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Dissolution performance of cellulose in MIM plus tetrabutylammonium propionate solvent

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Novel cellulose solvents, MIM-$[N_{4444}][CH_3CH_2COO]$, were developed by coupling *N*-methylimidazole (MIM) with tetrabutyl ammonium propionate ($[N_{4444}][CH_3CH_2COO]$). The solubilities of cellulose in MIM-$[N_{4444}][CH_3CH_2COO]$ solvents were determined at 25 °C. The effect of MIM content on cellulose solubility and the possible dissolution mechanism of cellulose in MIM-$[N_{4444}][CH_3CH_2COO]$ solvent have been investigated. It was found that $[CH_3CH_2COO]^-$ anion in MIM-$[N_{4444}][CH_3CH_2COO]$ solvent is the main driving force of the cellulose dissolution by interacting with the hydroxyl hydrogen atom in cellulose, and the role of MIM is mainly to disassociate/dilute $[N_{4444}][CH_3CH_2COO]$. In addition, the morphology and structure of the regenerated cellulose materials from MIM-$[N_{4444}][CH_3CH_2COO]$ solvent were characterized by scanning electron micrograph (SEM), Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray diffraction (XRD).

1. Introduction

With the gradual depletion of fossil resources, the production of chemicals and materials from renewable lignocellulosic biomass in place of fossil resources is receiving much attention [1]. Cellulose, the most abundant biopolymer in nature, is expected to act as an alternative to fossil resources. However, the further utilization of cellulose is actually limited owing to its insolubility in water and most organic solvents caused by the intra- and inter-molecular hydrogen bond network and hydrophilicity of cellulose [2]. For this reason, considerable efforts have been devoted to the development of effective solvents for cellulose. Among them are *N*-methylmorpholine-*N*-oxide, lithium chloride + *N*,*N*-dimethylacetamide, tetrabutyl ammonium fluoride + dimethyl sulfoxide, NaOH/Thiourea, and so on [3–6]. However, these solvents have disadvantages including toxicity, hazardous vapor, high cost, and thermal instability [7].

Over the past years, ionic liquids (ILs) have received considerable attention due to their unique properties such as negligible vapor pressure, non-flammability, wide liquid range, high chemical and thermal stability, and strong dissolution ability for various organic and inorganic materials [8–13]. The ILs used for cellulose processing include imidazolium-based carboxylates [14–19], bio-derived choline-based ILs composing of ions derived from naturally occurring bases (e.g., choline) and acids (e.g., amino acids and carboxylic acids) [20,21], and quaternary ammonium chlorides [22]. Among them, the imidazolium-based carboxylate ILs show powerful dissolving capacity for cellulose, but poor cellulose dissolution performance for the choline-based ILs, and the temperature for cellulose dissolution reach up to 120 °C in the quaternary ammonium chlorides. Recently, some efforts have been made to develop more efficient cellulose solvent systems by combining co-solvent with IL. Typical combinations include 1-butyl-3-methylimidazolium chloride + aprotic polar solvent (dimethyl sulfoxide DMSO, *N*,*N*-dimethylformamide DMF, etc.) [23] and 1-butyl-3-methylimidazolium acetate + DMSO (DMF or *N*,*N*-dimethylacetamide DMAc [24–27]. Compared with ILs, the IL + cosolvent systems have remarkable advantages such as ease of dissolution for cellulose at low temperature, lowered viscosity, and cellulose dissolution efficiency.

Tetrabutylammonium hydroxide aqueous solution is commercially available and apparently cheap compared with imidazolium-based aqueous solution. Moreover, $[CH_3CH_2COO]^-$ anion has stronger hydrogen bond accepting ability which is favorable to cellulose dissolution than other carboxylate anions [15,16]. Herein, $[CH_3CH_2COO]^-$ anion was selected to paired with tetrabutylammonium cation $[N_{4444}]^+$ to gain $[N_{4444}][CH_3CH_2COO]$. The dissolution performance of cellulose in $[N_{4444}][CH_3CH_2COO]$ was examined. At the same time, a series of novel solvents were designed by coupling $[N_{4444}][CH_3CH_2COO]$ with polar aprotic solvents like *N*-methylimidazole (MIM), dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), *N*-methyl pyrrolidone (NMP) and 1,3-dimethyl-2-imidazolidinone (DMI). The dissolution behavior of cellulose, the effect of polar aprotic solvent content on cellulose dissolution and the possible dissolution mechanism of cellulose in such solvents were investigated. Moreover, morphology and structure of the regenerated cellulose were characterized by SEM, ATR-FTIR and XRD.

