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A possible means of realizing a sacrifice-free three component separation of lignocellulose from wood biomass using an amino acid ionic liquid†

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Lignocellulose materials are potentially valuable resources for transformation into many bio-products. However, because of the difficulty in fractionating them into cellulose, hemicellulose, and lignin by a simple method directly from wood biomass, their economical conversion into high value-added products has been greatly limited. We found that *N*-methyl-*N*-(2-methoxyethyl)-pyrolidin-1-ium 2,6-diaminohexanoate ([P_{1ME}][Lys]) dissolved lignin very well below 60 °C, but that 80 °C was required for it to dissolve cellulose. Taking advantage of this difference in dissolution ability, direct extraction of lignin from wood biomass has been accomplished under mild conditions without the use of any hazardous reagents. Since lignin acts as the essential glue that binds cellulose and hemicellulose and gives plants their structural integrity, we have achieved the demonstration of the sacrifice-free separation of cellulose, hemicellulose, and lignin from wood biomass (Japanese cedar: *Cryptomeria japonica*).

Introduction

The main components in wood biomass are cellulose, hemicellulose, and lignin. The high crystallinity of cellulose, complex chemical cross-linking between components, and sheathing of cellulose by hemicellulose and lignin contribute to the challenge of isolating it from the biomass without using a hazardous mechanical or chemical treatment.[1] Although the lignocellulose industry has a long history, the difficulty of separating each component limits their utilization and prevents their economically feasible conversion into value-added products. No method has been reported for fractionating these three compounds from the biomass without sacrificing one of them.[1] We hypothesized that direct separation of cellulose, hemicellulose, and lignin might be possible if we remove the lignin using an appropriate extracting solvent, because lignin works as the essential glue that binds cellulose and hemicellulose and gives plants their structural integrity.[1–5] Furthermore, since lignin is a highly branched amorphous polymer composed of polyphenol derivatives found in a plant biomass, it is viewed as an important bio-renewable resource of aromatic compounds.[2] However, traditional methods to isolate lignin from plant biomass have serious drawbacks: all known procedures require hazardous reagents and are energetically wasteful.[2] The most serious problem has been that significant damage occurred to the cellulose or hemicellulose or to lignin itself during the extraction process.[1,2] Therefore, an environmentally benign method of isolating lignin in its unaltered structure without sacrificing cellulose or hemicellulose from the plant biomass has been the target of much research.

Ionic liquids (ILs) usually melt below 100 °C and ILs are becoming attractive alternatives to volatile and unstable organic solvents due to their high thermal stability, actually, nearly non-volatility. Furthermore, due to their unique solubility in many inorganic and organic materials,[6] it has been anticipated that ILs might dissolve lignin. In 2006 and 2007, early examples of lignin dissolution in ILs were reported independently by several groups (Xie,[7] Kilpeläinen,[8] Rogers,[9] Argyropoulos,[10] and Pu[11]). Since then, extensive studies have been carried out to develop ILs that possess the capability to dissolve lignin with the aim of extracting it from plant biomass.[3–5,12–30] Fig. 1 shows a list of ILs that have been used as such extracting solvents: most are salts of imidazolium cations with chloride,[7–10,13–18,21–24] methylsulfate,[11] acetate,[9,13,19,20,23,24,26,28] dicyanoamide,[8] alkylbenzenesulfonate,[12] glycolate,[20] succinate,[20] propionate,[29] lactate,[24] acesulfamate (ace),[25] alkylphosphate,[24] or glycinate.[29] Very recently, Liu and co-workers reported that amino acid salt ionic liquids with cholinium cation dissolved lignin.[30] However, these solvents generally require a high temperature (>90 °C–100 °C) for

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†Electronic supplementary information (ESI) available: Detailed method of lignin dissolution in ILs. XRD and IR spectra of lignin regenerated and lignin extracted from Japanese cedar (Fig. S-1, S-2, S-3, and S-4). Results of XRD and IR analyses of hemicellulose and cellulose obtained by the Japanese cedar (Fig. S-5, S-6, S-7, and S-8), and TOF-MS spectra of the lignin extracted from Japanese cedar (Fig. S-9). See DOI: 10.1039/c3gc40445e

