Research Article

Dissolution Behavior of Cellulose in IL + DMSO Solvent: Effect of Alkyl Length in Imidazolium Cation on Cellulose Dissolution

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Four cellulose solvents including [C₂mim][CH₃COO] + DMSO, [C₄mim][CH₃COO] + DMSO, [C₆mim][CH₃COO] + DMSO, and [C₈mim][CH₃COO] + DMSO were prepared by adding dimethyl sulfoxide DMSO in 1-ethyl-3-methylimidazolium acetate [C₂mim][CH₃COO], 1-butyl-3-methylimidazolium acetate [C₄mim][CH₃COO], 1-hexyl-3-methylimidazolium acetate [C₆mim][CH₃COO], and 1-octyl-3-methylimidazolium acetate [C₈mim][CH₃COO], respectively. The solubilities of cellulose in these solvents were determined at 25°C. The effect of the alkyl chain length in imidazolium cation on cellulose solubility was investigated. With increasing alkyl chain length in imidazolium cation, the solubility of cellulose increases, but further increase in alkyl chain length results in decreases in cellulose.

1. Introduction

Recently, considerable attention has been received in the research related to the application of imidazolium-based carboxylate ionic liquids (ILs) in the dissolution of cellulose and delignification of lignocellulosic biomass [1]. This is mainly ascribed to the fact that, for the ILs with the same imidazolium-based cation backbone, imidazolium-based carboxylate ILs generally have lower melting points and higher capacity of cellulose dissolution compared to imidazolium-based chloride or bromide ILs. Fukaya et al. firstly reported the imidazolium-based formate ILs which were liquid at room temperature and could efficiently dissolve cellulose [2]. Xu et al. studied the effect of anionic structure and alkyl chain length of 1-butyl-3-methylimidazolium carboxylate ILs on cellulose solubility and found that cellulose solubility increased due to the replacement of H in the [CH₃COO][−] anion of [C₄mim][CH₃COO] by an electron-donating group but decreased because of the replacement of H in the [CH₃COO][−] anion of [C₄mim][CH₃COO] by an electron-withdrawing group [3, 4]. By NMR spectroscopic studies technique, Zhang et al. studied the dissolution mechanism of cellulose in [C₂mim][CH₃COO] and suggested

that the hydrogen bonding of hydroxyls with [CH₃COO][−] anion and [C₂mim]⁺ cation of [C₂mim][CH₃COO] was the major force for cellulose dissolution [5]. Lu et al. studied the effect of cationic structure of acetate ILs on cellulose dissolution and found that 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 [6]. Zhang et al. studied the structure-property relationship of 1-allyl-3-methylimidazolium carboxylate ILs, and the carboxylate ILs had less viscosity and higher cellulose solubility than 1-butyl-3-methylimidazolium carboxylate ILs [7]. Moreover, imidazolium-based carboxylate IL such as [C₂mim][CH₃COO] also could be used to dissolve or partition lignocellulosic biomass like wood [8, 9].

However, the imidazolium-based carboxylate ILs still show defects: high viscosity which would make cellulose difficultly disperse in ILs and thus help to dissolve cellulose more effectively and high processing temperatures which would consume/waste energy. To overcome the disadvantages, Rinaldi developed (IL + aprotic polar solvent including dimethyl sulfoxide DMSO and DMF) systems which have lower viscosity and higher dissolving rate than

neat ILs [10]. Later on, Xu et al. [11] designed novel $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]/\text{DMSO}$ solvents by adding an aprotic polar solvent DMSO to $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$ and found that the solvents could effectively dissolve cellulose at ambient temperature without heating. Based on molecular dynamics simulations and quantum chemistry calculations, Zhao et al. investigated the mechanism of cellulose in (IL + aprotic polar solvent) systems and concluded that the solvation of $[\text{C}_4\text{mim}]^+$ and $[\text{CH}_3\text{COO}]^-$ by the aprotic solvents makes it possible to produce more “free” $[\text{CH}_3\text{COO}]^-$ anions from anion-cation pairs, which would readily interact with cellulose, leading to the increase in cellulose solubility [12].

