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Extraction of Polysaccharides from Japanese Cedar Using Phosphonate-Derived Polar Ionic Liquids Having Functional Groups

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Abstract

Extraction of polysaccharides from Japanese cedar using ionic liquids has been demonstrated. To this aim, eleven types of phosphonate ionic liquids have been synthesized, their properties investigated, and applied to biomass processing. All ionic liquids prepared display strong hydrogen-bonding characteristics of Kamlet–Taft parameters ($\beta > 1.1$) which enabled the effective extraction of polysaccharides from Japanese cedar. In particular, 15 wt% of polysaccharides was extracted from Japanese cedar powder using 1-(3-methoxypropyl)-3-methylimidazolium ethyl ethylphosphonate. Since the ionic liquid is easily prepared using conventional reagents and might be applicable to large-scale reactions, it is expected that practical polysaccharide extraction using the ionic liquid might be possible from a wide variety of biomass resources.

1. Introduction

As one of the fundamental technologies to realize "sustainable society", research studies on the conversion of renewable resources to functional materials and even energy are explosively increasing today.[1] Cellulosic biomass, which is composed mainly of cellulose, hemicellulose and lignin, is the most abundant renewable resources on this planet. These components are scarcely soluble in conventional molecular liquids. Since polysaccharides and lignin form supramolecular structures,[2] it is difficult to dissolve them by conventional molecular liquids and this allows only limited use of them.

There has been a great deal of interest in ionic liquids (ILs)[3] as potential solvents for cellulosic biomass.[4,5] ILs are designer liquids which have the potential of designable properties, such as polarity and affinity with other compounds;[6] this makes it possible for us to design "polar" ILs that enable dissolution of cellulose and cellulosic biomass. Multiple inter-chain hydrogen bonds are known to make cellulose insoluble in conventional molecular liquids.[7] ILs precisely designed to display strong hydrogen-bonding basicity have been revealed to disrupt the hydrogen bond network of the cellulose.[8] In regard to the preparation of such polar ILs, chloride,[5,9] carboxylate,[10] and phosphonate[11] are recognized as candidates.[12] We also established that amino acid salts ILs could dissolve cellulose well[13,14] and a mixture of dimethyl sulfoxide (DMSO) and *N*,*N*-diethyl-*N*-(2-methoxy)ethyl-*N*-methylammonium alanate ($[N_{221ME}][Ala]$)[13] dissolved cellulose at room temperature.[15] These polar ILs have been used for wide ranging purposes such as energy-saving biomass processing,[16] analysis of biomass components,[17] and so forth. The studies indicate that develop-

ment of more polar ILs for cellulosic biomass is required to achieve new technologies and methodologies in biomass sciences.

We herein turn our attention to phosphonate-type polar ILs as solvents for extraction of polysaccharides from woody biomass, Japanese cedar, because phosphonate ILs have been reported to dissolve cellulose under mild conditions[11] and these, in particular, have wide structural diversity. Extraction of polysaccharides from plant biomass, bran, was in fact demonstrated using such ILs,[18] while no systematic study has been conducted.

Our area, Tottori, is famous for having a forest of beautiful Japanese cedar that has been a producing center of high-quality lumber used for housing for hundreds of years. However, the forest industry in Tottori is now faced with a crisis of extinction due to low-cost imported lumber and the fact that the population of this area has decreased more and more over the years. Recently, more people have gradually reconsidered using high-quality lumber made in Japan. But in order to produce high-quality lumber, it is essential to continuously remove unnecessary trees until the forest has grown for 60–100 years. Therefore, the development of a means to utilize wooden wastes has strongly been needed. So we decided to investigate an extracting method of polysaccharides from Japanese cedar using ILs. With the aim of realizing extraction of polysaccharide from woody biomass, we prepared phosphonate-type ILs systematically by changing the combination of cations and anions and investigated the effect of ion structures on their physicochemical properties, focusing on their ability to dissolve cellulose and polysaccharides in Japanese cedar.

2. Experimental

2.1 Materials and Instruments. 1-Ethylimidazole and 1-methylimidazole were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Ethyl bromide, *n*-butyl bromide, *n*-hexyl bromide, bromoethyl methyl ether, 3-chloromethoxy propane, ethyl ethylphosphonate, ethyl phosphonate, ethyl phosphoramidate, and ethyl benzylphosphonate were also purchased from TCI, and used as received. Amberlite® IRN-78 was purchased from SUPELCO. Neutral activated alumina was purchased from Aldrich. The measurements of ^{1}H NMR and ^{13}C NMR spectra were carried out on a JEOL JNM-500. Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo Scientific Exactive spectrometer. The amount of water was confirmed by Karl Fischer coulometric titration on a Kyoto Electronics MLC-610 DT. The differential scanning calorimetry (DSC) measurements were conducted at a scanning rate for both heating and cooling of 5 °C min^{-1} in the temperature range −120 to 100 °C. Thermogravimetric analyses (TGA) were carried out using a RIGAKU Thermo Plus EVO II with a heating rate of 10 °C min^{-1} from 25 to 500 °C under dry argon gas. Visible spectrum was measured using a JASCO UV 550. Viscosity of ILs was measured using a Brookfield DV2-T Viscometer at valuable temperature.

