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Direct Extraction of Polysaccharides from Moso Bamboo (*Phyllostachys heterocycla*) Chips Using a Mixed Solvent System of an Amino Acid Ionic Liquid with Polar Aprotic Solvent

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Abstract

The cellulose-dissolving ability and some physical properties of mixed solvents of an amino acid IL, *N*-methyl-*N*-(2-methoxyethyl)pyrrolidin-1-ium 2,6-diaminohexanoate ([P_{1ME}][Lys]), with polar aprotic solvents, such as 1,3-dimethylimidazolidinone (DMI), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and acetonitrile (CH₃CN), have been investigated. The viscosity was significantly reduced by the increasing content of polar aprotic solvents, and a 1:1 mixture (molar ratio) of [P_{1ME}][Lys] with DMF showed 91.5 cP which corresponded to less than 1/10 compared to that of the pure IL at 25 °C (1058 cP). The β values of the mixed solvents, which have the IL contents over 0.1, exhibited β-values similar to that of the pure IL. On the other hand, the π-value was dependent on the ratio of the IL content, and the pure IL had the highest π-value.

We found that the mixed solvent of [P_{1ME}][Lys] with DMF (1:1) easily dissolved the cellulose and the mixed solvent could be used to extract cellulose from moso bamboo (*Phyllostachys heterocycla*) powder. The efficiency of the extraction of cellulose from the bamboo powder was significantly increased when a 1:1 mixture of the IL with a polar aprotic solvent was used as the extracting solvent at 60 °C; the extraction ratio of the 1:1 mixture (IL: DMF) reached twice that of the pure IL. We thus obtained cellulose in 18% (w/w) yield from the bamboo powder.

1. Introduction

Cellulose is the most abundant renewable resource on this planet.¹ However, its isolation from biomass generally requires

hazardous chemical reagents under harsh conditions.^{1–5} Therefore, development of an environmentally benign method to extract cellulose from various types of biomass waste is strongly needed. We focused on bamboo (*Phyllostachys heterocycla*) as a source of cellulose.^{6,7} Although bamboo is a very common plant in Asian countries and it causes serious damage to rural natural areas due to its rapid growth with low nutrients, it has been mostly used as construction material, for handicrafts products, or as food (bamboo shoots) and not been employed as a source of cellulose.

There has been a great deal of interest in ionic liquids (ILs).^{8–11} After the report of the dissolution of cellulose using an IL by Swatoski et al. in 2002,¹² extensive studies regarding the extraction of polysaccharides using various types of ILs from biomass have been reported.^{13–49} Although the perfect selective extraction of cellulose from bioresources has not yet been accomplished to date, IL is expected to be the only tool to realize this objective without scarifying lignin or hemicellulose.⁴⁷

Ohno et al. reported the synthesis of amino acid ILs.^{50,51} We reported that amino acid salt ILs could easily dissolve cellulose.^{52–54} Therefore, we attempted to extract cellulose using our amino acid ILs from moso bamboo powder. However, we found a serious difficulty in that the resulting IL solution formed a jelly-like gel that made it difficult to apply our ILs on a large-scale. Rinaldi reported that the addition of imidazolium ILs, 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) or 1-butyl-3-methylimidazolium acetate ([C₄mim][OAc]), to polar aprotic solvents caused the effective dissolution of cellulose.⁵⁵ We also found that a 1:1 (molar ratio) mixture of dimethylsulfoxide (DMSO) and *N,N*-diethyl-*N*-methyl-*N*-(2-methoxy)ethylammonium alanate ([N_{221ME}][Ala])⁵² easily dissolved the cellulose even at ambient temperature.⁵³ During a further study, we found that a mixed solvent of *N*-methyl-*N*-(2-methoxyethyl)pyrrolidin-1-ium alanate ([P_{1ME}][Ala]) and DMSO (1:1) more easily dissolved the cellulose compared to that of [N_{221ME}][Ala] and DMSO, although [N_{221ME}][Ala] exhibited a slightly better solubility than [P_{1ME}][Ala] when the pure ILs were used for the cellulose dissolution.⁵² Inspired by these results, we investigated the cellulose solubility for three types of [P_{1ME}] salts, i.e., [P_{1ME}][Ala], [P_{1ME}][Lys], and [P_{1ME}][OAc], because the [N_{221ME}] salts with these anions exhibited a good cellulose dissolution.⁵² We thus revealed that [P_{1ME}][Lys] displayed the best cellulose solubility among them (see, Table S1 in the supplementary information). Therefore, we decided to investigate the possibility of a mixed solvent of our amino acid IL, in particular, [P_{1ME}][Lys] with a polar aprotic solvent as the extracting agent of cellulose from the bamboo biomass. We now report the results of the successful selective extraction of cellulose from bamboo powder using a mixed solvent system of [P_{1ME}][Lys] with a polar aprotic solvent.