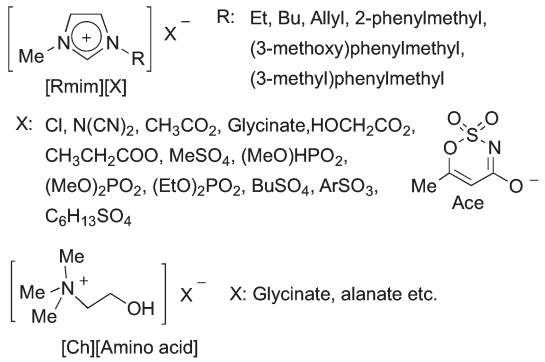

Fig. 1 List of ILs reported as lignin dissolution agents.

their dissolution, and development of ILs with the capability to dissolve this substance under mild temperature conditions is required from the standpoint of Green Chemistry.

Results and discussion

We recently reported that amino acid ILs[31] are strongly capable of dissolving cellulose:[32] *N*,*N*-diethyl,*N*-methyl,*N*-(2-methoxy)ethylammonium alanate ([N_{221ME}][Ala])[32] worked as an excellent solvent for cellulose dissolution among ILs whose anion part was a natural amino acid. We further revealed that a 1 : 1 mixture of [N_{221ME}][Ala] and dimethylsulfoxide (DMSO) dissolved cellulose very well even at room temperature.[33] During these investigations, we have recognized that ILs that possess a cellulose dissolution property also have the ability to dissolve lignin.[3–5] In fact, Muhammad and co-workers recently reported that [C_2mim][glycine] dissolved lignin and accomplished its extraction (24.45 wt%) from bamboo chips using this liquid.[29] The authors, however, used only [C_2mim][glycine] for their research and reported no result on the dissolution property of different types of amino acid ILs.[29] We, therefore, decided to investigate the dissolution property of these ILs *versus* lignin. We prepared alanine salts combined with six types of cations, *N*,*N*-diethyl-2-methoxy-*N*-methylethanaminium ([N_{221ME}]),[32] *N*,*N*-diethyl-*N*-methyl-2-(methylthio)-ethanaminium ([N_{221MTE}]),[32] *N*,*N*-diethyl-2-methoxy-*N*-(2-methoxyethyl)ethanaminium ([$N_{22(ME)2}$]),[32] *N*-ethyl-2-methoxy-*N*,*N*-bis-(2-methoxyethyl)ethanaminium ([$N_{2(ME)3}$]),[32] 3-(2-methoxyethyl)-1-methyl-1*H*-imidazol-3-ium ([(2-ME)mim],[32] and 1-(2-methoxyethyl)-1-methylpyrrolidin-1-ium alanine ([P_{1ME}][Ala]). Among these amino acid ILs (Fig. 2), [P_{1ME}][Ala] displayed the best solubility.[34] Hence, we next prepared [P_{1ME}] salts with natural amino acids, and then attempted to optimize the amino acid that contributed to good lignin dissolution.

In the preliminary experiments, we found that [P_{1ME}] salts dissolved lignin even at rt, while complete dissolution required a lengthy period. Therefore, the dissolution test was conducted at 60 °C and 100 °C and the results are summarized in Table 1. To 1.0 g of an ionic liquid in a 5 ml glass vial tube was added a lignin powder[34] and this was put on a hot stage of a microscope until the powder completely dissolved. The ionic

