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Communications

Superior Solubility of Polysaccharides in Low Viscosity, Polar, and Halogen-Free 1,3-Dialkylimidazolium Formates

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We successfully prepared low viscosity, polar, and halogen-free ionic liquids as potential solvents for a wide range of polysaccharides. A series of 1,3-dialkylimidazolium formates were produced as liquids having strong hydrogen bond acceptability. These formates had significantly lower viscosity than previously reported polar ionic liquids, in particular 1-allyl-3-methylimidazolium formate (viscosity 66cP at 25 °C) and 1-allyl-3-ethylimidazolium formate (67cP at 25 °C). Because of their strong hydrogen bond ability, various polysaccharides including amylose and (scarcely soluble) cellulose were dissolved in high concentrations under mild condition.

Introduction

In spite of a dramatic increase in studies on ionic liquids (ILs)[1] as solvents for chemistry,[2] few reactions have been carried out in ionic liquids alone. Evaluation of ionic liquids should therefore be high when some chemical reactions or processing were discovered exclusively in the ILs. Attention has focused on polar ILs that can dissolve compounds that were previously difficult to dissolve. Such compounds include synthetic polymers and biomacromolecules. In particular, many biomacromolecules are insoluble in conventional organic solvents, so that the development of ILs for biomacromolecules should be very helpful in the chemical modification and processing of biomacromolecules. The pioneering work by Rogers et al. demonstrated that heated 1,3-dialkylimidazolium chloride, hereafter referred to as [RR'im][Cl], dissolved cellulose.[3] [RR'im][Cl] can dissolve other biomacromolecules including *Bombyx mori* silk[4] and wool keratin.[5] In addition, DNA and RNA were confirmed to be soluble in [RR'im][Cl], which is the only nonaqueous solvent known for these important biomacromolecules.[6] These results all indicated that the [RR'im][Cl] salts are potential solvents for a variety of biomacromolecules. However, most [RR'im][Cl] salts are solid at room temperature, and those that are liquid have a high viscosity that limits their use as a solvent. Moreover, residual halogen in products synthesized or manufactured in chloride-containing ionic liquids may cause problems. Consequently, low viscosity and halogen-free ILs that dissolve biomacromolecules[7] are strongly desirable.

In a previous study, we found ILs composed of imidazolium cation with allyl group had low melting point and moderate viscosity at room temperature.[8] By comparing several saturated and unsaturated hydrocarbon chains on the imidazolium cation ring, we showed that the allyl group has a strong effect in lowering the melting point.[8] Allyl-imidazolium halide salts had greater viscosity than conventional ILs, however. We then sought to develop low viscosity ILs by changing anion species. Halogen-free ILs having carboxylic acid anions such as lactic acid[9] and amino acid[10] have been reported to be polar ILs with high hydrogen-bonding characteristic. Such anions are good candidates for polar and halogen-free ILs. For lowering of the viscosity, since there are a wide variety of carboxylic acid derivatives and they are commercially available, it is important to survey many carboxylic acids as suitable anions to produce low viscosity ILs.

Experimental Section

Materials and Instruments. Commercially available *N*-methylimidazole and *N*-ethylimidazole (Tokyo Chemical Ind. Co. Ltd.) were dried over KOH and distilled before use. A series of alkyl halides was shaken with aqueous $KHCO_3$ solution and then dried over $CaCl_2$ followed by distillation. Microcrystalline cellulose (Degree of Polymerization (DP) = ca. 250) was purchased from Aldrich Chemical Co., Inc. Inulin (DP

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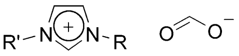
Chart 1. Chemical Structure of 1,3-dialkylimidazolium Formates.