2. Experimental Section

2.1 Materials and Instruments. 1,3-Dimethylimidazolidinone (DMI), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and acetonitrile (CH₃CN) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Amberlite® IRN-78 was purchased from SUPELCO. Neutral activated alumina was purchased from Aldrich. The bamboo (*Phyllostachys heterocycla*) powder was prepared using bamboo chips produced in

the Mochigase area of Tottori city and dried at 100 °C for 12 h under reduced pressure at 1.0 torr. The electro-spray ionization mass spectra (ESI-MS) were recorded with a Thermo Scientific Exactive spectrometer. The amount of water was confirmed by a Karl Fischer coulometric titration using a Kyoto Electronics MLC-610 DT. Differential scanning calorimetry (DSC) measurements were conducted at a scanning rate for both the heating and cooling of 5 °C min⁻¹ in the temperature range of -120 °C to 100 °C. The thermogravimetric analyses (TGA) were carried out using a RIGAKU Thermo Plus EVO II at the heating rate of 10 °C min⁻¹ from 25 °C to 500 °C under dry argon gas. The ¹H NMR and ¹³C NMR spectra were obtained using a JEOL JNM-500. Chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS) in CDCl₃ as the internal reference. The solid ¹³C NMR spectra were recorded with a Varian 400 MHz Solid NMR using glycine as the reference compound. The visible spectrum was measured using a JASCO UV 550. The viscosity of the ILs was measured using a Brookfield DV2-T viscometer.

2.2 Preparation of [P_{1ME}][Lys].⁵² An aqueous solution of *N*-methyl-*N*-(2-methoxyethyl)pyrrolidin-1-ium bromide ([P_{1ME}][Br]) (10.0 g, 44.6 mmol) in 290 ml of de-ionized water was passed through the column packed with 94 ml of activated Amberlite® IRN-78 slowly with the rate of 180 ml/day to afford the [P_{1ME}][OH] aqueous solution. Then deionized water was passed to the column until the eluent became neutral. The resulting aqueous solution (ca. 500 ml) was condensed to ca. 200 ml by evaporation. The aqueous solution of [P_{1ME}][OH] (0.22 M, 202 ml) was mixed with an aqueous solution of L-lysine (7.81 g, 53.5 mmol) in de-ionized water (50 ml) at 0 °C. The mixture was then stirred at 0 °C for 12 h, and the solvent was removed by evaporation to give [P_{1ME}][Lys] as a viscous oil. This was immediately diluted using a mixed solvent of acetonitrile and ethanol (9:1) (100 ml) and passed through a celite filter to remove the unreacted lysine precipitate. The filtrate was dried under reduced pressure at rt for 5 hr at 1.0 torr, then further dried by lyophilization to give [P_{1ME}][Lys] (8.93 g, 30.2 mmol) in 69% yield. The amount of water in the IL was confirmed as 399.6 ppm by a Karl Fischer coulometric titration. ¹H NMR (600 MHz, ppm, CD₃OD) 1.35–1.45 (6H, m), 2.17 (4H, s), 2.58 (2H, t, J = 6.9 Hz), 3.25 (1H, t, J = 1.8 Hz), 3.30 (2H, brs), 3.35 (2H, brs), 3.38 (3H, s), 3.53–3.56 (8H, m), 3.77 (2H, s); ¹³C NMR (150 MHz, ppm, CD₃OD, J = Hz) 182.49, 67.63, 66.31, 64.40, 59.21, 57.61, 49.34, 42.46, 36.62, 33.94, 24.31, 22.43; IR (neat, cm⁻¹) 3347, 3279, 2930, 2856, 2815, 2063, 1582, 1462, 1396, 1123, 1038; HRMS (ESI-TOF) *m/z* [M⁺] calcd for C₈H₁₈NO⁺ 144.1389, found 144.1380, *m/z* [X⁻] calcd for C₆H₁₃N₂O₂⁻ 145.0978, found 145.0971.

