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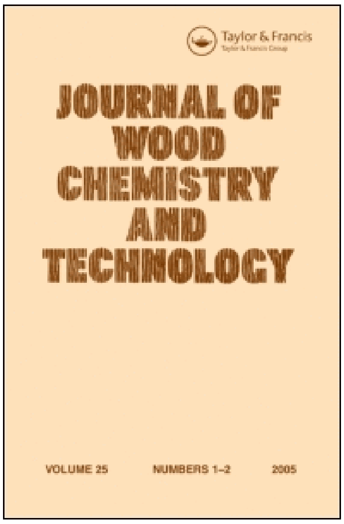

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Ionic Liquid as a Green Solvent for Lignin

Yunqiao Pu[a]; Nan Jiang[b]; Arthur J. Ragauskas[b]
[a] Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta, Georgia, USA [b] School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, USA

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Yunqiao Pu
Institute of Paper Science and Technology, Georgia Institute of
Technology, Atlanta, Georgia, USA

Nan Jiang and Arthur J. Ragauskas
School of Chemistry and Biochemistry, Georgia Institute of Technology,
Atlanta, Georgia, USA

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Abstract: This study examined the application of select ionic liquids (ILs) as aprotic green solvents for lignin. Dissolution experiments were carried out employing lignin isolated from pine kraft pulp. Up to 20 wt% lignin could be dissolved in [hmim][CF_3SO_3], [mmim][$MeSO_4$] and [bmim][$MeSO_4$]. For the $[bmim]^+$-containing ionic liquids, the order of lignin solubility for varying anions was: $[MeSO_4]^- > Cl^- \sim Br^- \ggg [PF_6]^-$, indicating that the solubility of lignin was principally influenced by the nature of the anions. Ionic liquids containing large, non-coordinating anions $[PF_4]^-$ and $[PF_6]^-$ were unsuitable as a solvent for lignin. ^{13}C nuclear magnetic resonance (NMR) analyses of lignin and model compounds showed that ^{13}C signals using ionic liquid as a solvent were shifted up-field by δ 0.1 to 1.9 ppm in comparison to ^{13}C NMR data acquired using dimethyl sulfoxide (DMSO) as the solvent.

Keywords: Ionic liquids, lignin, green solvent

INTRODUCTION

Lignin is one of three structural biopolymers present in all woody plants and is the second most abundant renewable biomaterial on Earth.[1] As a by-product

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Address correspondence to Arthur J. Ragauskas, School of Chemistry and Biochemistry, Georgia Institute of Technology, 500 10th Street, NW, Atlanta, GA 30332, USA. E-mail: arthur.ragauskas@chemistry.gatech.edu

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of biorefining, lignin has historically been utilized as a low value heating fuel, binder, dispersant, emulsifier, and sequestrant.[2,3] More recently, research studies have identified polyurethane and polyesters derived from lignin as a valuable renewable bioplastic resource.[4–6] Alkylated lignin derivatives have been shown to exhibit tensile strength properties similar to polystyrene and have been employed to prepare promising thermoplastic blends with aliphatic polyesters.[6,7] Alternatively, underivatized lignin has been blended with several commodity plastics yielding enhanced composites and is utilized as a resource for carbon-fiber synthesis.[8–10]

Lignin is an amorphous, polyphenolic polymer arising from a polymerization of phenylpropanoid monomers including: coniferyl, sinapyl, and p-coumaryl alcohol.[1,11,12] It is a unique biopolymer because it lacks clearly defined secondary and tertiary order found in many other natural polymers such as cellulose and proteins. Chemical pulping employs alkaline or acidic solutions to produce approximately 26 million tons of lignin annually from wood globally.[8,13] The growing interest in developing new lignin-based products is driven by the fact that lignin is a renewable, low-cost bioresource with unique functionalities, and is an environmentally benign material. However, many of the technologies currently used in lignin isolation or processing employ harsh alkaline or acidic conditions and/or organic solvents.[14–20] These processes are far from favorable and generally not considered green. Therefore, green solvents are needed that can dissolve lignin and facilitate new chemistries and are readily recyclable.