2.2 Preparation of ILs. As a typical procedure for preparing ILs, preparation of 1-ethyl-3-methylimidazolium ethyl ethylphosphonate (**8**) is described as follows: to 1-methylimidazole in toluene, an excess amount of ethyl bromide was added at room temperature, and the resulting mixture was stirred for 24 h. During the reaction, clear liquid was separated from reaction media and the precipitate formed was washed repeatedly with diethyl ether. The precipitate was dried in vacuo at 50 °C to give 1-ethyl-3-methylimidazolium bromide ([C_2mim]Br) as white solid. [C_2mim]Br was dissolved in Milli Q water, and the resulting solution was passed through a column filled with anion-exchange resin (Amberlite® IRN-78) to give 1-ethyl-3-methylimidazolium hydroxide ([C_2mim]OH) aqueous solution.

To the aqueous solution of [C_2mim]OH, an equivalent molar amount of diethyl ethyl ethylphosphonate was added, and the resulting mixture was stirred. After the pH of the reaction mixture became neutral, water and ethanol were removed by evaporation. The product was washed repeatedly with diethyl ether and dissolved into ethanol, and the resulting solution was stirred with active carbon. After removal of the active carbon by filtration, ethanol was removed by evaporation and the residue was then dissolved in dichloromethane, and the resulting solution was passed through a short column filled with neutral activated alumina. The solvent was removed by evaporation, and the resulting liquid was dried under reduced pressure at 80 °C for 12 h, yielding 1-ethyl-3-methylimidazolium ethyl ethylphosphonate (**8**) as a colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.14 (3H, q, $J = 12.8$ Hz, PCH_2CH_3), 1.23 (3H, t, $J = 7.3$, $POCH_2CH_3$), 1.56 (3H, m, $NCHCH_3$), 3.66 (2H, dd, $J = 7.0$ Hz, PCH_2CH_3), 3.91 (2H, q, $J = 6.9$ Hz, NCH_2CH_3), 4.08 (3H, s, NCH_3), 4.39 (2H, dd, $J = 7.5$ Hz, $POCH_2$), 7.33 (2H, d, $J = 11$ Hz, NCH=CHN), 10.86 (1H, s, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$): δ 8.46 ($J_{C-P} = 5.9$ Hz, PCH_2CH_3), 15.61 (NCH_2CH_3), 17.11 ($J_{C-P} = 6.0$ Hz, $POCH_2CH_3$), 20.36 ($J_{C-P} = 134$ Hz, PCH_2CH_3), 36.42 (NCH_3), 45.02 (NCH_2CH_3), 58.56 ($J_{C-P} = 6.1$ Hz, $POCH_2CH_3$), 120.96, 123.02, 139.78. HRMS (ESI-TOF) m/z: [M^+] calcd for $C_6H_{11}N_2$, 111.0923; found, 111.0911. m/z: [X^-] calcd for $C_4H_{10}O_3P$, 137.0368; found, 137.0366.

2.2.1 1-Ethyl-3-methylimidazolium Ethylphosphonate (1):[11a–11c] ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 (3H, t, $J = 7.3$ Hz, CH_2CH_3), 1.58 (3H, t, $J = 7.5$ Hz, $POCH_2CH_3$), 3.92 (2H, q, $J = 7.4$ Hz, PCH_2CH_3), 4.07 (3H, s, NCH_3), 4.38 (2H, dd, $J = 7.3$, NCH_2), 6.95 (1H, d, $J_{PH} = 597$ Hz, PH), 7.27 (2H, m, NCH=CHN), 10.75 (1H, s, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.58 (NCH_2CH_3), 16.81 ($J_{C-P} = 6.0$ Hz, $POCH_2CH_3$), 18.51 (NCH_2CH_3), 36.38 (NCH_3), 45.00 (NCH_2CH_3), 59.16 ($J_{C-P} = 4.8$ Hz, $POCH_2CH_3$), 121.55, 123.54, 138.46. HRMS (ESI-TOF) m/z: [M^+] calcd for $C_6H_{11}N_2$, 111.0923; found, 111.0910. m/z: [M^-] calcd for $C_2H_6O_3P$, 109.0054; found, 109.0047.

2.2.2 1-Butyl-3-methylimidazolium Ethylphosphonate (2):[11a] ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.96 (3H, t, $J = 5.8$ Hz, CH_2CH_3), 1.25 (3H, q, $J = 4.0$ Hz, $POCH_2CH_3$), 1.36 (2H, m, $CH_2CH_2CH_3$), 1.86 (2H, m, NCH_2CH_2), 3.90 (2H, t, $J = 5.5$ Hz, $POCH_2$), 4.08 (3H, s, NCH_3), 4.29 (2H, t, $J = 6.75$ Hz, NCH_2), 6.95 (1H, d, $J_{PH} = 591$ Hz, PH), 7.24 (1H, s), 7.34 (1H, s), 10.83 (1H, s, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.48 ($NCH_2CH_2CH_2CH_3$), 16.85 ($J_{C-P} = 7.5$ Hz, $POCH_2CH_3$), 19.52, 32.21, 36.48 (NCH_3), 49.75 (NCH_2CH_3), 59.07 ($POCH_2CH_3$), 121.38, 123.04, 139.89. HRMS (ESI-TOF) m/z: [M^+] calcd for $C_8H_{15}N_2$, 139.1237; found, 139.1224. m/z: [M^-] calcd for $C_2H_6O_3P$, 109.0054; found, 109.0047.