1: R = C_2H_5 R' = CH_3 **3**: R = $CH_2CH{:}CH_2$ R' = CH_3
2: R = C_3H_7 R' = CH_3 **4**: R = $CH_2CH{:}CH_2$ R' = C_2H_5

= ca. 35), amylose (DP = ca. 1000), xylan (DP = ca. 3000), and pectin (DP = ca. 1500) were purchased from Tokyo Chemical Ind. Co., Ltd. Dextrin (DP = ca. 70) was a gift from Chiba Flour Milling Co., Ltd. All polysaccharides were used after drying but without further purification. ^{1}H NMR spectra were recorded on a JEOL α 500 instrument. Visible spectra were recorded on a Shimadzu UV-PC 2450 spectrophotometer. DSC measurement was carried out with a DSC-5200 (Seiko Instruments Inc.). TGA analysis was made on Seiko TG/DTA 220 instrument with heating rate of 10 °C/mim from 25 to 400 °C under nitrogen gas atmosphere. The viscosity measurement was carried out with Brookfield DV-I + viscometer at different temperature from 25 to 85 °C under nitrogen gas atmosphere. The water content of the ionic liquids was determined by using Karl Fischer moisture titrator (MKC-510N; Kyoto Electronics) and found to be below 0.2 wt %.

Preparation of Ionic Liquids. We prepared four different imidazolium formates as shown in Chart 1. The preparation procedure of 1-allyl-3-methylimidazolium formate (**3**) is as follows. First, 1-allyl-3-methylimidazolium bromide was prepared as in ref 8. Bromide anions were converted into hydroxide by passing an aqueous solution of the bromide salt through a column filled with anion exchange resin (Amberlite IRA 400-OH) to give 1-allyl-3-methylimidazolium hydroxide aqueous solution. This aqueous hydroxide solution was then neutralized with equimolar formic acid. After removal of water by evaporation under reduced pressure, the residual liquid was washed repeatedly with excess diethyl ether. The target salt was dissolved into chloroform containing 10% (v/v) methanol and was then passed through a column filled with neutral activated alumina. After removal of solvent by evaporation under reduced pressure, the ionic liquid thus obtained was dried in vacuo at 70 °C for 24 h. In the ^{1}H NMR spectra, there was no peak assigned to free formic acid. After adding $AgNO_3$ aqueous solution to the IL, no precipitation of AgBr was found. Other ionic liquids have been prepared similar to the above process. Characterizations (^{1}H NMR and elemental analysis data) of ILs are summarized in the Supporting Information.

Measurement of Kamlet−Taft Parameter. Since some solution properties determined by the solvatochromism of dye molecules in ILs depend strongly on the structure of dye molecules, it is necessary to determine such parameters using several different dye molecules. To calculate Kamlet−Taft parameters, we used three different dyes; 4-nitroaniline, *N,N*-diethyl-4-nitroaniline, and Reichardt's dye. To 0.2 mL of ionic liquid was added the dye as a concentrated dry methanol solution. The methanol was then carefully removed by vacuum drying at 40 °C for 12 h. These ionic liquid solutions were placed into quartz cells with 1.0 mm light-path length, and their visible spectra were recorded at 25 °C. The Kamlet−Taft parameters (α, β, and π^*) were calculated using the following equations:

$$\nu_{\text{(dye)}} = 1/(\lambda_{\max\text{ (dye)}} \times 10^{-4}) \qquad (1)$$

$$\alpha = 0.0649\ E_T(30)\text{-}2.03 - 0.72\pi^* \qquad (2)$$

$$E_T(30) = 28592/\lambda_{\max\text{ (Reichardt's dye)}} \qquad (3)$$

$$\pi^* = 0.314(27.52 - \nu_{N,N\text{-diethyl-4-nitroaniline}}) \qquad (4)$$

$$\beta = (1.035\nu_{N,N\text{-diethyl-4-nitroaniline}} + 2.64 - \nu_{\text{4-nitroaniline}})/2.80 \qquad (5)$$

Dissolution of Polysaccharides in Ionic Liquids. We mixed 1.0 g of dried ionic liquids with 10 mg of each polysaccharide under nitrogen gas atmosphere. The mixture was heated at approximately 5 °C intervals in a temperature controlled oil bath and was stirred for 15 min at each temperature until the solution became optically clear. The temperature was raised by 5 °C in case of insufficient dissolution. The lowest temperature to give a clear solution was recorded as the dissolution temperature.