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2. Materials and methods

2.1. Materials

Microcrystalline cellulose (MCC) with a 229 of viscosity-average degree of polymerization (DP) was purchased from Sigma-Aldrich. *N*-methylimidazole (99%) and tetrabutyl ammonium hydroxide aqueous solution (55 wt%) were purchased from Alfa Aesar Company. Ltd. Dimethyl sulfoxide, analytical reagent was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. *N,N*-dimethylformamide (>99.5%) was purchased from Tianjin Fengchuan Chemical Reagent Science and Technology Co., Ltd. *N,N*-dimethylacetamide (>99.5%) and propionic acid (99%) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. *N*-methyl pyrrolidone (>99.0%) and 1,3-dimethyl-2-imidazolidinone (≥99.5%) were purchased from Shanghai Aladdin biochemical technology co., Ltd. Deuterated DMSO (DMSO-d_6) (>99.9%) used for NMR samples was purchased from Qingdao Weibo Tenglong Technology Co., Ltd.

2.2. Preparation of MIM-[N_{4444}][CH_3CH_2COO] solvents

[N_{4444}][CH_3CH_2COO] was synthesized and purified as described below. Briefly, tetrabutyl ammonium hydroxide aqueous solution was neutralized with equal molar butyric acid. Activated carbon was added to the obtained [N_{4444}][CH_3CH_2COO] aqueous solution two to three times to remove possible residual impurities. After removing water by evaporation under reduced pressure, the [N_{4444}][CH_3CH_2COO] was finally dried under vacuum in the presence of P_2O_5 at 60 °C.

The MIM-[N_{4444}][CH_3CH_2COO] solvents were gained by adding MIM to dried [N_{4444}][CH_3CH_2COO] with a given MIM weight percentage under stirring.

2.3. Cellulose dissolution in MIM-[N_{4444}][CH_3CH_2COO] solvents

As an example, cellulose was added to a 25 mL colorimetric tube containing 2.0 g of MIM-[N_{4444}][CH_3CH_2COO], 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 ± 0.5 °C. Additional cellulose was added until the solution became 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, 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.

2.4. Measurements ^{13}C NMR spectra

Measurements of ^{13}C NMR spectra for [N_{4444}][CH_3CH_2COO] in MIM-[N_{4444}][CH_3CH_2COO] ($W_{MIM} = 75$) solvent and MIM-[N_{4444}][CH_3CH_2COO]($W_{MIM} = 75$)-cellulose(8 wt%) solution were performed on a Bruker DMX 300 spectrometer at room temperature. DMSO-d_6 was used as an external standard. Chemical shifts were given in ppm downfield from TMS.

2.5. Regeneration of cellulose film and characterization of the regenerated cellulose

8 wt% of cellulose solution was prepared by dissolving cellulose in MIM-[N_{4444}][CH_3CH_2COO] ($W_{MIM} = 75$) solvent at 25 °C. The solution was cast onto a glass plate to give a thickness of about 2 mm, took off air bubble in a vacuum oven for 30 min, and then immediately coagulated in the water to obtain a transparent regenerated cellulose gel film. The regenerated cellulose gel film was washed with running distilled water followed by drying at 60 °C in a vacuum oven. The dried cellulose film was coded as RC-A.

8 wt% of as-prepared cellulose solution was cast onto a glass plate to give a thickness of about 2 mm, took off air bubble in a vacuum oven for 30 min. Then, the cellulose solution film was frozen for 2 h at −20 °C and subsequently immersed in distilled water for regeneration-gelation. The gel was repeatedly washed by distilled water to remove off MIM-[N_{4444}][CH_3CH_2COO]. After being frozen for 2 h at in a refrigerator, the hydrogel was freeze-dried using a FD-10 freeze-dryer to obtain cellulose aerogel. The cold trap temperature was below −45 °C and the vacuum pressure was below 0.1 MPa during the freeze-drying process. The freeze-dried cellulose film was coded as RC-FF.