Ionic liquids (ILs) are liquids at or below 100°C that are comprised entirely of cations and anions.[21–25] They have been developed over the past decades as green solvents, with tunable solvation properties.[21,26–28] The potential of ionic liquids to act as solvents and catalysts for a wide range of chemical processes is attracting extensive attention from industry and academia, as they exhibit significant environmental and process benefits. Ionic liquids have been referred to as design solvents, which can be designed to optimize a variety of chemical reactions of interest. Recently, ionic liquids have been used as solvents for natural polymers,[29–34] including cellulose and starch. Xie and Shi [35] have reported that ionic liquids 3,3′-ethane-1,2-diylbis(1-methyl-1*H*-imidazol-3-ium) dichloride and 3,3′-ethane-1,2-diylbis(1-methyl-1*H*-imidazol-3-ium) dichloroaluminate have enhanced properties for wood liquefaction in comparison with the phenol/H_2SO_4 system. This article reports our studies directed at utilizing ionic liquids as a novel green solvent for lignin.

In this study, we examined the dissolution of a softwood lignin in several different ionic liquids, including: 1,3-dimethylimidazolium methylsulfate ([mmim][$MeSO_4$]), 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([hmim][CF_3SO_3]), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([bm_2im][BF_4]), 1-butyl-4-methylpyridinium hexafluorophosphate ([bmpy][PF_6]), and 1-butyl-3-methylimidazolium cations ($[bmim]^+$)

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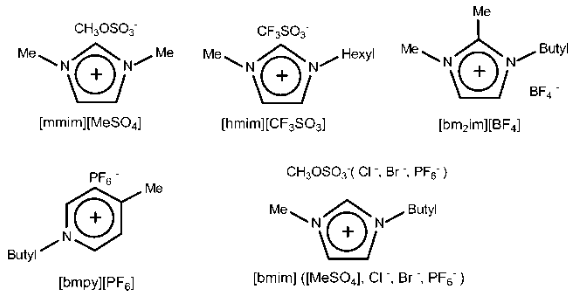


Figure 1. Ionic liquids.

with a range of anions (i.e., $[MeSO_4]^-$, Cl^-, Br^-, and PF_6^-). The applicability of these solvents systems for ^{13}C nuclear magnetic resonance spectroscopy of lignin was also examined.

MATERIALS AND METHODS

Lignin Dissolution in Ionic Liquids

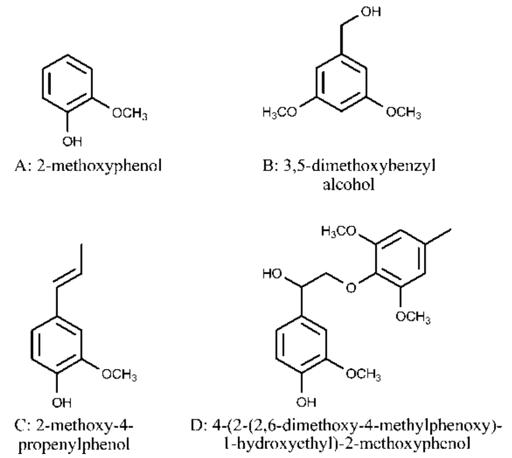
All the ionic liquids were purchased from Sigma-Aldrich and used as received, as summarized in Figure 1 and Table 1. A residual softwood lignin isolated from a southern pine kraft pulp following literature methods[36] and a softwood kraft black liquor lignin were used in this study. Lignin dissolution experiments were carried out using the residual softwood lignin. Samples of the ionic liquid (~0.50 g) were mixed with weighed lignin samples and if needed, were heated in an oven for accelerated dissolution.

