Preparation and Evaluation of Cellulose-Dissolving Magnetic Ionic Liquid

Jin Muraoka*[a], Noriho Kamiya[b,c], and Yuji Ito[a]

[a] Graduate School of Science and Engineering, Kagoshima University, Korimoto 1-21-35, Kagoshima, 890-0065 JAPAN
[b,c] Center for Future Chemistry, Kyushu University JAPAN
[a] Department of Applied Chemistry, Graduate School of Engineering, Kyushu University JAPAN

E-mail: k8033887@kadai.jp
Full postal address: Korimoto 1-21-35, Kagoshima, 890-0065 JAPAN
Phone number: +81-99-285-8105

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Abstract

Ionic liquids have attracted attention as potential pretreatment agents in cellulosic biomass processing. Here we report on a new magnetic ionic liquid that can dissolve crystalline cellulose and be collected by a magnet.

1. Introduction

Cellulose has been recognized as a potential second generation biomass over sugar. It has the advantage of not competing with food staples [1]. Cellulose consists of polydisperse linear glucose polymer chains which form inter- and intra-hydrogen-bonded supramolecular structures, making this natural resource insoluble in water and most common organic liquids. Various pretreatment techniques have been studied to improve cellulose dissolution in its biomass processing [2]. Since conventional physical, chemical, and physicochemical processing methods usually require high energy and harsh reaction conditions, an alternative strategy has been investigated. In recent progress in solvent engineering for cellulose dissolution, ionic liquids (ILs) have attracted significant interest because they can dissolve cellulose under more moderate conditions than can other pretreatment methods [3,4]. Furthermore, their compatibility with certain biocatalytic processes [5], enables highly selective cellulose hydrolysis with low energy consumption. The production cost of ILs has been recognized as one of the critical issues to be addressed.

In this paper, we discuss a proof-of-concept study for the design of magnetic ILs as simple, low-cost cellulose pretreatment agents. The ILs should dissolve cellulose and be recovered magnetically after cellulose dissolution. A magnetic IL, 1-butyl-3-methylimidazolium FeCl4 ([bmim]FeCl4), discovered in 2004, was synthesized by mixing 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and $FeCl_3$ [6]. N-butylpyridium tetrachloroferrate ([bPy]$FeCl_4$) and 1-butyl-1-methylpyrrolidium tetrachloroferrate ([bmP]$FeCl_4$) were also synthesized recently for some application [7]. The IL is potentially recyclable as it shows a strong response to a magnetic field. However, no reports exist on a magnetic IL that can dissolve cellulose.

2. Experimental

2.1. Materials

Monochloroacetic acid was purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. $FeCl_3 \cdot 6H_2O$, N-methylimidazole, n-chloroethanol, acetonitrile and ethyl acetate were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. All the chemicals were of analytical grade and were used without further purification. Avicel PH-101, as crystalline cellulose, was purchased from Sigma-Aldrich, St. Louis, Missouri.

2.2. Preparation of magnetic ionic liquids

We synthesized a new magnetic ILs, [cmmim]$FeCl_4$ (Fig. 1), and studied their basic magnetic properties and cellulose dissolution ability. The new magnetic IL was synthesized in two steps. [Cmmim]Cl [8] synthesized in the first step (yields of 57%) served as precursors to the synthesis of [cmmim]$FeCl_4$ in the second step [6]. The purification of these magnetic ionic liquids was performed using a 46 mm diameter neodymium magnet, which had magnetic flux density of 0.55 T at the center.

2.3. Characterization

Magnetic IL synthesis was evaluated by Nuclear Magnetic Resonance (NMR) Spectrometry, Raman near-infrared (RI) spectroscopy and magnetic susceptibility measurements. ^1H NMR spectra were registered and analyized by NMR Spectrometry (ECX-400, JOEL RESONANCE Inc., Tokyo, Japan). Samples were in D_2O solution and tetramethylsilane (TMS) was used as an external reference. The RI spectrum was measured using an FT-Raman system (RFT-6000; JACSO, Tokyo, Japan). The excitation light wavelength was 1064 nm. A magnetic property measurement system (MPMS-5, Quantum Design, Tokyo, Japan), based on a SQUID magnetometer, was used. Each sample (2.2 mg of [cmmim]Cl or [cmmim]$FeCl_4$) was placed in a cellulose capsule for measuring the IL magnetic susceptibility.

2.4. Evaluation of dissolving crystalline cellulose

The crystalline state of the regenerated cellulose was measured by X-ray diffractometer (Ultima IV; Rigaku, Tokyo, Japan).

3. Results and discussion

3.1. NMR spectra of the magnetic IL

The cationic structures and purities of the intermediates [cmmim]Cl primarily confirmed using the D_2O NMR spectra, and the data are listed as follow. [Cmmim]$FeCl_4$, ^1H NMR spectrum, δ, ppm: 3.78 s (3H, CH_3); 4.95 s (2H, CH_2); 7.34 (1H, CH); 7.35 (1H, CH); 8.46 (1H, CH). There are not additional peaks existing in the ^1H NMR spectra.