2.2.3 1-*n*-Hexyl-3-methylimidazolium Ethylphosphonate (3): ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, t, $J = 6.8$ Hz, CH_2CH_3), 1.25 (3H, t, $J = 7.0$ Hz, $POCH_2CH_3$), 1.31 (6H, m, $CH_2CH_2CH_2CH_3$), 1.89 (2H, q, $J = 7.3$ Hz, NCH_2CH_2), 3.91 (2H, q, $J = 7.3$ Hz, $POCH_2CH_3$), 4.08 (3H, s, NCH_3), 4.28 (2H, t, $J = 7.5$ Hz, NCH_2), 6.98 (1H, d, $J_{PH} = 588$ Hz, PH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.92 ($NCH_2(CH_2)_4CH_3$), 16.86 ($J_{C-P} = 7.3$ Hz, $POCH_2CH_3$), 22.38, 25.89, 30.24, 31.11, 36.35 (NCH_3), 49.88 (NCH_2CH_2), 58.96 ($J_{C-P} = 4.8$ Hz, $POCH_2CH_3$), 121.57, 123.38, 139.51. HRMS (ESI-TOF) m/z: [M^+] calcd for $C_{10}H_{19}N_2$, 167.1550; found, 167.1535. m/z: [M^-] calcd for $C_2H_6O_3P$, 109.0054; found, 109.0047.

2.2.4 1-(2-Methoxyethyl)-3-methylimidazolium Ethylphosphonate (4): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (3H, t, $J = 7.3$ Hz, $POCH_2CH_3$), 3.37 (3H, s, $CH_2CH_2OCH_3$), 3.77 (2H, t, $J = 5.0$ Hz, NCH_2CH_2), 3.92 (2H, q, $J = 7.3$ Hz, $POCH_2$), 4.06 (3H, s, NCH_3), 4.57 (2H, t, $J = 4.8$ Hz, NCH_2), 6.97 (1H, d, $J_{PH} = 592$ Hz, PH), 7.29 (1H, s), 7.42 (1H, s), 10.76 (1H, s, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.85 ($J_{C-P} = 7.3$ Hz, $POCH_2CH_3$), 36.39 (NCH_2CH_3), 49.72 (NCH_2CH_2), 58.98 (OCH_3), 59.05 ($J_{C-P} = 10.8$ Hz, $POCH_2CH_3$), 70.74 ($NCH_2CH_2CH_2OCH_3$), 122.32, 123.03, 139.75. HRMS (ESI-TOF) m/z: [M^+] calcd for $C_7H_{13}N_2O$, 141.1029; found, 141.1021. m/z: [M^-] calcd for $C_2H_6O_3P$, 109.0054; found, 109.0047.

2.2.5 1-(3-Methoxypropyl)-3-methylimidazolium Ethylphosphonate (5): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 (3H, t, $J = 6.8$ Hz, $POCH_2CH_3$), 2.19 (2H, q, $J = 6.2$ Hz, $NCH_2CH_2CH_2$), 3.32 (3H, s, $CH_2CH_2OCH_3$), 3.42 (2H, t, $J = 5.6$ Hz, $NCH_2CH_2CH_2$), 3.92 (2H, dd, $J = 7.5$ Hz, $POCH_2$), 4.08 (3H, s, NCH_3), 4.42 (2H, t, $J = 7.3$ Hz, NCH_2), 6.95 (1H, d, $J_{PH} = 594$ Hz, PH), 7.24 (1H, s), 7.28 (1H, s), 10.68 (1H, s, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.86 ($J_{C-P} = 6.0$ Hz, $POCH_2CH_3$), 30.28 ($NCH_2CH_2CH_2OCH_3$), 36.56 (NCH_3), 47.30 ($NCH_2CH_2CH_2OCH_3$), 59.00 ($J_{C-P} = 44.4$ Hz, $POCH_2CH_3$), 68.50 ($NCH_2CH_2CH_2OCH_3$), 122.07, 122.63, 139.85. HRMS (ESI-TOF) m/z: [M^+] calcd for $C_8H_{15}N_2O$, 155.1186; found, 155.1077. m/z: [M^-] calcd for $C_2H_6O_3P$, 109.0054; found, 109.0046.

2.2.6 1-(2-Phenoxyethyl)-3-methylimidazolium Ethylphosphonate (6): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (3H, t, $J = 7.3$ Hz, $POCH_2CH_3$), 3.91 (2H, q, $J = 7.3$ Hz, $POCH_2$), 4.01 (3H, s, NCH_3), 4.36 (2H, t, $J = 4.8$ Hz, NCH_2CH_2), 4.82 (2H, t, $J = 4.8$ Hz, NCH_2), 6.87 (2H, d, $J = 8.5$ Hz, CHCHCH), 6.96 (1H, t, $J = 7.5$ Hz, CHCHCH), 6.99 (1H, d, $J_{PH} = 588$ Hz, PH), 7.50 (1H, s), 7.64 (1H, s), 10.8 (1H, s, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.85 ($J_{C-P} = 7.3$ Hz, $POCH_2CH_3$), 36.45 (NCH_3), 49.32 (NCH_2CH_2), 59.13 ($J_{C-P} = 3.6$ Hz, $POCH_2CH_3$), 66.6 (NCH_2CH_2OPh), 114.47, 121.85, 122.51, 123.13, 129.8, 139.78, 157.56. HRMS (ESI-TOF) m/z: [M^+] calcd for $C_{12}H_{15}N_2O$, 203.1186; found, 203.1172. m/z: [M^-] calcd for $C_2H_6O_3P$, 109.0054; found, 109.0047.

