Extraction of polysaccharides from bran with phosphonate or phosphinate-derived ionic liquids under short mixing time and low temperature†

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A novel series of 1-alkyl-3-methylimidazolium phosphonate and phosphinate-type ionic liquids is able to extract polysaccharides from bran, which is a renewable biomass. In particular, 1-ethyl-3-methylimidazolium phosphinate is a novel low viscosity polar ionic liquid with which one can extract a series of polysaccharides from bran without heating. The physico-chemical properties of a series of these salts are also determined, in a study of the ability of these ionic liquids to extract cellulose and other polysaccharides from bran.

Introduction

Energy production from renewable biomass is a new and important undertaking. In view of the perpetual necessity for food, it is out of the question to treat foods as a starting material for energy production. Processes involving inedible biomass should be developed for that purpose. Use of immediately available plant biomass such as woods, hulls, straw and so on is a plausible strategy for providing energy. The polysaccharides in these categories of biomass are insoluble in water, so that a mixture of organic solvent/water/inorganic salt has generally been used together with heating to break the highly ordered crystalline structure, which is stabilized by multiple hydrogen bonds. Moreover, since polysaccharides exist as supramolecular complexes in nature, it is almost impossible to dissolve them at the molecular level or to extract them from biomass under mild conditions.[1] In any process to generate energy from the biomass, the minimum energy should be used to get the process going. At present, the energy necessary is greater than the total energy obtained from the polysaccharides.[2] This led us to seek solvents for extracting cellulose under mild conditions.

In recent years, ionic liquids (ILs),[3–5] which are low melting point organic salts designed to be liquid below 100 °C or (preferably) at room temperature, have been proposed as solvents for biopolymers such as DNA, RNA and proteins.[6–8] Some ILs are expected to act as solvents for polysaccharides.[9,10] The processing of cellulose and other polysaccharides in ILs is a step toward feasible and economic energy conversion systems such as biofuel cells. Three steps are involved. The first step is the extraction and dissolution of polysaccharides from biomass. The second step is hydrolysis of polysaccharides into mono-, di-, or oligo-saccharides. The third step is conversion of chemical energy, involving the resulting sugars, into electric energy. Biofuel cells based on ordinary molecular liquids, including water, have drawbacks that include the volatility of solvents, short lifetime of enzymes, and even algae growth.[11,12] Although ILs overcome these problems, they present others such as high viscosity. ILs are needed that facilitate these three steps.

In the present paper we focus on the first step, the extraction of polysaccharides from biomass under mild conditions. In a pioneering work, Rogers *et al.* found that 1-n-butyl-3-methylimdiazolium chloride dissolves cellulose.[13,14] Unfortunately, chloride salts have high melting temperatures and high viscosities. Energy is consequently needed in both the pre-treatment and main processes that use these chloride salts. A new class of room temperature ILs is desirable that can dissolve and isolate polysaccharides, including cellulose, from biomass with minimum energy.

Polar ILs with low melting points and relatively low viscosities have recently been synthesized that might be capable of overcoming the drawbacks of chloride salts. For instance, a series of alkylimidazolium carboxylates, such as acetate and formate salts, have been synthesized as room temperature ILs having relatively low viscosity.[15,16] Rogers *et al.* recently reported that some acetate salts dissolve cellulose from wood biomass in high concentrations.[16] These works all suggest that carboxylate salt-type ILs are good solvents for a series of polysaccharides. These carboxylates are not particularly thermally stable, however, which limits their usage. Our previous paper[17] reported the preparation of a series of alkylimidazolium cations coupled with alkylsulfates, alkylsulfonates, and alkylphosphates. Of these, 1-ethyl-3-methylimidazolium methylphosphonate was a good candidate for cellulose processing. This IL is thermally stable, and dissolves micro-crystalline cellulose under mild conditions. Since there is a wide variety of commercially available phosphonate-derived acid esters and alkylhalides, it is a good idea to combine diverse dialkylimidazolium cations with phosphonate-derived materials as anions in the search for polar ILs. Below, we set out our investigations of the extraction of polysaccharides from biomass using a series of dialkylimidazolium salts with phosphonate-derived anions,

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paying due attention to the requirements for efficient biomass processing under mild conditions, preferably without heating. We also determined the physico-chemical properties of a series of these salts, to consider their ability to extract polysaccharides, especially at low temperatures and with short mixing times.

Experimental

Materials

1-Methylimidazole was purchased from Wako Pure Chemical Co. Ltd. 1-Ethylimidazole, 1-n-butylimidazole, dimethyl phosphite, diisopropyl phosphite, diethyl phosphite, dibutyl phosphite and ethylbromide were purchased from Tokyo Chemical Industry, Co. Ltd. 1-Methylimidazole and 1-ethylimidazole were dried over KOH and distilled before use. The dimethyl phosphite was dried over K_2CO_3 then $CaCl_2$, and was distilled before use. Ethylbromide, allylbromide, n-propylbromide and n-butylbromide were all distilled before use. THF was purified before use with a solvent purifying system. All other commercially available chemicals were used as received.