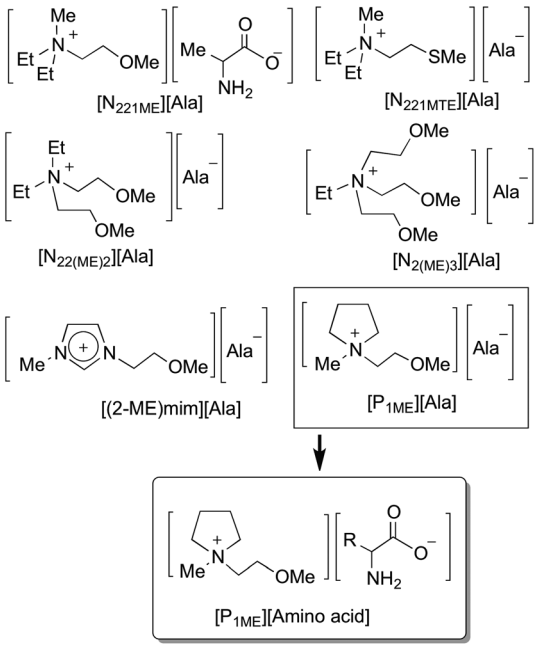

Fig. 2 Amino acid ionic liquids as lignin dissolution agents.

Table 1 Results of the dissolution test of lignin in various types of *N*-methyl-*N*-(2-methoxyethyl)pyrolidin-1-ium salts

Entry	IL([P_{1ME}][X]) Anion (X)	Solubility (wt% *vs.* solvent) 60 °C	100 °C	Total
1	Glycine	20	0[a]	20
2	Alanine	20	15	35
3	Valine	5	15	20
4	Leucine	25	10	35
5	Isoleucine	15	0[a]	15
6	Methionine	35	15	50
7	Proline	30	10	40
8	Phenylalanine	15	35	50
9	Tryptophan	0	20	20
10	Serine	30	15	45
11	Threonine	20	25	45
12	Asparagine	15	25	40
13	Glutamine	25	25	50
14	Aspartic acid	20	5[a]	25
15	Glutamic acid	15	30	45
16	Cysteine	5	5[a]	10
17	Tyrosine	35	15	50
18	Histidine	35	5[a]	40
19	Lysine	40	15	55
20	Arginine	35	20	55

[a] Since the resulting mixture was obtained as a black jelly-like sol, further dissolution of lignin could not be observed.

liquid solution was then diluted with ethanol, which caused the formation of regenerated lignin that was collected after centrifugation. XRD and IR analyses confirmed that no significant structural change of the lignin took place during the dissolution and regeneration process.[35]

As shown in Table 1, the lysine salt ([P_{1ME}][Lys]) best dissolved lignin (entry 19) and the arginine salt showed the second best result (entry 20). Methionine (entry 6), phenylalanine