2.3 Measurements of the Kamlet-Taft Parameters.^{56–59} 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 using the following equations:

$$\begin{aligned} \nu(\text{dye}) &= 1/(\lambda_{\max}(\text{dye}) \times 10^{-4}) \\ E_T(30) &= 0.9986(28592/\lambda_{\max}(\text{Reichardt's dye \#33})) \\ &\quad - 8.6878 \\ \pi^* &= 0.314(27.52 - \nu(N,N\text{-diethyl-4-nitroaniline})) \\ \alpha &= 0.0649E_T(30) - 2.03 - 0.72\pi^* \\ \beta &= (1.035\nu(N,N\text{-diethyl-4-nitroaniline}) + 2.64 \\ &\quad - \nu(4\text{-nitroaniline}))/2.80 \end{aligned}$$

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 60 °C in 5 °C increments under nitrogen in a temperature-controlled oil bath.

2.5 Extraction of Polysaccharides from Bamboo Powder. Bamboo powder (a g, particle diameter 53–112 μm ,) was added to a mixed solvent of $[\text{P}_{1\text{ME}}][\text{Lys}]\text{-DMF}$ (1:1, molar ratio) (b g), and the resulting mixtures were stirred at 60 °C for 24 h under dry nitrogen. After allowing it to cool to rt, the mixture was centrifuged at 10,000 rpm for 30 min., and the supernatant IL layer was collected (X g). The IL layer was diluted with water to form a precipitate. The precipitate was then repeatedly washed with water and dried by lyophilization to give the polysaccharide samples A (Y g). The degree of extraction was calculated by the following equation:²⁷ degree of extraction (%) = $[Y/(X + Y) \times b]/a \times 100$.

2.6 Extraction of Cellulose from the Bamboo Powder by the Mixed Solvent of $[\text{P}_{1\text{ME}}][\text{Lys}]$ and DMF (1:1). The bamboo (*Phyllostachys heterocycla*) powder was prepared using bamboo chips produced in the Mochigase area of Tottori city and dried at 100 °C for 12 h under reduced pressure at 1.0 torr before use. The sample (0.500 g) was dispersed into a mixed solvent (5.0 g of a mixed solvent of $[\text{P}_{1\text{ME}}][\text{Lys}]$ and DMF ($X_{\text{IL}} = 0.5$) in a 25 ml vial tube, then the mixture was stirred at 60 °C for 24 h. After being allowed to cool to rt, the mixture was centrifuged at 10,000 rpm for 10 min. The separated IL layer was placed in a vial tube and diluted with deionized water that caused precipitation of the cellulose which was collected and rinsed 10 times with water, then dried under reduced pressure and lyophilization to afford the pure cellulose (0.046 g). The remaining residue was rinsed 10 times with water, then dried under vacuum and was subjected to the 2nd extraction process. A 0.042 g cellulose sample was obtained by the second process from the residue. We finally obtained a total of 0.088 g (18 wt% (w/w)) of the extract (cellulose) and 0.364 g (72 wt% (w/w)) of residue (lignin-rich polysaccharide). $[\text{P}_{1\text{ME}}][\text{Lys}]$ was recovered in almost quantitative yield from the water layer and reused after drying by lyophilization and mixed with fresh DMF.