Extensive literature survey reveals that few researches have been conducted to investigate how the alkyl length of imidazolium cation in IL + DMSO solvent effect on cellulose dissolution. To have a better understanding of the alkyl length of imidazolium cation in IL + DMSO solvent effect on cellulose dissolution and provide wealthy knowledge for the design of novel IL + DMSO solvents, more detailed studies are still needed. Therefore, in the present work, four cellulose solvents including $[\text{C}_2\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$, $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$, $[\text{C}_6\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$, and $[\text{C}_8\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ were designed. The solubilities of cellulose in these solvents will be determined at 25°C. The effect of the alkyl chain length of imidazolium cation on cellulose solubility will be investigated in detail.

2. Experimental

2.1. Materials. Microcrystalline cellulose (MCC) with viscosity-average degree of polymerization (DP) being 229 was from Alfa Aesar. 1-Ethyl-3-methylimidazolium acetate $[\text{C}_2\text{mim}][\text{CH}_3\text{COO}]$ (99%), 1-butyl-3-methylimidazolium acetate $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$ (99%), 1-hexyl-3-methylimidazolium acetate $[\text{C}_6\text{mim}][\text{CH}_3\text{COO}]$ (99%), and 1-octyl-3-methylimidazolium acetate $[\text{C}_8\text{mim}][\text{CH}_3\text{COO}]$ (99%) were purchased from Linzhou Keneng Material Technology Co., Ltd. Dimethyl sulfoxide DMSO was from Tianjin Kemiou Chemical Reagent Co. Ltd. These materials were used as received.

2.2. Preparation of IL + DMSO Solvents. As an example, $[\text{C}_2\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ solvent was prepared by adding DMSO in dried $[\text{C}_2\text{mim}][\text{CH}_3\text{COO}]$ with a given molar ratio (2.5:1) of DMSO to $[\text{C}_2\text{mim}][\text{CH}_3\text{COO}]$ under stirring. $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$, $[\text{C}_6\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$, and $[\text{C}_8\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ solvents were prepared by using a similar process.

2.3. Dissolution of Cellulose. In a typical dissolution experiment, cellulose was added into a 25 mL colorimetric tube which contained 2.0 g of $[\text{C}_2\text{mim}]\text{Ac} + \text{DMSO}$, and the tube was sealed with parafilm. The tube was then immersed in an oil bath (DF-101S, Gongyi Yingyu Instrument Factory), and the bath temperature was controlled to be $25 \pm 0.5^\circ\text{C}$. The mixture was heated and stirred at a given temperature. Additional cellulose was added until the solution became

FIGURE 1: Schematic structures for the investigated ILs in the IL + DMSO solvents.

completely clear under polarization microscope (Nanjing Jiangnan Novel Optics Co., Ltd.). When cellulose became saturated, judged by the fact that cellulose could not be dissolved further within 2 h, its solubility (expressed by gram per 100 g of solvent) at 25°C could be calculated from the amount of the solvent and cellulose added.

3. Results and Discussion

The solubility values of cellulose in IL + DMSO solvents at 25°C are shown in Table 1. It can be seen from Table 1 that the alkyl chain length of imidazolium cation markedly affects the solubility of cellulose. Among the investigated IL + DMSO solvents, $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ is the most efficient for the dissolution of cellulose. With the exception of $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ solvent, the solubility of cellulose decreases with increasing alkyl chain length in the order: $[\text{C}_2\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO} > [\text{C}_6\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO} > [\text{C}_8\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$.