Synthesis of ILs

We prepared 1-ethyl-3-methylimidazolium phosphinate as follows. 1-Ethyl-3-methylimidazolium bromide was dissolved into Milli Q water, and the resulting solution was passed through a column filled with anion exchange resin (Amberlite IR-78) to give an aqueous solution of 1-ethyl-3-methylimidazolium hydroxide. This solution was roughly concentrated by evaporation. Phosphinic acid aqueous solution was added to the aqueous solution of 1-ethyl-3-methylimidazolium hydroxide and the resulting solution was stirred for 2 h at room temperature. After removal of water by evaporation, the residual liquid was repeatedly washed with excess amounts of anhydrous diethyl ether. The resulting liquid was fully mixed with dichloromethane (100 ml) and then passed through a short column filled with active alumina (20 ml). The dichloromethane was removed by evaporation and the resulting liquid was dried *in vacuo* at 80 °C for 24 h, yielding 1-ethyl-3-methylimidazolium phosphinate as a colorless liquid. 1-Ethyl-3-methylimidazolium i-propylphosphonate and 1-ethyl-3-methylimidazolium n-butylphosphonate were prepared using the same procedures with the corresponding alkyl phosphites. Other ILs were prepared *via* the procedures used in our previous study.[17] The chemical structure of 1-ethyl-3-methylimidazolium phosphinate was confirmed by ^{1}H-, and ^{13}C-NMR spectra. These spectra were observed using a JEOL ECX-400.

^{1}H- and ^{13}C-NMR data of ILs

1-Ethyl-3-methylimidazolium methylphosphonate (1). ^{1}H-NMR (400 MHz; $CDCl_3$; Me_4Si) $\delta_H = 1.58$ (3H, t, $J = 7.3$ Hz, $\mathrm{NCH_2C}H_3$), 3.55 (3H, d, $J = 11.9$ Hz, $\mathrm{POC}H_3$), 4.06 (3H, s, $\mathrm{NC}H_3$), 4.36 (2H, q, $J = 7.3$ Hz, $\mathrm{NC}H_2\mathrm{CH_3}$), 6.92 (1H, d, $J =$ 588.5 Hz, $\mathrm{P}H$), 7.58 (2H, d, $J = 11.3$ Hz, $\mathrm{NC}H\mathrm{C}H\mathrm{N}$), 10.66 (1H, s, $\mathrm{NC}H\mathrm{N}$). ^{13}C-NMR (100 MHz; $CDCl_3$; Me_4Si) $\delta_C = 15.22$ ($\mathrm{NCH_2}C\mathrm{H_3}$), 35.83 ($\mathrm{N}C\mathrm{H_3}$), 45.22 ($\mathrm{N}C\mathrm{HCH_3}$), 50.05 ($\mathrm{PO}C\mathrm{H_3}$), 121.35 ($\mathrm{N}C\mathrm{HCHN}$), 123.17 ($\mathrm{NCH}C\mathrm{HN}$), 138.40 ($\mathrm{N}C\mathrm{HN}$).

1-Allyl-3-methylimidazolium methylphosphonate (2). ^{1}H-NMR (400 MHz; $CDCl_3$; Me_4Si) $\delta_H = 3.24$ (3H, d, $J = 11.4$ Hz, $\mathrm{POC}H_3$), 3.91 (3H, s, $\mathrm{NC}H_3$), 4.92 (2H, t, $J =$ Hz, $\mathrm{NC}H_2\mathrm{CH}$), 5.32 (2H, dd, $J = 13.7$, 6.0 Hz, $\mathrm{CH{=}C}H_2$), 6.07 (1H, dq, $J =$ 22.4, 5.6 Hz, $\mathrm{CH_2C}H\mathrm{{=}CH_2}$), 6.82 (1H, d, $J = 559.6$ Hz, $\mathrm{P}H$), 7.87 (2H, d, $J = 8.7$ Hz, $\mathrm{NC}H\mathrm{C}H\mathrm{N}$), 10.69 (1H, s, $\mathrm{NC}H\mathrm{N}$). ^{13}C-NMR (100 MHz; $CDCl_3$; Me_4Si) $\delta_C = 35.63$ ($\mathrm{N}C\mathrm{H_3}$), 49.41 ($\mathrm{PO}C\mathrm{H_3}$), 50.56 ($\mathrm{N}C\mathrm{H_2CH}$), 119.94 ($\mathrm{CH{=}}C\mathrm{H_2}$), 122.34, 123.34 ($\mathrm{N}C\mathrm{H}C\mathrm{HN}$), 131.99 ($\mathrm{CH_2}C\mathrm{H{=}CH_2}$), 137.29 ($\mathrm{N}C\mathrm{HN}$).

1-*n*-Propyl-3-methylimidazolium methylphosphonate (3). ^{1}H-NMR (400 MHz; $CDCl_3$; Me_4Si) $\delta_H = 0.95$ (3H, t, $J =$ 7.2 Hz, $\mathrm{CH_2C}H_3$), 1.75 (2H, m, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 3.22 (3H, d, $J = 11.4$ Hz, $\mathrm{POC}H_3$), 3.82 (3H, s, $\mathrm{NC}H_3$), 4.33 (2H, t, $J =$ 7.2 Hz, $\mathrm{NC}H_2\mathrm{CH_2}$), 6.78 (1H, d, $J = 554.1$ Hz, $\mathrm{P}H$), 7.33 (2H, d, $J = 31.0$ Hz, $\mathrm{NC}H\mathrm{C}H\mathrm{N}$), 10.40 (1H, s, $\mathrm{NC}H\mathrm{N}$). ^{13}C-NMR (100 MHz; $CDCl_3$; Me_4Si) $\delta_C = 13.13$ ($\mathrm{CH_2}C\mathrm{H_3}$), 29.34 ($\mathrm{NCH_2}C\mathrm{H_2CH_3}$), 35.49 ($\mathrm{N}C\mathrm{H_3}$), 48.10 ($\mathrm{N}C\mathrm{H_2CH_2}$), 49.47 ($\mathrm{PO}C\mathrm{H_3}$), 123.78 ($\mathrm{N}C\mathrm{HCHN}$), 123.99 ($\mathrm{NCH}C\mathrm{HN}$), 137.30 ($\mathrm{N}C\mathrm{HN}$).