3. Results and Discussion

3.1 Extraction of Cellulose from the Bamboo Powder by $[\text{P}_{1\text{ME}}][\text{Lys}]$. With the aim of realizing the extraction of

polysaccharides from the bamboo powder, we initiated an extraction experiment using pure $[\text{P}_{1\text{ME}}][\text{Lys}]$ as illustrated in Figure 1, because this IL best dissolved the cellulose from among our prepared amino acid ILs. To 1.0 g of $[\text{P}_{1\text{ME}}][\text{Lys}]$ was added the bamboo powder (100 mg) and the resulting mixture was stirred at 60 °C for 24 h to form a viscous solution (I) in Figure 1). This was immediately centrifuged at 10,000 rpm for 30 min., and the supernatant (a in Figure 1) was separated. This IL layer (a) was diluted with water which caused formation of a precipitate that was collected and washed six times with water, then dried by lyophilization to afford a white powder (A: 5.3 mg, 5.3 wt % vs. bamboo powder). A jelly-like residue b remaining in the test tube was washed ten times with water, then the IL was recovered from the water layer. The residue was dried under reduced pressure at 70 °C at 1.0 torr for 6 h to afford lignin-rich polysaccharides B (92 mg, 92 wt % vs. bamboo powder).

The solid ^{13}C NMR study of extract A revealed that it consisted of cellulose with a very high purity (see, Figure S1). It was thus found that very pure cellulose was extracted by the $[\text{P}_{1\text{ME}}][\text{Lys}]$ from the bamboo powder, though the chemical yield was insufficient. It was also confirmed that the lignin was in fact included in residue B by ^{13}C NMR (see, Figure S1), because the signals due to the aromatic carbons indeed appeared. The results clearly indicated that separation of the cellulose and lignin might be possible using this protocol. However, a serious difficulty was found when we tried to increase the experimental scale; the resulting IL solution formed a jelly-like gel from which it was difficult to separate the IL layer from the gel. It has been reported that reducing the viscosity of the ILs is one of the important factors in increasing the solubility of biomass.^{60–62} Therefore, we next attempted to solve this problem by mixing the appropriate aprotic polar solvents.

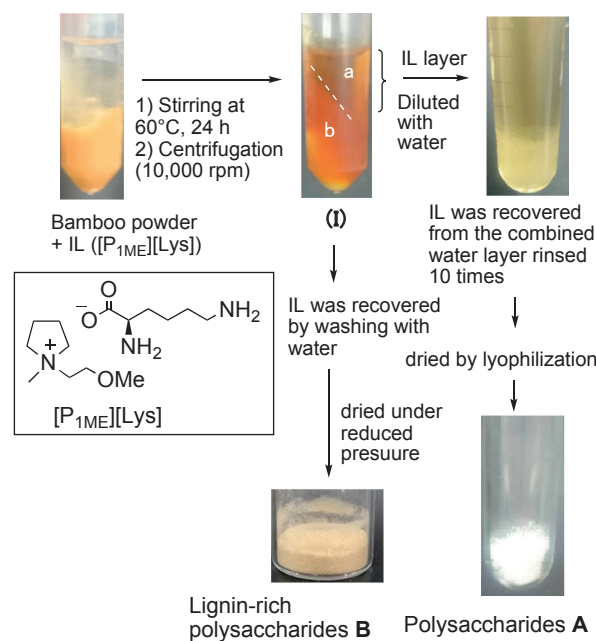


Figure 1. Extraction protocol of polysaccharides from bamboo powder using an IL.