Table 1. Physical properties of ionic liquids[a] used

Ionic liquids	Purity (%)	Melting point, °C
$[mmim][MeSO_4]$	≥97	RTL[b]
$[hmim][CF_3SO_3]$	≥95	~28
$[bm_2im][BF_4]$	≥97	38~40
$[bmpy][PF_6]$	≥97	~45
$[bmim][MeSO_4]$	>97	RTL
[bmim]Cl	>99	~70
[bmim]Br	>97	~60
$[bmim][PF_6]$	>96	RTL

[a] Typical water content ≤1%;

[b] liquid at room temperature.



A: 2-methoxyphenol

B: 3,5-dimethoxybenzyl alcohol

C: 2-methoxy-4-propenylphenol

D: 4-(2-(2,6-dimethoxy-4-methylphenoxy)-1-hydroxyethyl)-2-methoxyphenol

Figure 2. Lignin-related model compounds.

Model Compounds

Lignin-related model compounds (Figure 2) 2-methoxyphenol and 3,5-dimethoxybenzyl alcohol were purchased from Aldrich. 2-methoxy-4-propenylphenol was obtained from Pfaltz & Bauer and used as received. Model compound 4-(2-(2,6-dimethoxy-4-methylphenoxy)-1-hydroxyethyl)-2-methoxyphenol was synthesized according to reported procedures.[37]

^{13}C NMR Spectroscopy

Lignin/ionic liquid solutions were transferred into 5 mm NMR tubes fitted with a co-axial insert containing DMSO-d_6 for field-frequency lock. All ^{13}C NMR spectra were recorded on a Bruker Advance/DMX 400 NMR spectrometer at 70°C and 20,000 scans were collected for each lignin sample dissolved in the ionic liquid and DMSO-d_6. The ^{13}C NMR spectra of lignin-related model compounds in ionic liquid and DMSO-d_6 were performed in an analogous manner.

RESULTS AND DISCUSSION

The results obtained from solubilization of residual softwood kraft lignin in ionic liquids are summarized in Table 2. A softwood lignin sample was observed to dissolve in [mmim][MeSO$_4$] ($\sim$74 g/L) and [bmim][MeSO$_4$] ($\sim$62 g/L) at room temperature. Lignin could not be dissolved in [hmim][CF$_3$SO$_3$] under ambient conditions. Upon heating to desired

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Table 2. Solubility of residual softwood kraft pulp lignin in ionic liquids

Ionic liquid	Temp./°C	Solubility (g L^{-1})
[mmim][$MeSO_4$]	50	344
	25	74.2
[hmim][CF_3SO_3]	70	275
	50	<10
[bmim][$MeSO_4$]	50	312
	25	61.8
[bmim]Cl	75	13.9
[bmim]Br	75	17.5
[bmim][PF_6]	70–120	Insoluble
[bm_2im][BF_4]	70–100	14.5
[bmpy][PF_6]	70–120	Insoluble

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temperatures, lignin rapidly dissolved in [mmim][$MeSO_4$], [hmim][CF_3SO_3] and [bmim][$MeSO_4$] to yield increasingly viscous mixtures (i.e., 344 g/L in [mmim][$MeSO_4$] at 50°C, 275 g/L in [hmim][CF_3SO_3] at 70°C, and 312 g/L in [bmim][$MeSO_4$] at 50°C). The greatest lignin solubility was obtained using [mmim][$MeSO_4$] and [bmim][$MeSO_4$], at slightly elevated temperatures of 50°C.