1-*n*-Butyl-3-methylimidazolium methylphosphonate (4). ^{1}H-NMR (400 MHz; $CDCl_3$; Me_4Si) $\delta_H = 0.88$ (3H, t, $J = 7.1$ Hz, $\mathrm{CH_2C}H_3$), 1.16 (2H, m, $J = 15.0$, 7.6 Hz, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.75-1.81 (2H, br m, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 3.26 (3H, d, $J = 11.0$ Hz, $\mathrm{POC}H_3$), 3.80 (3H, s, $\mathrm{NC}H_3$), 4.11 (2H, t, $J = 7.3$ Hz, $\mathrm{NC}H_2\mathrm{CH_2}$), 6.55 (1H, d, $J = 559.2$ Hz, $\mathrm{P}H$), 7.35 (2H, d, $J = 32.1$ Hz, $\mathrm{NC}H\mathrm{C}H\mathrm{N}$), 10.35 (1H, s, $\mathrm{NC}H\mathrm{N}$). ^{13}C-NMR (100 MHz; $CDCl_3$; Me_4Si) $\delta_C = 13.21$ ($\mathrm{CH_2}C\mathrm{H_3}$), 18.73 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 31.40 ($\mathrm{NCH_2}C\mathrm{H_2CH_2}$), 35.54 ($\mathrm{N}C\mathrm{H_3}$), 48.31 ($\mathrm{N}C\mathrm{H_2CH_2}$), 49.32 ($\mathrm{PO}C\mathrm{H_3}$), 122.29 ($\mathrm{N}C\mathrm{HCHN}$), 123.57 ($\mathrm{NCH}C\mathrm{HN}$), 137.18 ($\mathrm{N}C\mathrm{HN}$).

1-Ethyl-3-methylimidazolium ethylphosphonate (5). ^{1}H-NMR (400 MHz; $CDCl_3$; Me_4Si) $\delta_H = 1.07$ (3H, t, $J = 7.1$ Hz, $\mathrm{OCH_2C}H_3$), 1.38 (3H, t, $J = 7.3$ Hz, $\mathrm{NCH_2C}H_3$), 3.72 (3H, d, $J = 11.9$ Hz, $\mathrm{POC}H_2\mathrm{CH_3}$), 3.89 (3H, s, $\mathrm{NC}H_3$), 4.25 (2H, q, $J = 7.3$ Hz, $\mathrm{NC}H_2\mathrm{CH_3}$), 6.73 (1H, d, $J = 592$ Hz, $\mathrm{P}H$), 7.29 (2H, d, $J = 11.4$ Hz, $\mathrm{NC}H\mathrm{C}H\mathrm{N}$), 10.42 (1H, s, $\mathrm{NC}H\mathrm{N}$). ^{13}C-NMR (100 MHz; $CDCl_3$; Me_4Si) $\delta_C = 15.43$ ($\mathrm{NCH_2}C\mathrm{H_3}$), 16.71 ($\mathrm{OCH_2}C\mathrm{H_3}$), 36.21 ($\mathrm{N}C\mathrm{H_3}$), 44.84 ($\mathrm{N}C\mathrm{H_2CH_3}$), 58.85 ($\mathrm{O}C\mathrm{H_2CH_3}$), 121.14 ($\mathrm{N}C\mathrm{HCHN}$), 123.09 ($\mathrm{NCH}C\mathrm{HN}$), 138.79 ($\mathrm{N}C\mathrm{HN}$).

1-Ethyl-3-methylimidazolium i-propylphosphonate (6). ^{1}H-NMR (400 MHz; $CDCl_3$; Me_4Si) $\delta_H = 1.05$ (6H, d, $J = 6.4$ Hz, $\mathrm{OCH(C}H_3\mathrm{)_2}$), 1.40 (3H, t, $J = 7.3$ Hz, $\mathrm{NCH_2C}H_3$), 3.91 (3H, s, $\mathrm{NC}H_3$), 4.22 (2H, q, $J = 7.5$ Hz, $\mathrm{NC}H_2\mathrm{CH_3}$), 4.34 (1H, m, $\mathrm{OC}H\mathrm{(CH_3)_2}$), 6.80 (1H, d, $J =$ 592 Hz, $\mathrm{P}H$), 7.25 (2H, d, $J = 10.5$ Hz, $\mathrm{NC}H\mathrm{C}H\mathrm{N}$), 10.53 (1H, s, $\mathrm{NC}H\mathrm{N}$). ^{13}C-NMR (100 MHz; $CDCl_3$; Me_4Si) $\delta_C =$ 15.45 ($\mathrm{NCH_2}C\mathrm{H_3}$), 24.33 ($\mathrm{OCH(}C\mathrm{H_3)_2}$), 36.24 ($\mathrm{N}C\mathrm{H_3}$), 44.85 ($\mathrm{N}C\mathrm{H_2CH_3}$), 66.41 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 121.08 ($\mathrm{N}C\mathrm{HCHN}$), 123.03 ($\mathrm{NCH}C\mathrm{HN}$), 139.02 ($\mathrm{N}C\mathrm{HN}$).