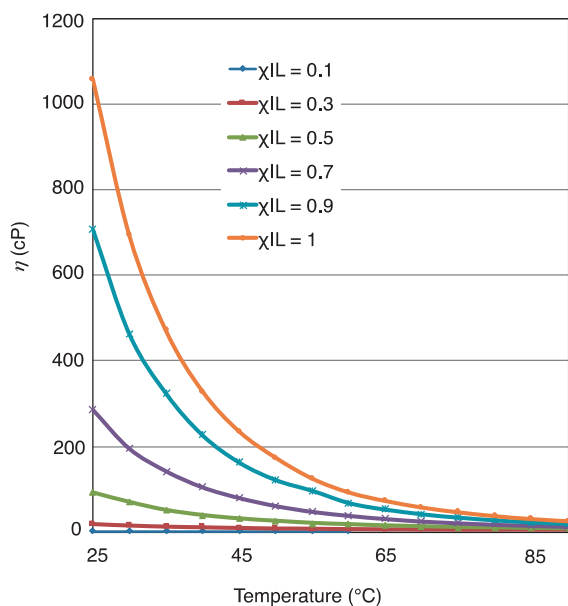


Figure 2. Temperature dependence of viscosity vs. content ratio of DMF in $[P_{1ME}][Lys]$. The water contents of the mixed solvents are as follows: $X_{IL} = 0.1$ (400 ppm); $X_{IL} = 0.3$ (474 ppm); $X_{IL} = 0.5$ (1026 ppm); $X_{IL} = 0.7$ (980 ppm); $X_{IL} = 0.9$ (774 ppm); $X_{IL} = 1.0$ (400 ppm). X_{IL} is the molar fraction of IL in the DMF solution proposed by Rinaldi.⁵⁵

3.2 Properties of Mixed Solvents of $[P_{1ME}][Lys]$ with Aprotic Polar Solvents. We prepared the mixed liquids of $[P_{1ME}][Lys]$ with *N,N*-dimethylformamide (DMF) as a model aprotic polar solvent and measured the temperature dependence of the viscosity of the mixtures (Figure 2). Although the viscosity of pure $[P_{1ME}][Lys]$ is very high (1,058 cP at 25 °C), this was drastically reduced by increasing the DMF contents, and a 1:1 mixture (molar ratio) showed only 91.5 cP at the same temperature.

The solvent polarity is well known as an important factor to determine the solubility of biopolymers in the solvents.^{63,64} Ohno and co-workers reported that cellulose could be dissolved in ionic liquids which have high hydrogen bond basicity β -values (>0.8) for the Kamlet-Taft parameter.⁶⁵ Therefore, we next investigated the β -values and π -values using different DMF contents of the mixed liquid of $[P_{1ME}][Lys]$ (Table 1). Rinaldi reported that for the mixed solvent of 1,3-dimethyl-2-imidazolidinone (DMI) with 1-ethyl-3-methylimidazolium acetate ($[C_2mim][OAc]$), the β -values are identical to those of the neat IL when the ratio of the IL was increased from around $X_{IL} = 0.1$,⁵⁵ where X_{IL} denotes the molar ratio of the IL in the solvent system. As shown in Table 1, the mixed solvent, which has an X_{IL} over 0.1, exhibited β -values similar to that of the pure IL. On the other hand, the π -value was dependent on the ratio of the IL content and the pure IL reached the highest π -value.

3.3 Extraction of Cellulose from the Bamboo Powder by a Mixed Solvent of $[P_{1ME}][Lys]$ with Polar Aprotic Solvents. Based on the results, we tested the extraction of cellulose from the bamboo powder using various mixed solvents of $[P_{1ME}][Lys]$ and DMF at different mixture ratios (Table 2).

Table 1. β -Value and π -value change versus different ratios of $[P_{1ME}][Lys]$ with DMF. Here, X_{IL} is the molar fraction of IL in the DMF solution. $X_{IL} = 0$ denotes the pure DMF and $X_{IL} = 1.0$ indicates the pure $[P_{1ME}][Lys]$.

X_{IL} (IL: DMF)	Kamlet-Taft parameters at 25 °C	
	π^* -value	β -value
0	0.88	0.69
0.1	0.96	1.21
0.3	1.01	1.21
0.5	1.07	1.19
0.7	1.06	1.20
0.9	1.07	1.19
1.0	1.11	1.18

Here, $X_{IL} = 0$ denotes pure DMF and $X_{IL} = 1.0$ indicates the pure $[P_{1ME}][Lys]$.