For the $[bmim]^+$-containing ionic liquids, the order of lignin solubility for varying anions was: $[MeSO_4]^- > Cl^- \sim Br^- \ggg [PF_6]^-$, indicating that the solubility of lignin was principally influenced by the nature of the anions. All the studied ionic liquids containing large, non-coordinating anions such

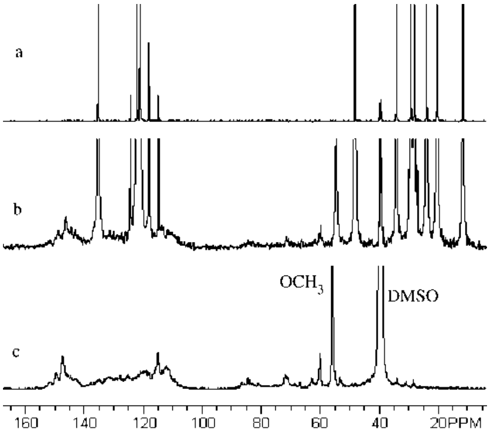

Figure 3. ^{13}C NMR spectra of residual softwood kraft lignin. a: ionic liquid [hmim]CF_3SO_3; b: residual lignin in [hmim]CF_3SO_3; c: residual lignin in DMSO.

as $[BF_4]^-$ and $[PF_6]^-$ exhibited no or very limited ability to dissolve the residual softwood kraft lignin.

The residual softwood kraft lignin in ionic liquid [hmim][CF_3SO_3] was characterized by ^{13}C nuclear magnetic resonance (Figure 3). The residual lignin in this ionic liquid exhibited comparable spectral information when compared to that acquired with DMSO-d_6 as a solvent. Small changes in chemical shifts were noted. For example, the typical ^{13}C signal for the OCH_3 group of lignin was shifted up-field $\sim\delta$ 1.2 ppm in the ionic liquid, compared with chemical shift observed in DMSO. No chemical shift changes in the ^{13}C NMR signals for [hmim][CF_3SO_3] were detected after the lignin was dissolved in this ionic liquid. A softwood kraft black liquor lignin in ionic liquid [mmim][$MeSO_4$] was also examined by ^{13}C NMR. Similarly, comparable spectral information of the black liquor lignin was observed in both ionic liquid and DMSO as a solvent (Figure 4). The chemical shifts of black liquor lignin signals in the ionic liquid demonstrated δ 0.8 $\sim$1.2 ppm up-field shift, compared with that in DMSO. Figure 4 demonstrates that no chemical shift changes were observed for [mmim][$MeSO_4$] after the black liquor lignin was dissolved in this ionic liquid.

Four representative lignin-related model compounds were characterized in the ionic liquid [hmim][CF_3SO_3] using ^{13}C NMR, as well as in DMSO-d_6. Compounds A, B, and C were well dissolved in [hmim][CF_3SO_3] at room temperature, whereas D dissolved at 70°C. The assignments and chemical shifts of ^{13}C NMR signals for the model compounds are summarized in Table 3. Figure 5 shows the ^{13}C NMR spectra of model compound 3,5-dimethoxybenzyl alcohol in [hmim]CF_3SO_3 and DMSO,

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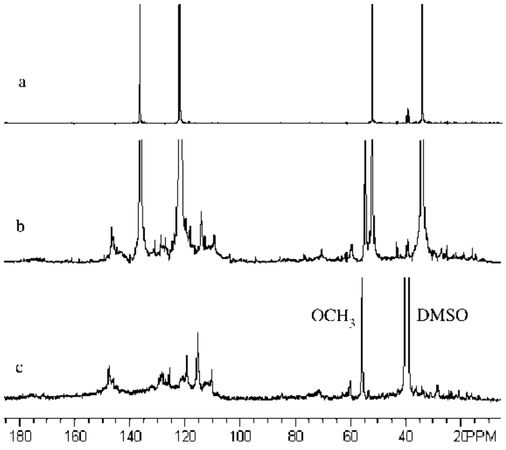

Figure 4. ^{13}C NMR spectra of softwood black liquor lignin. a: ionic liquid [mmim][$MeSO_4$]; b: black liquor lignin in [mmim][$MeSO_4$]; c: black liquor lignin in DMSO.