Table 1. Physical Properties and Kamlet−Taft Parameters of the Ionic Liquids

ILs	T_g/°C[a]	T_m/°C[a]	T_d/°C[b]	η/cP (25 °C)	Kamlet−Taft parameters α	β	π^*
1	*c*	52	212	*d*	*d*	*d*	*d*
2	−73	*c*	213	117	0.46	0.99	1.06
3	−76	*c*	205	66	0.48	0.99	1.08
4	−76	*c*	205	67	0.47	0.99	1.06
[Amim][Cl][e]	−51	*c*	256	2090	0.46	0.83	1.17
[C4mim][Cl][f]	*c*	66	262	*d*	0.44[g]	0.84[g]	1.14[g]

[a] Temperature at signal peak. [b] Temperature for 10% weight loss under N_2 gas. [c] Not observed. [d] Not measured. [e] 1-Allyl-3-methylimidazolium chloride. [f] 1-Butyl-3-methylimidazolium chloride. [g] Measured under a supercooled state.

Results and Discussion

Of the ILs prepared in this study (Chart 1), **1** was a white solid at room temperature and **2**−**4** were room-temperature ionic liquids (RTILs). Differential scanning calorimetry analysis revealed that the melting temperature (T_m) of **1** was 52 °C, whereas the others had only a low glass transition temperatures (T_g) of −73 °C or lower (Table 1). The latter ILs remained liquid even after storing them at −20 °C for several months, indicating a molten state or a stable supercooled state.

Table 1 also lists the Kamlet−Taft parameters[11] for **2**−**4**. RTILs **2**−**4** have the same or slightly lower α values (hydrogen bond acidity) and lower π^* values (dipolarity) than the two [RR'im][Cl] ILs, but they have higher β values (hydrogen bond basicity). In general, β is governed by the nature of the anions.[11] Formate anion is the conjugate base of formic acid that is a weaker acid than HCl. Hence, **2**−**4** exhibited higher β values than a series of [RR'im][Cl] type ILs.

Although ILs with high hydrogen bonding ability are expected to have high viscosity, these formates exhibited relatively low viscosities. ILs **3** and **4** had the particularly low viscosity of 66 and 67 cP at 25 °C, respectively. We attribute the low viscosity to the small ion size, the configurational rotation of the allyl group, and the flat shape of both anion and cation. In general, the imidazolium cation having an allyl group generally showed lower viscosity than those having propyl or propargyl groups.[8] On the other hand, **1**−**4** showed a 10 wt % weight loss near 200 °C, which is lower than the values of 256 °C for [Amim][Cl] and 262 °C for [C4mim][Cl]. This difference might be due to the nucleophilicity (hydrogen bond basicity) of the anion as well as the number of atoms forming the anion.[12]

As a result of the strong hydrogen bond acceptability of these ILs, these formates are potential solvents for biomacromolecules such as cellulose,[13] silk, DNA, etc. We also investigated the solubility of polysaccharides including cellulose which is nearly insoluble. To dissolve cellulose, hydrogen bond basicity is necessary to weaken the inter- and intramolecular hydrogen bonds of the cellulose chains.[3] Because 1,3-dialkylimidazolium formate has a stronger hydrogen bond basicity than chloride salts (as shown by its lower viscosity), the IL **3** dissolved cellulose at lower temperature than [Amim][Cl] and dissolved greater concentrations of cellulose than [Amim][Cl]. Figure 1 shows, for example, that to solubilize 10 wt % cellulose, the