Table 2. Solubility of AvicelTM and the amounts of polysaccharide extracted from the bamboo powder using $[P_{1ME}][Lys]$ including DMF at different content ratios.

X_{IL} (IL: DMF) ^{a)}	β -value (Kamlet-Taft parameter at 25 °C)	Solubility of cellulose (Avicel)	The degree of extraction (%) ^{b)}
0	0.69	0	0
0.1	1.21	2.7	0
0.3	1.20	26	6.0
0.5	1.21	28	9.2
0.7	1.19	24	7.8
0.9	1.20	23	7.2
1.0	1.18	21	5.2

^{a)} $X_{IL} = 0$ denotes pure DMF and $X_{IL} = 1.0$ indicates pure $[P_{1ME}][Lys]$. ^{b)}The reaction was conducted at 60 °C. The degree of extraction was calculated following the method of Abe.²⁷ We conducted dissolution experiments using the IL solvent which included less than 800 ppm water.

We also investigated the solubility of the model cellulose (AvicelTM) in the same solvents (Table 2). As shown in the table, no extract was obtained when a mixed solvent of $X_{IL} = 0.1$ was used, although this liquid possesses a high β -value (1.2) almost equal to that of the pure IL. Interestingly, a solvent of $X_{IL} = 0.1$ dissolved 2.7% (w/w) cellulose. Since the viscosity decreased, as expected, the degree of extraction was indeed increased for the mixed liquid ($X_{IL} = 0.3$) to 6.0%, and reached a maximum rate (9.2%) which was 1.8-fold higher than that of the pure IL when a mixed liquid of $X_{IL} = 0.5$ was employed as the extracting solvent as shown in the Table 2. On the other hand, the cellulose solubility reached 28% when a mixed solvent of $[P_{1ME}][Lys]$ with DMF = 1:1 ($X_{IL} = 0.5$) was used as the solvent (Table 2).

We next investigated the viscosity of four types of mixed solvents of $[P_{1ME}][Lys]$ with DMI, DMF, DMSO, and CH_3CN all of which have $X_{IL} = 0.5$ at 60 °C, and the results of the extractions are shown in Table 3. Among the tested solvents, the lowest viscosity was obtained for the mixture with DMF (Entry 3), though the differences between the others were not significant. Table 3 also shows the β -values of $[P_{1ME}][Lys]$, four aprotic solvents, and the mixed solvents. As shown, all

Table 3. Relationship of degree of extraction of polysaccharides from the bamboo powder between the viscosity and β -value

Entry	Mixed solvent (XIL = 0.5) ^{a)}	Viscosity (η (cP))	β -value (Kamlet-Taft parameter at 25 °C)	The degree of extraction (%) ^{b)}
1	IL: [P _{1ME}][Lys]	84.65	1.18	5.2 ± 0.80
2	IL-DMI	17.56	1.20	7.6 ± 0.77
3	IL-DMF	15.72	1.19	9.2 ± 0.28
4	IL-DMSO	22.87	1.15	8.5 ± 0.44
5	IL-CH ₃ CN	18.22	1.19	7.8 ± 0.20

^{a)}XIL = 0.5. Viscosity was determined at 60 °C. Extraction test was conducted by stirring for 24 h at 60 °C. ^{b)}Average value of three experiments.

the mixed solvents and the IL displayed similar high β -values (ca. 1.2) and no significant difference was observed among these four mixed solvents.

We tested the extraction of polysaccharides using these mixed solvents from the bamboo powder (Table 3). The best result was obtained when the mixture of IL-DMF, XIL = 0.5, was used as the extracting solvent, and a 9.2 ± 0.28 degree of extraction (average of three experiments) was obtained (Entry 3), which was 1.8-fold higher than that of the pure IL (Entry 1). The next result was recorded for the mixture of IL with DMSO, and all the mixed solvents extracted the polysaccharides more efficiently than the pure IL. The results indicated that the extraction efficiency depends on the viscosity of the solvent, though the difference is not significant because all of these four solvents have very high β -values.