1-Ethyl-3-methylimidazolium n-butylphosphonate (7). ^{1}H-NMR (400 MHz; $CDCl_3$; Me_4Si) $\delta_H = 0.70$ (3H, t, $J = 7.5$ Hz, $\mathrm{CH_2CH_2CH_2C}H_3$), 1.21 (2H, m, $J =$ 14.9, 7.3 Hz, $\mathrm{CH_2CH_2C}H_2\mathrm{CH_3}$), 1.42 (5H, m, $J = 17.2$, 4.4 Hz, $\mathrm{CH_2C}H_2\mathrm{CH_2CH_3}$, $\mathrm{NC}H_3$), 3.67 (2H, t, $J =$ 7.0 Hz, $\mathrm{POC}H_2$), 3.88 (3H, s, $\mathrm{NC}H_3$), 4.21 (2H, q, $J = 7.3$ Hz, $\mathrm{NC}H_2\mathrm{CH_3}$), 6.78 (1H, d, $J = 592$ Hz, $\mathrm{P}H$), 7.24 (2H, d, $J = 10.1$, 1.8 Hz, $\mathrm{NC}H\mathrm{C}H\mathrm{N}$), 10.48

(1H, s, NCHN). ^{13}C-NMR (100 MHz; CDCl$_3$; Me$_4$Si) δ_C = 13.71 ($\mathrm{CH_2CH_2CH_2}C\mathrm{H_3}$), 15.43 ($\mathrm{NCH_2}C\mathrm{H_3}$), 18.98 ($\mathrm{CH_2CH_2}C\mathrm{H_2CH_3}$), 32.98 ($\mathrm{CH_2}C\mathrm{H_2CH_2CH_3}$), 36.21 ($\mathrm{N}C\mathrm{H_3}$), 44.87 ($\mathrm{N}C\mathrm{H_2CH_3}$), 63.03 ($\mathrm{O}C\mathrm{H_2CH_2}$), 121.09 (N$C$HCHN), 123.03 (NCH$C$HN), 138.93 (N$C$HN).

1-Ethyl-3-methylimidazolium phosphinate (8). ^{1}H-NMR (400 MHz; CDCl$_3$; Me$_4$Si) δ_H = 1.30 (3H, t, J = 7.4 Hz, $\mathrm{NCH_2C}H_3$), 3.81 (3H, s, $\mathrm{NC}H_3$), 4.11 (2H, q, J = 7.4 Hz, $\mathrm{NC}H_2\mathrm{CH_3}$), 7.19 (2H, s, J = 384 Hz, $\mathrm{P}H_2$), 7.26 (2H, d, J = 6.9 Hz, NCHCHN), 10.20 (1H, s, NCHN). ^{13}C-NMR (100 MHz; CDCl$_3$; Me$_4$Si) δ_C = 15.43 ($\mathrm{NCH_2}C\mathrm{H_3}$), 36.27 ($\mathrm{N}C\mathrm{H_3}$), 44.97 ($\mathrm{N}C\mathrm{H_2CH_3}$), 121.13 (N$C$HCHN), 123.03 (NCH$C$HN), 138.69 (N$C$HN).

Physicochemical property measurements

Physico-chemical properties of these ILs were measured using the procedures described in our previous study.[17] The amount of water contamination was measured by Karl Fischer coulometric titration (Kyoto Electronics MKC-510N). The differential scanning calorimetry (DSC) measurements were made using a DSC-6200 (SEIKO Instruments) at a scanning rate for heating and for cooling of 2.5 °C min^{-1} in the range of temperatures from −100 to 100 °C. The thermogravimetric analysis (TGA) was performed using a SEIKO TG/DTA 220 instrument with a heating rate of 10 °C min^{-1} from 25 to 500 °C under nitrogen gas. Visible spectra were observed using a Shimadzu UV 2450. Viscosities were measured using a Brookfield DV-I+ viscometer from 25 to 90 °C under dry nitrogen gas. Hydrogen bonding ability was quantified *via* the Kamlet–Taft parameters.[17]

Extraction of polysaccharides from bran

Each IL (1.90 g) was mixed with bran (0.10 g, powder with particle diameter 150 ± 50 μm) and stirred gently at 50 °C or at 25 °C. After stirring, the insoluble part was filtered off to give the sample solution (A g). Excess ethanol was added to the resulting IL solutions with stirring. After repeated washing with hot ethanol to remove residual IL, the regenerated precipitate was collected by filtration (B g). The degree of extraction was calculated from the following eqn (1).

$$\text{Degree of extraction (\%)} = \frac{B/(A-B)\times 1.9}{0.1}\times 100 \qquad (1)$$

Results and discussion

Effect of cation structure on the extraction of polysaccharides from bran

We first studied the effect of the side chain that is attached to the N-position of the imidazolium ring on the extraction of polysaccharides from bran. Bran is the hard shell of wheat and comprises a complex of polysaccharides and lignin, making it a scarcely soluble material. In the extraction of polysaccharides from bran, the hydrophobic parts of the IL should match the lignin in inducing swelling and increasing the amount of polysaccharides extracted. We chose four cations having different alkyl side chain lengths in order to study the effect of the lignin affinity in increasing the amount of polysaccharide extracted. As shown in Chart 1, we prepared and determined the properties of 1-ethyl-3-methyl-imidazolium (**1**), 1-allyl-3-methylimidazolium (**2**), 1-n-propyl-3-methylimidazolium (**3**), and 1-n-butyl-3-methyl-imidazolium (**4**) salts.