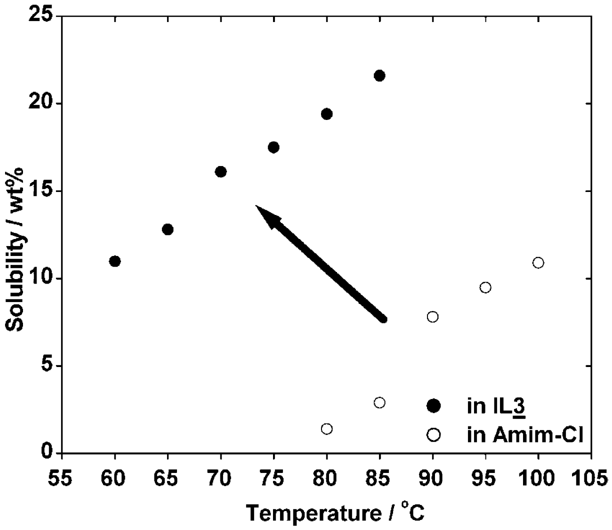


Figure 1. Temperature dependence of solubility (wt %) of cellulose in IL **3** and [Amim][Cl].

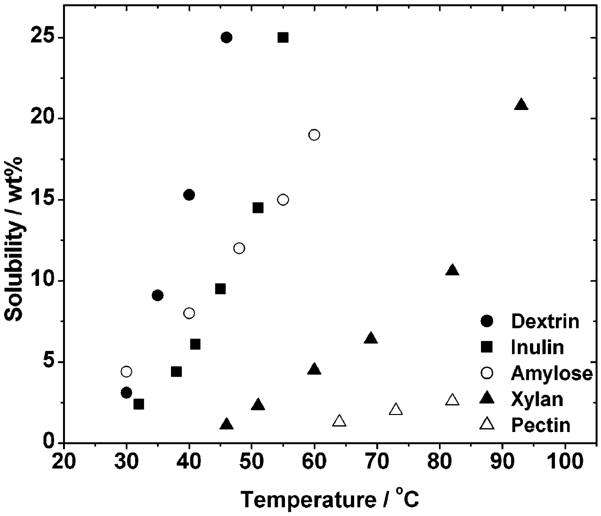


Figure 2. Temperature dependence of solubility (wt %) of a series of polysaccharides in IL **3**.

sample of [Amim][Cl] had to be heated up to 100 °C, whereas the sample of IL **3** had to be heated only to 60 °C.

IL **3** solubilized not only cellulose but also many other polysaccharides. Figure 2 shows the solubility of a series of polysaccharides in IL **3**. Dextrin, amylose, and inulin were the most soluble polysaccharides tested, having solubilities of 2−4 wt % at around room temperature. The dissolution temperatures of xylan and pectin were higher than those of dextrin, amylose, and inulin. The hydrophilicity of these polysaccharides might be one of the reasons for this difference. Xylan has only two hydroxyl groups in its sugar unit, whereas dextrin and inulin have three hydroxyl groups. The interaction between the hydroxyl group of cellulose and ILs is crucial for dissolution, based on the dissolution mechanism of cellulose in [Amim][Cl] by Zhang et al.[14] This mechanism is consistent with our findings, and also with the findings of Armstrong et al.,[15] who reported that the solubility of biomaterials in [C4mim][Cl] decreased after methylation of the hydroxyl groups of cyclodextrins. The relatively low density of hydroxyl groups might therefore explain the relatively low solubility of xylan. The solubility of pectin was even lower than that of xylan, being only 3 wt % even after heating. This low value was due to gelation.

At 3−20 wt %, these solutions showed no phase separation upon cooling to room temperature. They also remained homogeneous even after storing them at 5 °C for several months. If solvents such as methanol or ethanol were added, however, the solution would quickly be separated into phases. We also confirmed that polysaccharide-based films or beads could be prepared using these ILs by following the procedure reported by Rogers.[16] The high solubility of these ILs is another advantage for many types of processing after dissolution.

In conclusion, a series of novel ILs with the formate anion have been prepared. These halogen-free ILs had lower viscosities than previously reported polar ILs. Because the polarities were high, due to the especially strong hydrogen bond basicity, many kinds of polysaccharides were solubilized with high concentrations under relatively low temperatures.

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Supporting Information Available. ^{1}H NMR data of ionic liquids. This material is available free of charge via the Internet at http://pubs.acs.org.

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