Base on the results, we attempted to extract of the cellulose and obtain lignin-rich bamboo powder by repeating the extraction process using the mixed solvent of [P_{1ME}][Lys]-DMF (XIL = 0.5), since this solvent showed the lowest viscosity. As expected, no formation of the jelly-like gel was obtained and separation of the IL layer was easily accomplished by centrifugation for just 5 min at 10,000 rpm, while it took 30 min for the pure IL. As illustrated in Figure 3, we obtained cellulose in an 18% (w/w) total yield. Since the estimated cellulose content of the biomass is generally ca. 50–60% (w/w),⁶⁶ this indicates that nearly 30–36% of the cellulose could be extracted by this process.

The intensity of the aromatic region in the ¹³C NMR spectra of the residue **B2** (below of Figure 4) was, in fact, increased compared to that of **B1** (for the spectra, see upper portion of Figure 4). It has thus been confirmed that the lignin contents could be increased by this process. Although we attempted to investigate the structure of **B2** by MALDI-TOF MS, it was unsuccessful to obtain the signal. Since the amount of the residue (72%(w/w)) was still higher than that of the amount of lignin estimated by the experiment using the Klarson method (31 wt%),⁶⁷ we further tried to extract cellulose from the residue **B2**, but unfortunately, this was unsuccessful due to formation of a viscous jelly-like gel when the process was carried out at 60 °C. Although it was successful to suppress the formation of the viscous jelly-like gel when the extraction process was conducted at rt, the extraction efficiency was very poor and

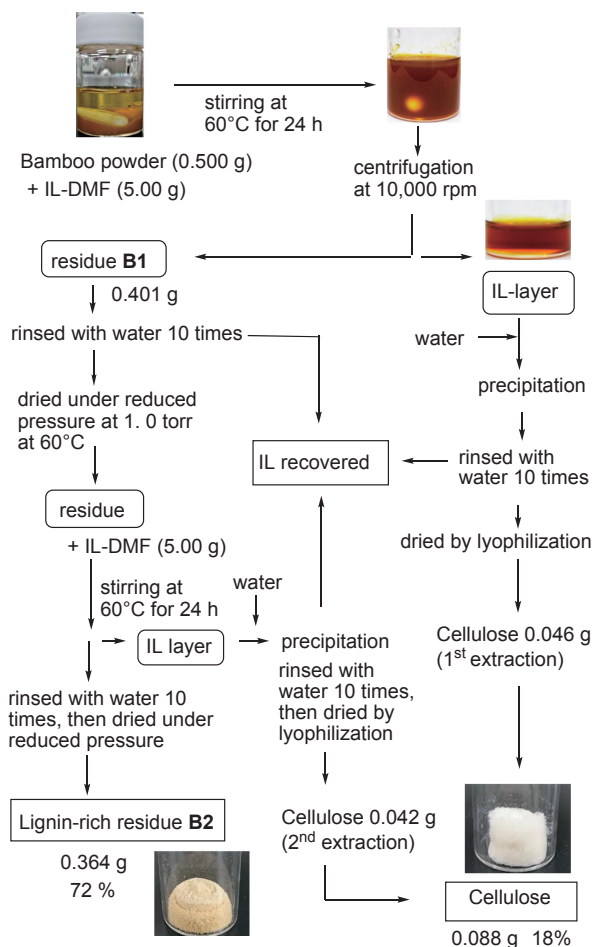


Figure 3. Extraction protocol of lignin-rich polysaccharides **B2** using the mixed solvent of [P_{1ME}][Lys]-DMF (XIL = 0.5).

only a trace amount of cellulose was obtained from **B2**. We tested different mixed solvents for the extraction of cellulose from **B2**, but it was also unsuccessful to suppress formation of the viscous jelly-like gel. We also demonstrated the extraction of cellulose using larger scale experiment conditions; 0.847 g of cellulose was extracted by the duplicated process in a similar yield (17 wt%(w/w)) as shown in Figure 3 when 5.0 g of the dry bamboo powder was treated with a 50 g of the 1:1 mixture of [P_{1ME}][Ly] and DMF.