It is well known that the electron-donating capacity of alkyl group increases as alkyl chain length increases. Therefore, as the alkyl chain length in imidazolium cation increases, the electron cloud density of carbon atoms C_2 and C_4 (see Figure 1) bounded to nitrogen atom N_3 decreases, which results in an increase in acidity of hydrogen atoms H_2 and H_4 . Furthermore, the increased acidity of hydrogen atoms in imidazolium cation contributes to the hydrogen bond formation between acidic hydrogen and hydroxyl oxygen of cellulose and thus cellulose dissolution [5]. Therefore, the solubility of cellulose in $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ solvent is higher than that in $[\text{C}_2\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ solvent. However, as alkyl chain length further increases, the steric hindrance of the hydrogen bond formation between acidic hydrogen and hydroxyl oxygen increases, and the hydrophilicity of imidazolium cation decreases [6]. Therefore, further increase in alkyl chain length conversely can cause a decrease in cellulose solubility. That is why the cellulose solubility decreases with increasing alkyl chain length in the order: $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO} > [\text{C}_2\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO} > [\text{C}_6\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO} > [\text{C}_8\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$. Similar trend was also observed for the 1-alkyl-3-methylimidazolium chlorides in which $[\text{C}_n\text{mim}]^+$ cation has varying alkyl chain lengths [13].

TABLE 1: The solubility (g per 100 g of solvent) of MCC in IL + DMSO solvents at 25°C.

Entry	Solvent	R_{DMSO}^a	Solubility
1	$[\text{C}_2\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ ($R_{\text{DMSO}} = 2.5:1$)	2.5:1	12.5
2	$[\text{C}_4\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ ($R_{\text{DMSO}} = 2.5:1$)	2.5:1	15.0
3	$[\text{C}_6\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ ($R_{\text{DMSO}} = 2.5:1$)	2.5:1	11.0
4	$[\text{C}_8\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ ($R_{\text{DMSO}} = 2.5:1$)	2.5:1	10.0

^a R_{DMSO} is the molar ratio of DMSO to IL.

In addition, it is also found that, at 25°C, cellulose is not dissolved in all the ILs $[\text{C}_2\text{mim}][\text{CH}_3\text{COO}]$, $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}]$, $[\text{C}_6\text{mim}][\text{CH}_3\text{COO}]$, and $[\text{C}_8\text{mim}][\text{CH}_3\text{COO}]$. However, after DMSO was added in these ILs, respectively, cellulose becomes readily soluble. This is due to the fact that, upon adding DMSO in IL, DMSO serves to partially dissociate the strong ion pairs in IL into solvated cations and anions, and the solvated cations and anions in IL + DMSO solvent are more accessible to the hydroxyl proton of cellulose than those in neat IL, which is beneficial to the disruption of the hydrogen bonds in cellulose and thus to the cellulose dissolution [11, 12, 14]. This is the reason why cellulose becomes readily soluble in $[\text{C}_2\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$, $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$, $[\text{C}_6\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$, and $[\text{C}_8\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ solvents.

4. Conclusions

In this work, four cellulose solvents including $[\text{C}_2\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$, $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$, $[\text{C}_6\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$, and $[\text{C}_8\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$ were prepared to investigate the effect of the alkyl chain length of imidazolium cation on cellulose solubility. With increasing alkyl chain length in imidazolium cation, the cellulose solubility decreases in the order: $[\text{C}_4\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO} > [\text{C}_2\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO} > [\text{C}_6\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO} > [\text{C}_8\text{mim}][\text{CH}_3\text{COO}] + \text{DMSO}$. This is mainly ascribed to the fact that the increasing alkyl chain length leads to an increase in the acidity of the hydrogen atoms H_2 and H_4 in imidazolium cation which contributes to the hydrogen bond formation between acidic hydrogen and hydroxyl oxygen of cellulose and thus cellulose dissolution. However, as alkyl chain length further increases, the steric hindrance of the hydrogen bond formation between acidic hydrogen and hydroxyl oxygen increases, and the hydrophilicity of imidazolium cation decreases, which goes against cellulose dissolution.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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