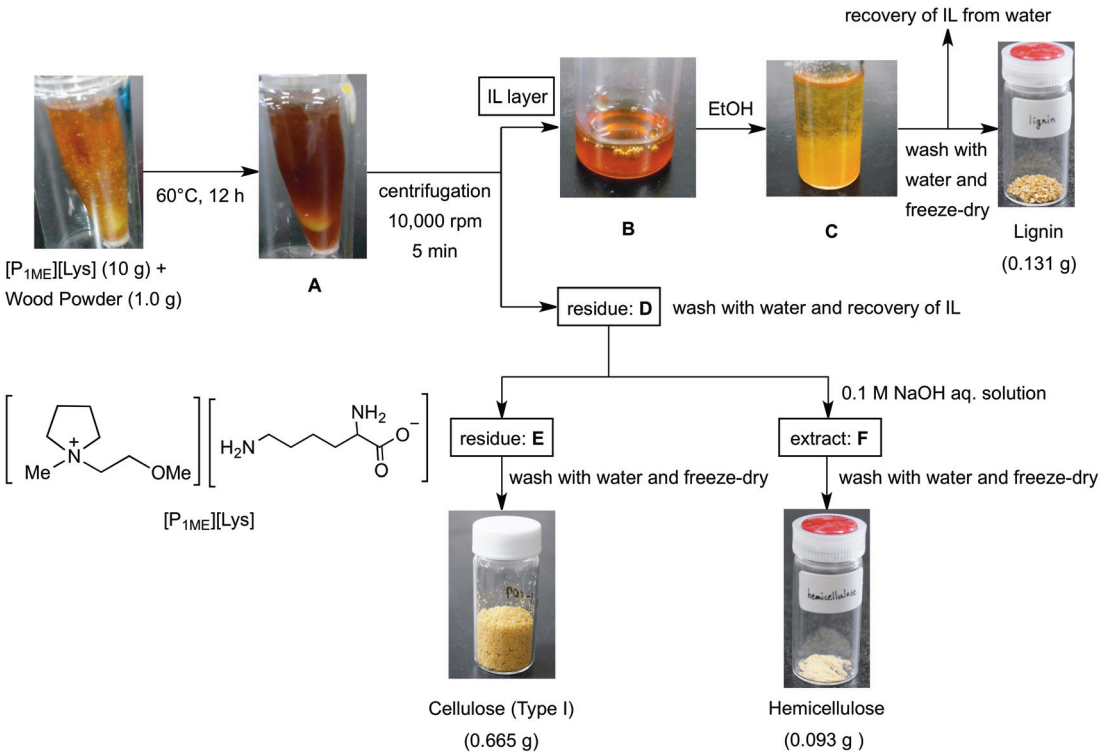

Fig. 3 Separation protocol of the three components of lignocellulose using $[P_{1ME}][Lys]$ as a key extracting agent.

(entry 8), glutamine (entry 13) and tyrosine (entry 17) salts also dissolved lignin very well. It should be noted that most amino acid salts with the $[P_{1ME}]$ cation dissolved lignin at 60 °C except for the tryptophan salt (entry 9). In particular, $[P_{1ME}]$-[Lys] dissolved lignin very well (40 wt% *vs.* solvent) below 60 °C, while all salts required a high temperature of least 80 °C to dissolve cellulose.

Hence, based on the difference in dissolution ability between cellulose and lignin in the ionic liquid, we attempted to isolate lignin selectively from wood powder using $[P_{1ME}]$-[Lys] as the extraction solvent. This extraction was achieved following the route illustrated in Fig. 3. To 10.0 g of $[P_{1ME}][Lys]$ was added wood powder (1.0 g, Japanese cedar: *Cryptomeria japonica*) and the mixture was stirred at 60 °C for 12 h to form a viscous sol (A in Fig. 3).

This was immediately centrifuged at 10 000 rpm for 5 min, and the supernatant (ionic liquid layer, B in Fig. 3) was separated. Dilution of this IL solution with ethanol or methanol caused the formation of a precipitate (C in Fig. 3) which was collected and washed with water three times and then dried under vacuum to give lignin (0.131 g, 13.1 wt% *vs.* wood powder).[36]

Since it had been shown that lignin accumulated 16.5% by weight in the wood chips we used by the Clarson method,[37] *ca.* 79% of lignin was found to be extracted by this simple method (Fig. 3). It should be emphasized that we succeeded in using the IL five times after recovery without any loss of its ability to dissolve lignin.[38]

A jelly-like residue remaining in the test tube after separation of the ionic liquid layer (D in Fig. 3) by centrifugation was washed three times with water and ionic liquid was recovered from the water layer. Since lignin had been successfully removed, the separation of cellulose and hemicellulose in residue D was easily accomplished (Fig. 3): it was first extracted with a 0.1 M sodium hydroxide aqueous solution (0.1 M NaOH) and the extract F was dried under vacuum and then washed with water three times and dried under vacuum to give hemicellulose as a light yellow powder (0.093 g, 9.3 wt% *vs.* wood powder).[39] The residue E was washed with water three times and dried under vacuum to give cellulose (0.665 g, 66.5 wt% *vs.* wood powder). The crystalline form of cellulose obtained was identified as Type I by XRD analysis,[40] thus indicating that no significant modification of the crystalline form of the cellulose had taken place during the present lignin extraction process. However, some components (*ca.* 10 wt%) were missing during the process. The average amount of hemicellulose was reported as 20–30 wt%,[1] while we obtained it in 9.3 wt%. Therefore, we assume that the unstable nature of hemicellulose during the extraction process might be attributable to the reduced total amount of components.