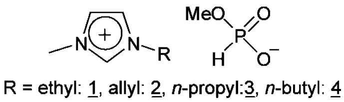

Chart 1 Chemical structure of dialkylimidazolium methylphosphonate.

All the ILs prepared here were obtained as liquids at room temperature ILs (RTILs). Table 1 shows melting temperature (T_m), glass transition temperature (T_g), and decomposition temperature (T_{dec}) of these four ILs. Every IL has one T_g around −80 °C, and no crystallization was detected while when these ILs were stored at −20 °C for more than three months. It means that every IL stably exists in a supercooled state, because of their asymmetric structure of both the anion and cations. The thermogravimetric analysis (TGA) showed that all these ILs were stable up to 250 °C.

It is necessary to design ILs with relatively strong hydrogen bond basicity to dissolve polysaccharides. Strong hydrogen bond basicity is effective in weakening the hydrogen-bonding network of the polymer chains.[18,19] The Kamlet–Taft parameters (α: hydrogen bond acidity, β: hydrogen bond basicity, π^*: dipolarity/polarizability) are commonly used to specify the hydrogen-bonding ability of the ILs as well as their polarity.[17,20] Table 1 also lists the Kamlet–Taft parameters of these four ILs. These ILs are characterized by β values greater than those for conventional ILs. It is generally believed that the β value depends mainly on the anion species, but also on the cation structure.[20] In considering the β value, we have already reported

Table 1 Physico-chemical properties of ILs examined in this study

				Kamlet–Taft parameters at 25 °C		
ILs	T_g ^{a}/°C	T_m/°C	T_{dec} ^{b}/°C	α	β	π^*
1	−86	—	278	0.52	1.00	1.06
2	−82	—	256	0.51	0.99	1.06
3	−79	—	277	0.54	1.00	1.02
4	−77	—	277	0.52	1.02	1.01

[a] Temperature at the signal peak. [b] Temperature at 10% weight loss.

that a methylphosphonate anion generates strong hydrogen bond basicity. The series of methylphosphonate salts prepared here also had stronger hydrogen bond basicity than conventional ILs. The π^* value of the present ILs decreased with increasing alkyl side chain length on the cation. This fact suggests that the π^* value reflects the degree of delocalization of charge on the cation.

We next determined the viscosity of these ILs. In the extraction of polysaccharides from bran under mild conditions in short periods of time, the dispersibility of the bran powder is important. Fig. 1 shows the viscosity of the ILs prepared here. The viscosity of these ILs depends on the cation structure. At 25 °C the viscosity of these salts is in the order: **1** (107 cP) < **2** (123 cP) < **3** (219 cP) < **4** (287 cP). It is generally accepted that cation size affects the viscosity of the resulting ILs.

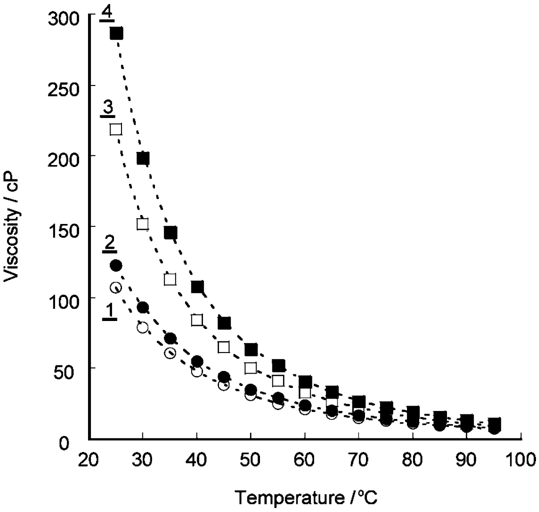

Fig. 1 Viscosity of ionic liquids evaluated here.

These physicochemical properties clearly indicate that the ILs prepared here include potential solvents for cellulose and other polysaccharides. Previously, the extraction of polysaccharides from plant biomass using ILs necessitated at least 24 h of stirring at temperatures above 100 °C[14,16] To reduce energy loss, extraction should be taken more rapidly at 50 °C or below.

To each IL (2.85 g), bran (0.15 g) was mixed (Fig. 2-1) and stirred at 50 °C. The bran in the ILs was dispersed, and some polysaccharides were extracted within 10 min at 50 °C (Fig. 2-2). We have confirmed that these ILs dissolve major component polysaccharides of bran such as cellulose, hemicellulose, and residual starch. The insoluble portion is expected to comprise lignin and its complexes. After stirring of the sample solution, the insoluble part was filtered off (Fig. 2-3), and excess ethanol was added to the IL solutions with gentle stirring (Fig. 2-4). The resulting precipitate was collected by filtration and washed repeatedly with ethanol to remove residual ILs.

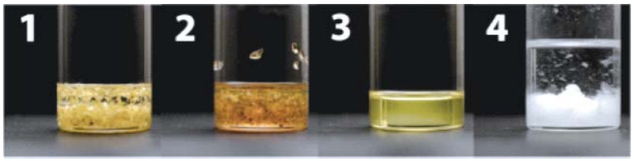

Fig. 2 Extraction of polysaccharides from bran. 1: Before heating, 2: after heating for 10 min, 3: filtrate, 4: after addition of ethanol to the filtrate.