2.2.7 1-Ethyl-3-methylimidazolium Ethyl Phosphoramidate (7): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (3H, t, $J = 6.3$, OCH_2CH_3), 1.54 (3H, t, $J = 6.9$ Hz, NCH_2CH_3), 3.92 (2H, m, PCH_2CH_3), 4.10 (3H, m, NCH_3), 4.38 (2H, d, $J = 7.5$ Hz, OCH_2CH_2), 7.43 (1H, s), 7.49 (1H, s), 11.0 (1H, s, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.67 (NCH_2CH_3), 16.88 ($J_{C-P} = 8.4$ Hz, $POCH_2CH_3$), 36.38 (NCH_3), 44.93 (NCH_2), 59.96 ($J_{C-P} = 4.8$ Hz, $POCH_2$), 121.05, 123.20, 138.91. HRMS (ESI-TOF) m/z: [M^+] calcd for $C_6H_{11}N_2$, 111.0923; found, 111.0903. m/z: [X^-] calcd for $C_2H_7NO_3P$, 124.0164; found, 124.0156.

2.2.8 1-Ethyl-3-methylimidazolium Ethyl (Methoxymethyl)phosphonate (9): ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.05 (3H, t, $J = 7.0$ Hz, PCH_2CH_3), 1.41 (3H, t, $J = 7.3$ Hz, NCH_2CH_3), 3.17 (2H, d, $J = 8$ Hz, PCH_2OCH_3), 3.22 (3H, s, OCH_2CH_3), 3.67 (2H, q, $J = 7.1$ Hz, $POCH_2$), 3.86 (3H, s, NCH_3), 4.20 (2H, dd, $J = 7.2$ Hz, NCH_2), 7.72 (1H, s), 7.80 (1H, s), 9.37 (1H, s, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.62 (NCH_2CH_3), 17.17 ($J_{C-P} = 7.2$ Hz, $POCH_2CH_3$), 36.45 (NCH_3), 45.04 (NCH_2CH_3), 60.91 ($J_{C-P} = 13.2$ Hz, PCH_2OCH_3), 60.28 ($J_{C-P} = 5.9$ Hz, PCH_2OCH_3), 69.64 ($J_{C-P} = 13.2$ Hz, $POCH_2CH_3$), 120.94, 123.02, 139.77. HRMS (ESI-TOF) m/z: [M^+] calcd for $C_6H_{11}N_2$, 111.0923; found, 111.0912. m/z: [X^-] calcd for $C_4H_{10}O_4P$, 153.0317; found, 153.0316.

2.2.9 1-Ethyl-3-methylimidazolium Ethyl Benzylphosphonate (10): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (3H, t, $J = 7.0$ Hz, PCH_2CH_3), 1.55 (3H, t, $J = 7.5$ Hz, NCH_2CH_3), 3.40 (3H, s, PCH_2OCH_3), 3.60 (2H, d, $J = 2.8$ Hz, PCH_2Ph), 3.71 (3H, s, NCH_3), 3.84 (2H, q, $J = 11.3$ Hz, NCH_2CH_3), 4.38 (2H, q, $J = 11.3$ Hz, $POCH_2CH_3$), 7.29 (1H, s), 7.33 (1H, s), 10.73 (1H, s, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.51 (NCH_2CH_3), 17.14 ($J_{C-P} = 6.0$ Hz, $POCH_2CH_3$), 35.81 ($J_{C-P} = 51.5$ Hz, PCH_2PH), 36.60 (NCH_3), 44.67 (NCH_2), 59.97 ($J_{C-P} = 14.8$ Hz, $POCH_2$), 120.82, 124.80, 124.83, 138.1 ($J_{C-P} = 8.3$ Hz), 139.75. HRMS (ESI-TOF) m/z: [M^+] calcd for $C_6H_{11}N_2$, 111.0923; found, 111.0912. m/z: [X^-] calcd for $C_9H_{12}O_3P$, 199.0524; found, 199.0521.