The results of TOF-MS experiments for the lignin obtained from three different sources, Japanese cedar, Japanese cypress, and lauan are shown in Fig. 4. We found that lignin obtained from cedar and cypress were composed of two types of polymers, $m/z = 196 + 197 \times n$ and $m/z = 110 + 197 \times n$, while lignin from lauan was a single polymer, $m/z = 196 + 197 \times n$. Therefore, it is expected that the present lignin extraction protocol from wood biomass might provide a useful means to make a lignin library of resource plants. Furthermore, the molecular

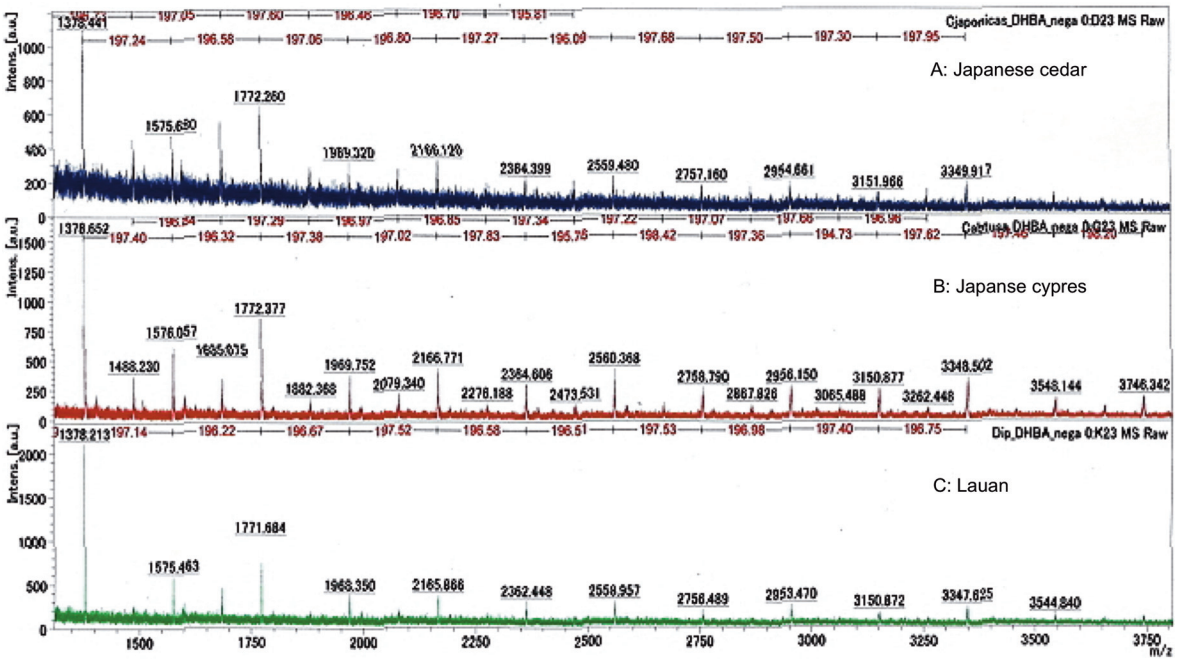

Fig. 4 MALDI-TOF-MS spectra of lignin obtained from three different sources.

weight of the extracted lignin reached a minimum of 25 kDa.[41] This suggests that our method allows lignin to be obtained without significant damage to its original structure.

Conclusions

In conclusion, we succeeded in developing a new ionic liquid which can dissolve lignin efficiently: *N*-methyl-*N*-(2-methoxyethyl)-pyrolidin-1-ium lysine ([P_{1ME}][Lys]) proved to be an excellent solvent for this dissolution, extracting lignin from wood biomass at 60 °C and making it possible to separate cellulose, hemicellulose, and lignin in the lignocellulose very simply. It should be emphasized that this ionic liquid is a halogen free and safe solvent, consisting of non-toxic ammonium cations with natural amino acids, and is recyclable. Separation of cellulose, hemicellulose, and lignin without sacrificing any component to the others has, to date, been considered but a dream in the field of lignocellulose chemistry. In this paper, we have shown a possible means to realize such a method using an amino acid ionic liquid as the key solvent. Since we used a sodium hydroxide solution for the separation of cellulose and hemicellulose in the present study, we are now investigating a design of the IL that would show a high capability to selectively dissolve hemicellulose. We hope that further investigation of our ionic liquid technology will make it even more beneficial in biomass sciences.