3.2. Raman spectra of the magnetic IL

The characteristic band of the Raman spectrum shows that the anion was $FeCl_4^-$ (330 cm^{-1} in Fig. 2), which was identified in a previous report [6]. The Raman spectrum of [cmim]$FeCl_4$ in the range of 400–3150 cm^{-1} was very similar to that of [cmmim]Cl and the liquid could therefore contain $[cmmim]^+$ as cations. From these results, it could be confirmed that $[cmmim]^+$ have been synthesized successfully.

3.3. Magnetic property of analysis of the magnetic IL

Magnet behaviors of [Cmmim]Cl and [cmmim]$FeCl_4$ were examined. The magnetic field range was -10,000 to 10,000 Oe and the temperature was set at 273 K. [Cmmim]Cl showed no response. On the other hand, [cmmim]$FeCl_4$ showed a linear response (Fig. 3a). From those measurement data, the magnetic susceptibility of [cmmim]$FeCl_4$ was calculated to be 16.3×10^{-5} emu g^{-1}, which is almost the same strength as that of [bmim]$FeCl_4$ [6]. These results indicate that the ILs containing the $FeCl_4^-$ anion showed a magnetic susceptibility, while those with chloride anion did not (Fig. 3a). From these results, it was confirmed that the ILs exhibit a magnet behavior.

To test the recovery of the ILs in water, the ionic liquid was slowly deposited at the bottom of glass bottle and the phase separation was achieved. The ionic liquid phase (the bottom phase) was magnetically collected (Fig. 3b). However, once mixed the solution vigorously, emulsion was formed, and eventually about 80% of the ionic liquid was distributed to the water phase (data not shown).

3.4. Evaluation of dissolving crystalline cellulose by the magnetic IL

Different amounts (0, 2, 5 and 10 mg) of crystalline cellulose were dissolved by the addition of magnetic ILs (102 mg each) and the solutions were heated for 1 hour at 80°C. After cooling to room temperature, 1 ml of sodium acetate buffer (10 mM, pH 5.0) was added to the cellulose and magnetic IL mixture to regenerate the dissolved cellulose. After being washed 3 times with 1 mL of the sodium acetate buffer, the regenerated sample was dried in a box with molecular sieve.
The diffractogram of the cellulose itself showed three typical peaks indicating the presence of crystalline cellulose type I. When the crystalline cellulose becomes amorphous, these peaks become indistinct. Figure 4 shows that both magnetic ILs dissolved the cellulose depending on the amount present. The diffractogram height at the position of the highest peak ($2\theta = 22.6°$) and at the locations for the amorphous background ($2\theta = 19.0°$) were used to estimate the crystallinity index (CI) of the different cellulose samples [9]. The measurement of the diffractogram by XRD was performed three times.

The averaged CI of the regenerated cellulose samples pretreated with [cmim]$FeCl_4$ at 10 wt% cellulose solution was 74% (Fig. 4b,i). This value was comparable with that of the untreated sample (74%, Fig. 4a,i). In contrast, pretreatment in 5 wt% cellulose solution by [cmmim]$FeCl_4$ yielded CI values of 68% (Fig. 4b,ii). A further decrease in CI value (31% with [cmmim]$FeCl_4$) was observed when smaller amounts of cellulose were pretreated (Fig. 4b,iii). The CI value of regenerated cellulose pretreated with [bmim]$FeCl_4$ was 77% even under pretreatment at 1 wt% cellulose solution (Fig. 4a,iii) implying that this IL cannot dissolve the cellulose. These results indicate that [cmmim]$FeCl_4$ can dissolve crystalline cellulose under the aforementioned conditions.

4. Conclusions

1-butyl-3-methylimidazolium chloride ([bmim]Cl) has been reported to be an effective IL for dissolving cellulose [3,10]. The anions of ILs affect its ability to dissolve cellulose [11,12]. In these magnetic ILs, it was suggested that the cationic moiety may play a key role in cellulose dissolution. In summary, we synthesized a magnetic IL, and validated its basic chemical and physical properties. The new magnetic IL could dissolve crystalline cellulose, highlighting their potential as cost-effective ILs that can be reused in cellulosic biomass conversion processes.

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Figure captions

Figure 1. Chemical structures of synthesized magnetic ionic liquids ([cmmim]$FeCl_4$).

Figure 2. Raman near-infrared spectra showing characteristic peak of $FeCl_4^-$ at 330 cm^{-1}. (a) [cmmim]$FeCl_4$ and (b) [cmmim]Cl.

Figure 3. **(**a) Synthesized magnetic ionic liquids showing magnetic moment. (b) [Cmmim]$FeCl_4$ in distilled water deposited at the bottom of a glass bottle(i), and attracted by a neodymium magnet (ii).

Figure 4. XRD spectra of cellulose pretreated with different magnetic ionic liquids. Different weight percent solutions of cellulose were prepared for regeneration. XRD spectrum of untreated cellulose shown in (a,i). (a) [bmim]$FeCl_4$: 5 wt% (ii), 1 wt% (iii) cellulose; (b) [cmmim]$FeCl_4$: 10 wt% (i), 5 wt% (ii), 2 wt% (iii) cellulose.