4. Conclusion

In this study we investigated the properties of mixed solvents of an amino acid IL, [P_{1ME}][Lys], with four types of aprotic solvents, DMI, DMF, DMSO, and CH₃CN. The viscosities of all the mixed solvents were much lower than the pure [P_{1ME}][Lys], while having a high hydrogen bonding basicity (β value 1.2). Among these mixed solvents, the viscosity of [P_{1ME}][Lys]-DMF (XIL = 0.5) was the lowest at 8.8% compared to the pure IL. We have thus succeeded in obtaining a highly-pure cellulose from the bamboo powder by duplicating the extraction process. Since the lignin contents in the residue were increased by repeating the extraction process, the possibility of separating the lignocellulosic biomass was revealed. The amino acid IL, [P_{1ME}][Lys], is easily prepared using

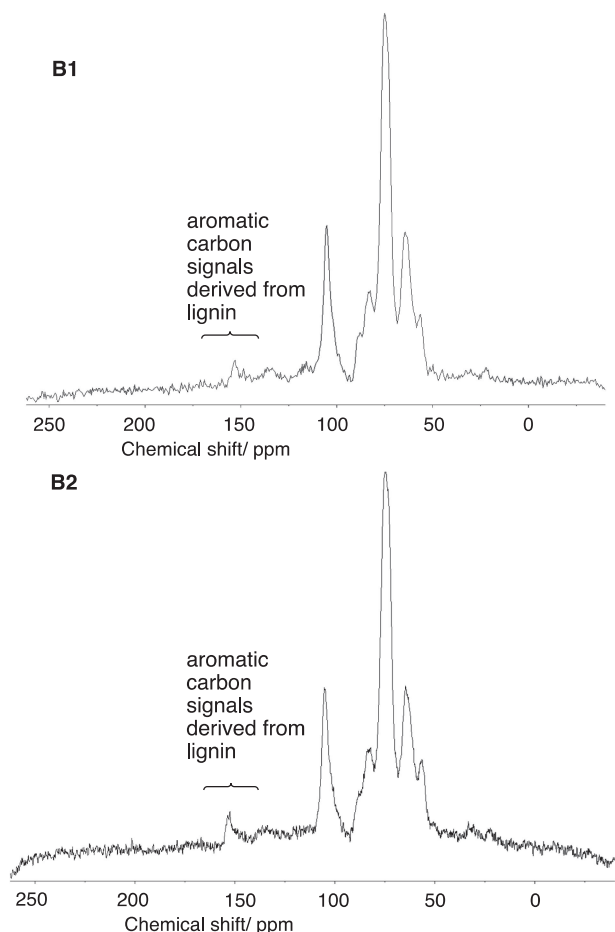


Figure 4. ^{13}C NMR spectra of the residues **B1** and **B2** from extraction of bamboo powder using the $[\text{P}_{\text{IME}}][\text{Lys}]$ -DMF solution. The intensity ratio of the aromatic region of **B1** increased at least ca. 55% compared to **B1** for the same amount.

conventional reagents and a very safe liquid; polysaccharide extraction using the mixed solvent of IL-DMF from a wide variety of biomass resources might be expected. Recently, the production of cellulose nanocrystals using IL was reported.⁶⁸ Further investigation of an optimizing combination of the IL with an aprotic polar solvent will make it even more beneficial in separating the desired resources from a biomass.

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Supporting Information

Results of cellulose dissolution test using three types of $[\text{P}_{\text{IME}}]$ salts (Table S1). Details of the extraction process and IR spectra, ^{13}C NMR, and SEM image of the extracted cellulose. This material is available on <http://dx.doi.org/10.1246/bcsj.20170383>.

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