Table 1
The cellulose solubility (g/100 g) in MIM-[N_{4444}][CH_3CH_2COO] solvents at 25 °C.

Solvents	W_{MIM} (wt%)	Solubility (g/100 g)
MIM-[N_{4444}][CH_3CH_2COO] ($W_{MIM} = 75$)	75	15.7
MIM-[N_{4444}][CH_3CH_2COO] ($W_{MIM} = 80$)	80	11.1
MIM-[N_{4444}][CH_3CH_2COO] ($W_{MIM} = 85$)	85	8.9
MIM-[N_{4444}][CH_3CH_2COO] ($W_{MIM} = 90$)	90	5.6
MIM	100	0

W_{MIM} represents the weight percentage of MIM in MIM-[N_{4444}][CH_3CH_2COO].

The RC-A and RC-FF films were employed for the measurements of SEM, XRD, and ATR-FTIR spectroscopy. Scanning electron micrograph (SEM) of regenerated cellulose films in the dry state were frozen in liquid nitrogen, immediately snapped. The fracture surfaces of the films were sputtered with gold, and then photographed. The XRD patterns were collected on a BrukerD8Advance diffraction spectrometer with Cu-Ka radiation (λ = 1.54 Å) over the range 3–60° (2θ) at a scan speed of 2° (2θ) per minute. An ATR-FTIR (Nicolet iN10, Thermo Fisher Scientific, USA) system with Ge crystal ATR accessory, MCT (mercury–cadmium telluride) detector, and OMINC picta workstation were employed for IR observation. Spectra were collected in high-resolution mode (4 cm^{-1} resolution and 64 scans) under ATR 5% maximum pressure. Background was subtracted for every measurement. Triplicate tests were performed at different sites for every sample.

3. Results and discussion

3.1. Effect of MIM content in MIM-[N_{4444}][CH_3CH_2COO] solvent on cellulose solubility

To investigate how MIM content impacts cellulose solubility, MIM-[N_{4444}][CH_3CH_2COO] solvents were designed and shown in Table 1. Based on experimental observations, cellulose is not soluble in MIM, and [N_{4444}][CH_3CH_2COO] is solid at room temperature. Moreover, it is also observed that [N_{4444}][CH_3CH_2COO] converts into liquid at 100 °C, but the [N_{4444}][CH_3CH_2COO] + cellulose liquid mixture turns black color upon adding 1 wt% cellulose to [N_{4444}][CH_3CH_2COO] at this temperature. Therefore, [N_{4444}][CH_3CH_2COO] is improper to be used as cellulose solvent. At the same time, it is also found that [N_{4444}][CH_3CH_2COO] can not completely be dissolved in MIM when MIM content in MIM-[N_{4444}][CH_3CH_2COO] solvent is <75 wt%. Therefore, the MIM-[N_{4444}][CH_3CH_2COO] solvents containing ≥75 wt% of MIM is employed in this work.

Table 1 summarizes the solubility data of cellulose in MIM-[N_{4444}][CH_3CH_2COO] solvent at 25 °C. As shown in Table 1, MIM content evidently affects cellulose solubility. MIM-[N_{4444}][CH_3CH_2COO] ($W_{MIM} = 75$) displays efficient dissolution capacity for cellulose and gives the maximum solubility value of as high as 15.7 g/100 g.

Table 2
The ^{13}C NMR chemical shifts (δ (ppm) relative to TMS) of [N_{4444}][CH_3CH_2COO] in MIM-[N_{4444}][CH_3CH_2COO]($W_{MIM} = 75$) solvent and MIM-[N_{4444}][CH_3CH_2COO]($W_{MIM} = 75$)-cellulose(8 wt%) solution at room temperature.

Cellulose concentration (wt%)	C1	C2	C3	C4	C5	C6	C7
0	57.59	23.16	19.03	12.77	11.49	32.30	175.85
8	57.57	23.07	18.98	12.77	10.96	31.98	177.11
Δδ	−0.02	−0.09	−0.05	0	−0.53	−0.32	1.26