2.2.10 1-(3-Methoxypropyl)-3-methylimidazolium Ethyl Ethylphosphonate (11): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.14 (3H, dt, $J = 6.1$ Hz, $POCH_2CH_3$), 1.23 (3H, t, $J = 7.0$ Hz, PCH_2CH_3), 1.60 (2H, m, NCH_2CH_2), 2.20 (2H, m, PCH_2), 3.32 (3H, s, $CH_2CH_2OCH_3$), 3.41 (2H, t, $J = 5.8$ Hz, $NCH_2CH_2CH_2OCH_3$), 3.92 (3H, m, $POCH_2$), 4.10 (3H, s, NCH_3), 4.30 (2H, t, $J = 7.0$ Hz, $NCH_2CH_2CH_2$), 7.30 (1H, s), 7.45 (1H, s), 11.19 (1H, s, NCHN), ^{13}C NMR (125 MHz, $CDCl_3$): δ 8.61 ($J_{C-P} = 5.9$ Hz, PCH_2CH_3), 17.10 ($J_{C-P} = 5.9$ Hz, $POCH_2CH_3$), 20.46 ($J_{C-P} = 133$ Hz, PCH_2CH_3), 30.24 ($NCH_2CH_2CH_2OCH_3$), 36.32 (NCH_3), 47.02 ($NCH_2CH_2CH_2OCH_3$), 58.45 ($NCH_2CH_2CH_2OCH_3$), 59.37 ($J_{C-P} = 4.8$ Hz, $POCH_2CH_3$), 68.40 ($NCH_2CH_2CH_2OCH_3$), 121.97, 122.81, 140.42. HRMS (ESI-TOF) m/z: [M^+] calcd for $C_8H_{15}N_2O$, 155.1186; found, 155.1170. m/z: [X^-] calcd for $C_4H_{10}O_3P$, 137.0368; found, 137.0368.

2.3 Measurements of the Kamlet–Taft Parameters.[19] The Kamlet–Taft parameters of ILs were determined as follows. Spectroscopic grade solvatochromic dyes, 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)-phenolate (Reichardt's dye #33) (from Fluka), 4-nitroaniline (from Tokyo Chemical Ind. Co., Ltd), and *N*,*N*-diethyl-4-nitroaniline (from Kanto Chem.), were used as received. A concentrated dry methanol solution of the dye was added to the ILs, and the methanol was removed under reduced pressure at 40 °C. To prevent dye aggregation, the dye concentration in any series of ILs was chosen to be low but sufficient to allow an absorbance greater than 0.15.

These dye solutions were placed in quartz cells with an optical path length of 1 mm. The temperature of the quartz

cell was maintained at 25 °C. Once the maximum absorption wavelength (λ_{max}) was determined, the Kamlet–Taft parameters (α: hydrogen-bonding acidity, β: hydrogen-bonding basicity, and π^*: dipolarity) were calculated from the following equations:

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

$$E_T(30) = 0.9986[28592/\lambda_{max}(\text{Reichardt's dye \#33})] - 8.6878 \quad (2)$$

$$\pi^* = 0.314[27.52 - \nu(N,N\text{-diethyl-4-nitroaniline})] \quad (3)$$

$$\alpha = 0.0649E_T(30) - 2.03 - 0.72\pi^* \quad (4)$$

$$\beta = [1.035\nu(N,N\text{-diethyl-4-nitroaniline}) + 2.64 - \nu(\text{4-nitroaniline})]/2.80 \quad (5)$$

2.4 Dissolution of Cellulose. Suspensions of microcrystalline cellulose (Cellulose powder C, ADVANTEC; 2.0 wt %) in dried ILs were prepared and the mixtures were stirred for 1 h at each temperature until the solution became a homogeneous clear solution by heating from 25 to 100 °C in 5 °C increments under nitrogen in a temperature controlled oil bath. The lowest temperature to give a clear solution was recorded as the dissolution temperature.

2.5 Extraction of Polysaccharides from Japanese Cedar. A powder of Japanese cedar (0.11 g, particle diameter 53–112 μm,) was added to dry ILs (2.0 g), and the resulting mixtures were stirred at 100 °C for 24 h under dry nitrogen. After allowing it to cool to rt, the insoluble part was filtered off and to the resulting filtrate (X g) was added hot ethanol to form a precipitate; the precipitate was then washed repeatedly with hot ethanol and dried under reduced pressure at 70 °C to give the polysaccharide samples (Y g). The degree of extraction was calculated from the following equation:

$$\text{Degree of extraction (\%)} = [Y/(X - Y) \times 2.0]/0.11 \times 100 \quad (6)$$

3. Results and Discussion

3.1 Effect of Cation Structures. First, we prepared six types of ethylphosphonate salts coupled with alkylimidazolium cations that have different side chains as shown in Figure 1; we then investigated the effect of the side chain on the imidazolium ring with their physicochemical properties and the dissolution property versus micro crystalline cellulose. Then we attempted to use them for the extraction of polysaccharide from Japanese cedar. Their thermal properties are summarized in Table 1. DSC analysis revealed that these ILs showed only glass-transition points. No crystallization was observed even after storing them at −20 °C for several weeks, indicating that the ILs existed in a stable super cooled state. TGA showed that these ILs were stable up to 220 °C; it was thus found that these phosphonate type ILs are more thermally stable than ILs derived from carboxylates.[20]

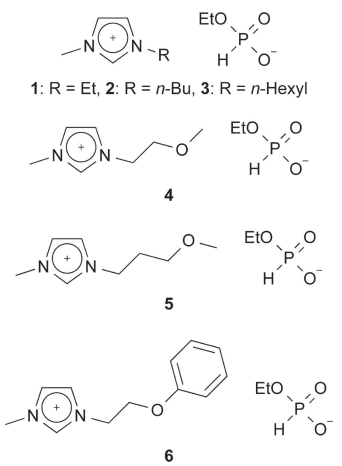


Figure 1. List of ethylphosphonate salts prepared in this study.