To confirm the IL stability, we measured NMR spectra of the IL **1** after extraction experiments. From the NMR spectra (see ESI, Fig. S1†), methylphosphonate salt was confirmed not to be hydrolyzed in the extraction process of polysaccharides. Next, we have conducted characterization of the extracted materials by FT-IR, NMR, and TGA measurements. These experiments clarified that the extracted materials are the mixture of cellulose, hemicellulose, and residual starch. These spectra are attached in the ESI (Fig. S2–4).

The extent of extraction of polysaccharides from bran in these four ILs depends on the cation structure. Fig. 3 shows the degree of extraction of polysaccharides from bran in the present series of methylphosphonate salts at 50 °C. The extent of extraction of polysaccharides after 120 min is shown in this ordering: **4** (20%) < **3** (30%) < **2** (35%) < **1** (39%). Moreover, these ILs dissolved polysaccharides at 50 °C within 10 min.

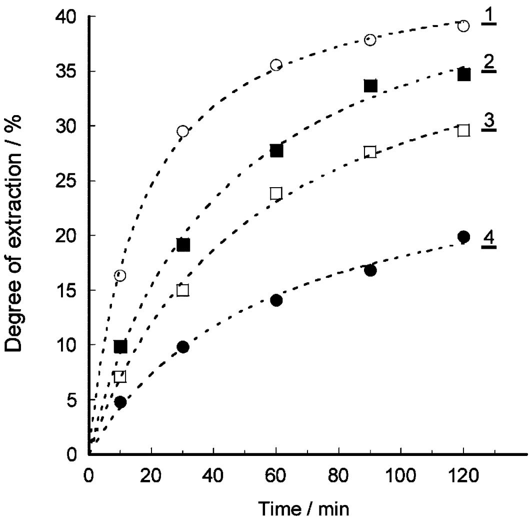

Fig. 3 Degree of extraction for bran with a series of ILs.

Hydrogen bond basicity is the most important property influencing the solubility of cellulose and other polysaccharides in ILs. The degree of extraction using these four ILs was however independent from their β value. Furthermore, there is no relation between the hydrophobicity of the cations and the degree of extraction. According to Fig. 1 and 3, lower viscosity ILs extracted more amount of polysaccharides. This may be due to better dispersion state of bran in less viscous ILs.

Effect of anion structure on the extraction of polysaccharides from bran

To determine the principal factor governing the degree of extraction and find ILs better suited for extraction, we modified the anion structure. As described above, among the phosphonate salts the 1-ethyl-3-methylimidazolium salt (**1**) has good capacity to extract polysaccharides. As shown in Chart 2, four 1-ethyl-3-methylimidazolium salts, containing methylphosphonate (**1**), ethylphosphonate (**5**), i-propylphosphonate (**6**) or n-butylphosphonate (**7**) anions have been studied in order to

Table 2 Physico-chemical properties of ILs examined in this study

ILs	$T_g{}^a$/°C	T_m/°C	$T_{dec}{}^b$/°C	Kamlet–Taft parameters at 25 °C α	 β	 π*
1	−86	—	278	0.52	1.00	1.06
5	−79	—	266	0.55	1.02	1.02
6	−71	—	256	0.55	1.03	1.00
7	−77	—	259	0.56	1.06	0.97

^{a} Temperature at the signal peak. ^{b} Temperature at 10% weight loss.

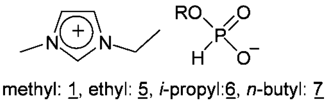

Chart 2 Chemical structure of alkylphosphonate salts.

investigate the effect on the degree of extraction of hydrogen bonding ability, viscosity and ion size and characteristics.

These ILs were also obtained as RTILs. Table 2 summarizes the physicochemical properties of these ILs. They have a glass transition temperature at around −80 °C. They remained liquid state even after storage at −20 °C for a month, indicating a highly stable supercooling state. Also, TGA analysis revealed that these ILs were stable up to 250 °C.

Table 2 also summarizes the Kamlet–Taft parameters for this series of ILs. These ILs have been designed to show relatively strong hydrogen bonding characteristics, especially the β value. The β value of ILs is in general affected mainly by the nature of the anion species.[17,19,20] The β values of these ILs were similar, but increased slightly in the order: **1** (β = 1.00) < **5** (β = 1.02) < **6** (β = 1.03) < **7** (β = 1.06). Since the series of anions studied here has the same unit structure ([(R)(H)$PO_2{}^-$]), the differing β values of these ILs should be explicable by the difference in the electron-releasing ability of the alkyl side chain. The π* values of the ILs decreased with an increasing number of carbon atoms in the alkyl side chain of the anion. The difference in the π* values should therefore reflect the extent of delocalization of charge on the anion. The proton at the 2-position of the imidazolium ring contributes to the hydrogen bond acidity.[21,22] The ILs studied here have the same 1-ethyl-3-methylimidazolium cation, but the α value was affected slightly by the anion structure. This should also show in the value of π*, since the value of α depends on π*.[20]

Fig. 4 shows the viscosity of these ILs. The viscosity of these ILs clearly depends on their anion structure. This is expected to be due to the bulkiness of the alkoxy group on the anion. In preparing low-viscosity ILs, it is important to use alkylphosphonate with a shorter alkyl chain.