Experimental

Synthesis of *N*-methyl-*N*-(2-methoxyethyl)pyrolidin-1-ium 2,6-diaminohexanoate ([P_{1ME}][Lys])

N-Methyl-*N*-(2-methoxyethyl)pyrolidin-1-ium hydroxide ([P_{1ME}][OH]) was prepared based on the anion-exchange method developed by Ohno and his colleagues:[31] an aqueous solution of *N*-methyl-*N*-(2-methoxyethyl)pyrolidin-1-ium bromide ([P_{1ME}][Br]) (1.79 g, 8.0 mmol) in 15 ml of de-ionized water was passed through the column packed with 50 ml of activated amberlite IRA400CL to afford a [P_{1ME}][OH] aqueous solution. The aqueous solution was then mixed with an aqueous solution of L-lysine (1.17 g, 8.0 mmol) in de-ionized water (50 ml) at 0 °C, then the mixture was stirred at 0 °C for 19 h, and the solvent was removed by evaporation to give [P_{1ME}][Lys] and sodium bromide (NaBr) as a partially melted solid. This was diluted with a mixed solvent of acetonitrile and methanol (9 : 1) and passed through a celite filter to remove NaBr. The filtrate was lyophilized and further dried under reduced pressure at 50 °C for 5 h at 1.0 torr to give [P_{1ME}][Lys] (2.24 g, 7.7 mmol) in 96% yield. Activation of amberlite IRA400CL was accomplished using 170 ml of a 1.7 M sodium hydroxide aqueous solution *vs.* 50 ml of IRA400CL: ^{1}H NMR (500 MHz, ppm, CD_3OD) 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); ^{13}C NMR (125 MHz, ppm, CD_3OD, 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; 680 cP (25 °C), T_g −72 °C. Anal. calcd for $C_{14}H_{31}N_3O_3$: C, 58.10; H, 10.80; N, 14.52. Found: C, 58.16; H, 11.03; N, 14.42.

The water content of all ionic liquids was in the range of 200–300 ppm after drying, but, due to their hygroscopic nature, reached *ca.* 9000 ppm (0.09 wt%) after the bottle cap was left off for 48 h at room temperature in our laboratory (though it was confirmed that these levels of water content had no influence on the dissolution property).

Extraction of lignin from wood chips (Fig. 3)

To 10 g of [P_{1ME}][Lys] was added wood powder (1.0 g) and the mixture was stirred at 60 °C for 12 h to form a viscous mixture (A in Fig. 3). This was immediately centrifuged at 10 000 rpm for 5 min and then the supernatant (ionic liquid layer) (B in Fig. 3) was separated. The residue was diluted with 2.0 ml of the IL, then warmed at 60 °C for 1 h and centrifuged at 10 000 rpm for 5 min; the same process was repeated and the IL layer was collected (we used a total of 14 g of IL). Dilution of this IL solution with ethanol or methanol caused the formation of a precipitate (C in Fig. 3), which was collected, washed with water three times and dried under vacuum to give lignin (0.131 g, 13 wt% *vs.* wood powder). The residue remaining in the test tube after the separation of the ionic layer (D in Fig. 3) was then washed with water 3 times to recover the IL and then extracted with a 0.1 M sodium hydroxide (NaOH) aqueous solution. The extract was dried under vacuum, washed with water and finally dried under vacuum to afford hemicellulose as a light yellow powder (0.093 g, 9.3 wt% *vs.* wood powder). Residue E was washed with water three times and dried under vacuum to give cellulose (0.665 g, 66.5 wt% *vs.* wood powder). The sample of wood powder (*ca.* 50 μ) was prepared from Japanese cedar (*Cryptomeria japonica*) and dried under vacuum (1.0 torr) at rt for 12 h and used for the extraction process.

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40 For the XRD and IR spectra of cellulose, see ESI, Fig. S-5 and S-6.†
41 See the ESI, Fig. S-9.†