We next evaluated their hydrogen-bonding ability using the Kamlet–Taft parameters (α; hydrogen-bonding acidity, β; hydrogen-bonding basicity, and π^*; dipolarity) and the results are shown in Table 1.[14] These ILs showed moderate α value which was caused by the presence of an acidic hydrogen atom at the 2 position of the imidazolium ring.[21] As for β value, the series of ILs prepared here had greater hydrogen-bonding basicity than conventional ILs. The β value of ILs generally depends mainly on the species of anions, however, this value also depends on the cation structure. Among these ILs, IL **5** showed the highest β value and the lowest observed for IL **1**.

It has been reported that viscosity of ILs is one of the important factors in dissolving cellulose and other biomass, hence, we then measured that element of these ILs. Figure 2 shows the temperature dependence of their viscosity. The viscosity increased with increasing alkyl chain length and the lowest value was obtained for IL **1**. Moreover, viscosity was slightly lower for IL **4** than for IL **2**, and IL **5** also had much lower viscosity than IL **2**. This should be explicable in terms of size of the cation, van der Waals interaction, and T_g value. Among these ILs, IL **6** showed the highest viscosity among the ethylphosphonate salts studied here. This might be due to the relatively strong interaction between phenyl groups. However, viscosity of these ILs dropped with rising temperature and all showed similar values above 90 °C (Figure 2).

We then evaluated the solubility of these ILs versus micro crystalline cellulose; Table 2 shows dissolution temperature of the cellulose in them. We mixed cellulose powder with each IL at concentrations of 2.0 wt %, and the resulting mixtures were stirred at 25 °C. ILs **1**, **2**, **4**, and **5** successfully dissolved cellulose at 25 °C. On the other hand, complete dissolution of cellulose in IL **3** and IL **6** required heating at 50 and 60 °C, respectively. The solubility of polysaccharides generally depends on the β value of the ILs. However, the dissolution

Table 1. Physicochemical properties of ethylphosphonate salts

ILs	T_g/°C[a)]	T_{dec}/°C[b)]	Kamlet–Taft parameters at 25 °C		
			α	β	π^*
1	−74	266	0.55	1.02	1.02
2	−68	239	0.52	1.05	1.04
3	−66	221	0.54	1.07	0.95
4	−63	234	0.52	1.05	1.04
5	−70	250	0.46	1.12	1.02
6	−31	228	0.43	1.03	1.06

a) Temperature at signal peak. b) Temperature for 10% weight loss.

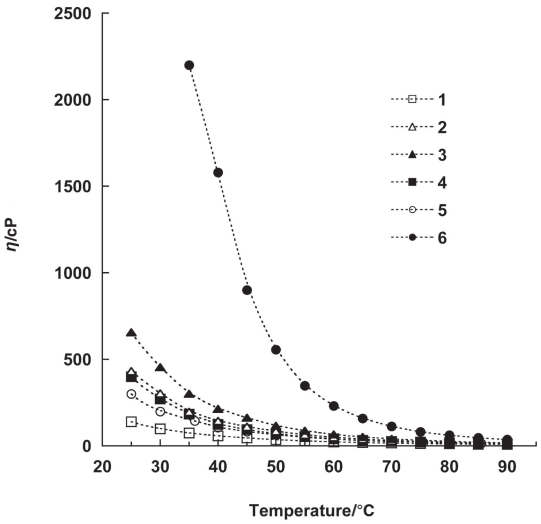


Figure 2. Temperature dependence of viscosity.

Table 2. Solubility of the model cellulose and the degree of extraction of polysaccharides from Japanese cedar

ILs	Dissolution temp. /°C	Degree of extraction /%
1	25	5.4
2	25	7.3
3	50	7.1
4	25	8.8
5	25	13.3
6	60	6.2

temperature of cellulose in the ILs evaluated here did not directly depend on the β value. Previous studies have revealed that ILs with sufficient β value to dissolve cellulose, the dissolution temperature over limited time depends on their viscosity.[11] IL **3** and IL **6** had higher viscosity than others evaluated here; cellulose powder dispersed more easily in lower viscosity ILs, so that higher dissolution temperature might be observed in IL **3** and IL **6** over short mixing time.

From these results, it was anticipated that these ILs might allow extraction of polysaccharides from Japanese cedar. Hence, we next evaluated them as solvents for such extraction by mixing the cedar powder with the ILs at concentrations of 5 wt % at 100 °C for 24 h with stirring. After being allowed to cool to rt, the remaining insoluble portion was removed by filtration, and excess ethanol was added to the filtrate with continuous stirring. The resulting precipitate was collected by a second filtration and washed repeatedly with hot ethanol to remove residual ILs. The extracted materials were analysed using FT-IR and NMR, and the results indicated that the extracted materials were a mixture of cellulose, hemicellulose, and a slight amount of lignin (Figures S1 and S2 in ESI), though it was not possible to determine the ratio of each contents.