Fig. 5 shows the degree of extraction of polysaccharides from bran by this series of phosphonate-derived salts at 50 °C. The degree of extraction was influenced by the anion structure of the IL, and the value after two hours mixing is the following order: **6** (16%) < **7** (19%) < **5** (30%) < **1** (39%).

The solubility of polysaccharides depends mainly on the β value of the ILs. However, the degree of extraction of polysaccharides from bran in this experiment did not directly depend on the β value. Among these four ILs, the β value was the highest for **7** and the lowest for **1**. In spite of this, **1** successfully extracted more polysaccharide than **7**. We infer that for a series of IL having the β value within a certain range, the amount of polysaccharide extracted from bran in a limited time varies depending on the viscosity more strongly than other parameters. Of these ILs, **7** has the largest alkyl side chain, but **7** has better capacity to extract polysaccharides than **6**. The properties and interaction force derived from size of the ion are therefore concluded not to be the primary determinants of the degree of extraction.

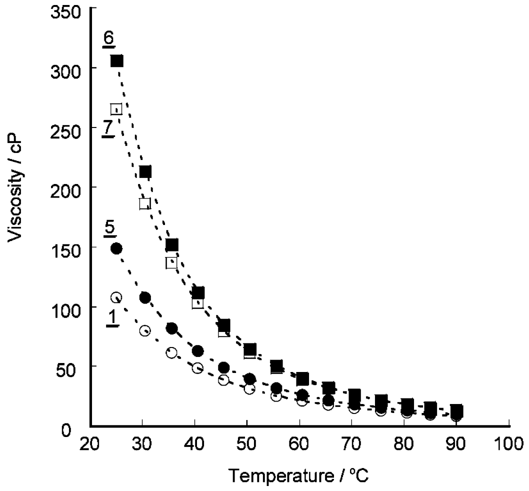

Fig. 4 Viscosity of ionic liquids evaluated here.

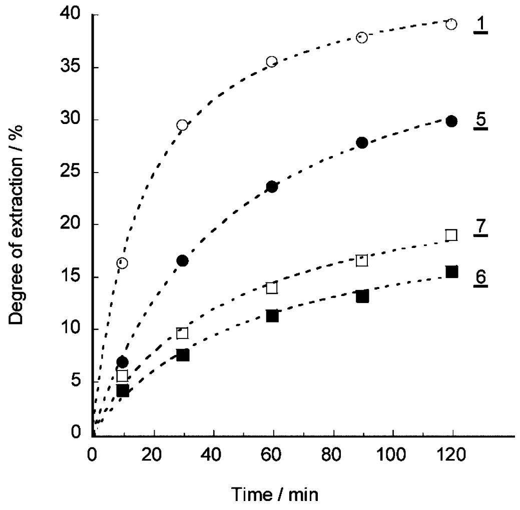

Fig. 5 Degree of extraction of polysaccharides from bran with a series of ILs as a function of treatment time at 50 °C.

Table 3 Physico-chemical properties of phosphate-derived ILs

				Kamlet–Taft parameters at 25 °C		
Ionic Liquid	T_g/°C	$T_m{}^a$/°C	$T_{dec}{}^b$/°C	α	β	π*
8	—	17	260	0.52	0.97	1.09

[a] Temperature at the signal peak. [b] Temperature at 10% weight loss.

The degree of extraction of polysaccharides is closely related to the viscosity as seen in Fig. 4. The IL with lowest viscosity had good capacity to extract polysaccharides in short times under mild conditions. Fig. 6 shows the relation between the extent of polysaccharide extraction (2 h after) and IL viscosity. It can be seen that low-viscosity ILs are able to extract a large amount of polysaccharides at 50 °C.

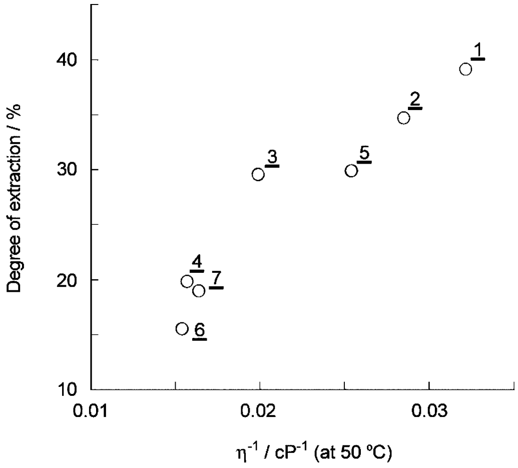

Fig. 6 Relationship between degree of extraction of polysaccharides and inverse viscosity of a series of ILs at 50 °C.

For polar ILs with similar β values, the degree of extraction over limited time depends strongly on their viscosity. ILs **1** and **6** have similar β values, of 1.00 and 1.03 for **1** and **6**, respectively, **6** ($\eta = 65$ cP at 50 °C) needs 120 min stirring at 50 °C to extract *ca.* 15% of polysaccharides from bran, **6** ($\eta = 65$ cP at 50 °C) necessitates 2 h stirring at 50 °C, whereas **1** ($\eta = 31$ cP at 50 °C) needs only 10 min under the same condition. The solubility of cellulose in these ILs should be independent from their viscosity, but solubilization of celluloses is faster in less viscous ILs. The bran dispersed more easily in lower viscosity ILs, so that greater solubility was observed in these under mild conditions and over short times.

