepting ability, it is electron-donating group rather than electron-withdrawing group that would be incorporated into side chains of anions of those ILs.

To the best of our knowledge, the ILs developed in the present work are the most powerful ILs solvents for the dissolution of cellulose at around room temperature to date. For example, at 30 °C the solubility of cellulose in $[Amim][CH_3CH_2COO]$ was about 4.7 times that of cellulose in $[C_2mim][(MeO)(H)PO_2]$ (Fukaya et al., 2008) which was the only IL reported to have the capacity to dissolve cellulose at around room temperature. Therefore, the ILs reported here are expected to offer a more effective and sustainable way to dissolve cellulose under ambient conditions, although the dissolution mechanism needs to be further investigated.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.08.101.

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