The extraction degree of polysaccharides from cedar depends on the cation structure. For instance, this degree was influenced by the cation structure of the ILs in the following value order: IL **1** (5.4%) < IL **6** (6.2%) < IL **3** (7.1%) < IL **2** (7.3%) < IL **4** (8.8%) < IL **5** (13.3%). As mentioned, it is

7: R = NH_2, **8**: R = Et, **9**: R = CH_2OCH_3, **10**: R = CH_2Ph

Figure 3. List of phosphonate salts prepared in this study.

well known that ILs with lower viscosity allow good polysaccharide extraction because of better dispersion in ILs. Since IL **1** had the lowest viscosity, we anticipated that this IL might show better extraction. However, the degree of extraction of polysaccharides from Japanese cedar powder was independent of their viscosity. No relationship was observed between the IL viscosity and the degree of extraction because we examined the extraction experiment from Japanese cedar conducted at 100 °C with stirring for 24 h: their viscosity thus might not influence the extraction under these conditions. On the other hand, the degree of extraction of polysaccharides from Japanese cedar strongly depended on the β value of their ILs. IL **5** which has the highest hydrogen-bonding activity (β value = 1.12) showed the best extraction of polysaccharides from Japanese cedar.

3.2 Effect of Anion Structure. The cation structure of ILs has now been revealed to affect their physicochemical properties and the dissolution ability of polysaccharides and ILs with greater hydrogen-bonding basicity (β value) successfully extracted polysaccharides from Japanese cedar powder, though this value strongly depends on the anion structure. In fact, we found that the cation structure significantly affected the cellulose dissolution property for amino acid ILs.[13] Hence, we next investigated the cellulose dissolution ability of four 1-ethyl-3-methylimidazolium salts (**7**–**10**) coupled with the phosphonates shown in Figure 3.

Among the series of 1-ethyl-3-methylimidazolium salts, only IL **7** was obtained as a solid at room temperature and showed a melting point at 85 °C. This high melting temperature might be due to the strong interaction between phosphoamide groups. Since IL **7** had a high melting point, further investigation on it was cancelled. On the other hand, ILs **8**–**10** are liquids at room temperature and show only a glass-transition temperature. They remained liquids even after being kept at −5 °C for several weeks, indicating they are in a super cooled state at room temperature. Their TGA analysis showed that they are stable up to 250 °C.

The polarity of the ILs prepared here was estimated via the Kamlet–Taft parameters. Table 3 also lists the Kamlet–Taft parameters of the series of ILs. All the ILs **8**–**10** studied herein showed strong hydrogen-bonding characteristics. The β value of newly developed 1-ethyl-3-methylimidazolium salts was over 1.12, greater than those of 1-ethyl-3-methylimidazolium ethylphosphonate (**1**).[11a] As described above, ethylphosphonate anion has greater hydrogen-bonding basicity. Because the series of anions studied here have the same basic unit structure ([(EtO)(R)PO_2]), the disparity among β values of these ILs can be explained by the difference in the electron-releasing capability of their side chains.

As seen in Figure 4, substitution of the ether group and alkyl group on anionic parts resulted in the increase of their viscosity. The highest viscosity was recorded for IL **10**. These results might be attributable to the increased interaction of polar groups and the size of ions.

Table 3. Physicochemical properties of ethylphosphonate salts

ILs	T_g /°C[a)]	T_m /°C[a)]	T_{dec} /°C[b)]	Kamlet–Taft parameters at 25 °C		
				α	β	π^*
7	—[c)]	85	250	Not measured		
8	−60	—[c)]	272	0.52	1.16	1.02
9	−62	—[c)]	267	0.46	1.14	1.02
10	−33	—[c)]	258	0.42	1.12	1.02

a) Temperature at signal peak. b) Temperature for 10% weight loss. c) Not detected.

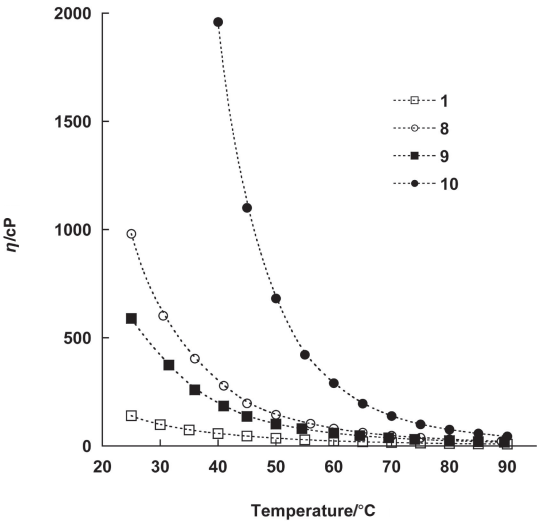


Figure 4. Temperature dependence of viscosity.

Table 4. Solubility of the model cellulose and the degree of extraction of polysaccharides from Japanese cedar

ILs	Dissolution temp /°C	Degree of extraction /%
8	25	7.7
9	25	7.0
10	50	6.5

All these new ILs **8**–**10** dissolved cellulose well under mild conditions and ILs **8** and **9** dissolved it even at room temperature (Table 4). However, IL **10** required heating at 50 °C to obtain a homogeneous solution of cellulose. This might be due to the higher viscosity of IL **10** than that of other ILs evaluated herein. In regard to the degree of extraction of polysaccharides from Japanese cedar, there are slight differences according to the anion structure: the degree of extraction is highest for IL **8** and lowest for IL **10**. With increasing β value, the degree of extraction gradually increased from 5.3 to 7.7%.