Design of a new IL and extraction of polysaccharides without heating

For ILs with adequate polarity, those with low viscosity have good ability to extract polysaccharides in short times. We have therefore successfully designed a novel IL having high polarity and low viscosity. Imidazolium cations with short alkyl side chains generally give low viscosity ILs, as we confirmed with a short alkyl side chain of phosphonate-derived anions.

The IL, 1-ethyl-3-methylimidazolium phosphinate, hereafter **8** (Chart 3), has been newly designed. It was obtained as RTILs, and DSC analysis showed that $T_m = 17$ °C for **8**. This IL was crystallized by keeping it at −20 °C for several days. TGA measurement revealed that **8** was stable up to 250 °C. The Kamlet–Taft polarity parameters of **8** are also shown in Table 3. IL **8** exhibits relatively strong hydrogen bonding basicity. Compared to the alkylphosphonate series salts ($1.00 < \beta < 1.06$; see Table 1), the β value of IL **8** is a little low at 0.97. We have reported previously that 1-allyl-3-methylimidazolium formate has essentially similar hydrogen-bonding basicity (0.99), and that it successfully dissolved cellulose in high concentrations.[15] We believe IL **8** has polarity sufficient to extract polysaccharides from bran.

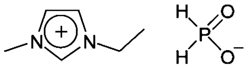

Chart 3 Chemical structure of 1-ethyl-3-methylimidazolium phosphinate (**8**).

Fig. 7 shows the viscosity of both **8** and **1**. IL **8** has the lowest viscosity of all the ILs considered in this paper. The viscosity of **8** is approximately 60% of that of **1**. As a result of lower viscosity and strong hydrogen bonding properties of **8**, this IL is expected to be a good solvent for polysaccharides.

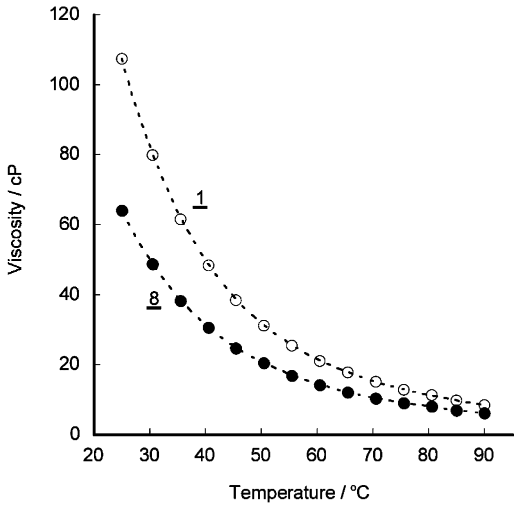

Fig. 7 Temperature dependence of viscosity of the IL **8** and **1**.

Fig. 8 shows the experimentally determined extent of extraction of polysaccharides from bran using **8**. As expected, **8** extracted polysaccharides better than **1**. As shown in Fig. 8, IL **8** extracted 42% of polysaccharides from bran, whereas **1** extracted only 39% at 50 °C with gentle stirring for 2 h.

In our previous paper, we successfully dissolved cellulose using a series of alkylphosphonate derivative salts.[17] IL **1** has been found to dissolve a certain amount of pure cellulose

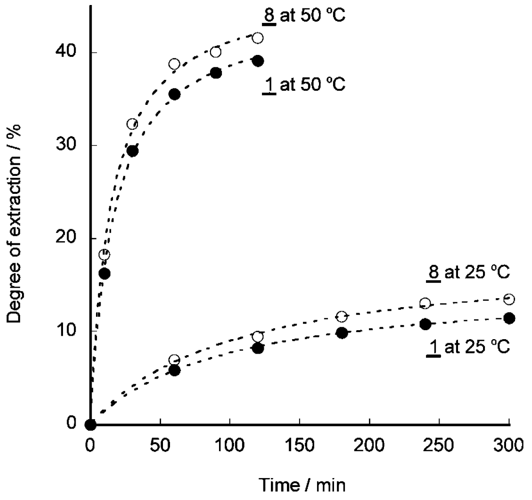

Fig. 8 Extraction of polysaccharides from bran with **8** and **1**.

powder without heating. We expected that **8** would also extract polysaccharide components from bran without heating. Fig. 8 shows the solubility of polysaccharides from bran in these ILs at 25 °C. This clearly shows that no heating is needed for dissolution. About 14% of polysaccharides were extracted from bran by gentle stirring in **8**, and 11% in **1**, at room temperature during 5 h mixing. Almost no heat was generated during gentle stirring, and there was no increase in the solution temperature. Although the extent of extraction is much lower than that at 50 °C (>35% for 2 h), this should be excellent first step for ecological energy conversion followed by hydrolysis and electrochemical energy conversion without heating (giving excess energy). Detailed investigation of extracts is under way and will be reported soon.

Conclusions

We report that biomass processing is readily performed with certain phosphonate-derived salts at low temperature and short mixing times. Although the β value is held to be important in the dissolution of polysaccharides, when the ILs have sufficient polarity, we found that the viscosity of the ILs dominates the ability to extract polysaccharides over limited time. We accordingly designed a low viscosity and highly polar IL, 1-ethyl-3-methylimidazolium phosphinate (**8**). This novel IL rapidly extracted cellulose and other polysaccharides from bran under mild conditions.

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