As mentioned, the degree of extraction of polysaccharides from Japanese cedar is related to the Kamlet–Taft β value. Figure 5 shows the relation between the degree of extraction from Japanese cedar and the Kamlet–Taft β value; ILs with high β value had good capacity to extract polysaccharides from Japanese cedar. However, it should be noted that the Kamlet–Taft β value is not the only determinant of the degree of extraction. As seen in this Figure, compared to the influence

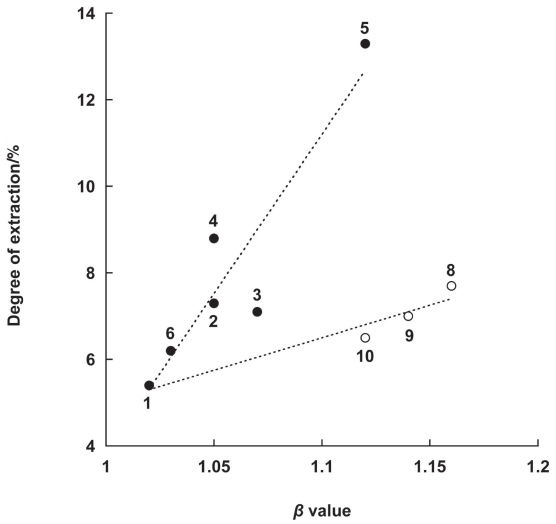
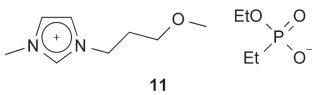


Figure 5. Relationship of β value between the degree of extraction of the ILs.



11

Figure 6. Chemical structure of IL **11**.

Table 5. Physicochemical properties of 1-(3-methoxypropyl)-3-methylimidazolium ethyl ethylphosphonate (**11**)

IL	T_g/°C[a)]	T_{dec}/°C[b)]	Kamlet–Taft parameters at 25 °C		
			α	β	π^*
11	−63	2.39	0.49	1.21	0.95

a) Temperature at signal peak. b) Temperature for 10% weight loss.

of anion structures, the degree of extraction is influenced more by the cation structure. This difference might be explained by compatibility and the affinity of side chain of imidazolium cation to the polysaccharide–lignin supramolecular complex in Japanese cedar powder.

Considering the above mentioned tendency, we prepared 1-(3-methoxypropyl)-3-methylimidazolium ethyl ethylphosphonate (**11**) shown in Figure 6. It was obtained as a liquid at room temperature. From the results of DSC analysis, IL **11** was revealed to show only a glass transition at −63 °C, indicating a stable super cooling state. TGA analysis revealed that IL **11** is thermally stable up to 239 °C. It exhibits strong hydrogen-bonding characteristics, displaying the highest β value of 1.21 among ILs evaluated in this study (Table 5).

As expected, we succeeded in extracting polysaccharides from Japanese cedar using IL **11** (Figure 7). The degree of extraction of IL **11** reached ca. 15% at 100 °C, this is three times higher than that of IL **1**. NMR spectra of this after extraction experiments were examined to confirm the stability of the newly designed IL **11**, and the results confirm that there was no structural change in it during the polysaccharide extraction process (see ESI). This observation strongly indicates that IL **11** can be recycled and reused efficiently in biomass processing.

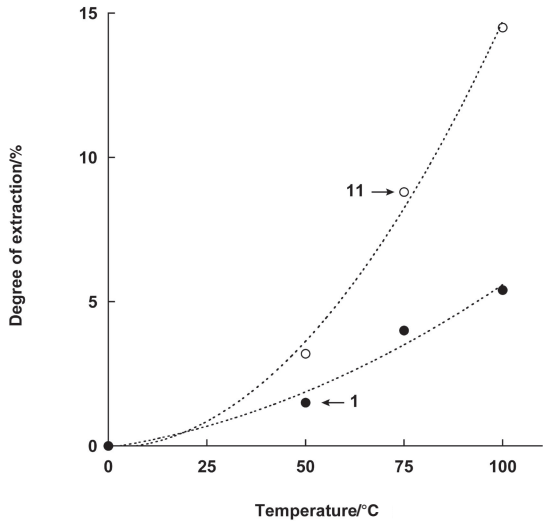


Figure 7. Temperature dependence of the degree of extraction.

4. Conclusion

In this study we prepared a series of novel highly polar phosphonate ILs and investigated their dissolution properties of cellulosic biomass. We have established that 1-(3-methoxypropyl)-3-methylimidazolium diethylphosphonate (**11**) displayed higher hydrogen-bonding basicity (β value 1.21) and most effectively extracted polysaccharides from Japanese cedar (15 wt %). Since IL **11** is easily prepared using conventional reagents and might be applicable to large-scale reactions, it is expected that practical polysaccharide extraction using this IL might be possible from a wide variety of biomass resources.

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Supporting Information

^{13}C NMR and IR spectra of extracts and microcrystalline cellulose. ^{1}H NMR spectra of IL **11** (recycled and the fresh one). ^{1}H and ^{13}C NMR spectra of IL **1**–IL **11**, and ESI-MS spectra of IL **8**–IL **11**. This material is available on http://dx.doi.org/10.1246/bcsj.20160073.

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