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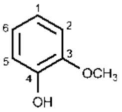
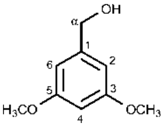
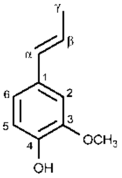
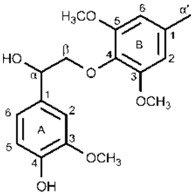
Table 3. Assignments and chemical shifts (ppm) of ^{13}C NMR signals of model compounds in DMSO and ionic liquid [hmim]CF_3SO_3

Model compounds	C	δ^a	δ (in IL)	$\Delta\delta^b$
	1	120.9	119.8	1.1
	2	112.9	111.0	1.9
	3	146.7	144.9	1.8
	4	147.7	146.2	1.5
	5	115.6	113.8	1.8
	6	119.1	118.6	0.5
	OMe	55.7	54.4	1.3
	1	144.8	143.4	1.3
	2,6	104.2	103.5	0.7
	3,5	160.2	159.6	0.6
	4	98.6	97.5	1.1
	α	62.7	62.3	0.4
	OMe	54.7	53.6	1.2
	1	129.2	128.1	1.1
	2	110. 1	108.4	1.7
	3	147.5	146.3	1.2
	4	145.8	144.2	1.6
	5	115.4	113.8	1.6
	6	118.6	117.6	1.0
	α	130.6	129.3	1.3
	β	121.7	121.5	0.2
	γ	17.3	15.9	1.4
	OMe	55.6	54.4	1.2
	A1	135.0	133.7	1.3
	A2	111.2	109.6	1.2
	A3	147.0	146.1	0.9
	A4	145.5	144.4	1.2
	A5	114.8	113.5	1.3
	A6	118.7	118.0	0.7
	α	71.1	70.8	0.3
	β	78.2	77.5	0.7
	A OMe	55.6	54.5	1.1
	B1	132.4	131.8	0.6
	B2,6	106.9	105.6	1.3
	B3,5	152.3	151.4	0.9
	B4	132.8	132.7	0.1
	α′	20.7	19.4	1.3
	B OMe	55.8	54.6	1.2

[a] Chemical shift (in DMSO).[39]

[b] Chemical shift changes.

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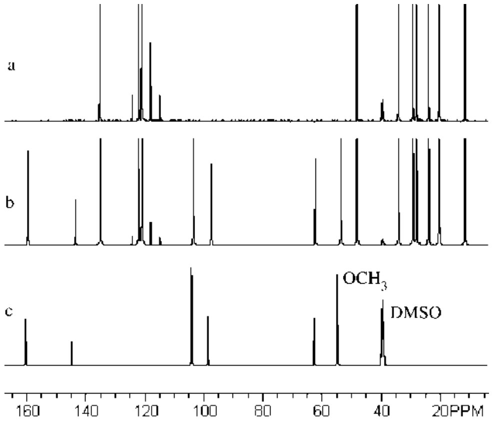

Figure 5. ^{13}C NMR spectra of model compound 3,5-dimethoxybenzyl alcohol. a: ionic liquid [hmim]CF_3SO_3; b: 3,5-dimethoxybenzyl alcohol in [hmim]CF_3SO_3; c: 3,5-dimethoxybenzyl alcohol in DMSO.

respectively. All the ^{13}C NMR signals for the model compounds dissolved in the ionic liquid were shifted up-field by δ 0.1 to 1.9 ppm in comparison to ^{13}C NMR data acquired using DMSO as the solvent. The ^{13}C NMR signals of OCH_3 group in model compounds dissolved in DMSO were shifted up-field δ 1.1$\sim$1.3 ppm of chemical shifts in the ionic liquid, which correlated with the observed results for the ^{13}C NMR signals of the OCH_3 group of lignin. Rogers' group has reported that the solvation of cellulose by ionic liquid [bmim]Cl involves hydrogen-bonding between the carbohydrate hydroxyl protons and chloride ion of the ionic liquid.[29,38] Whether the dissolution of lignin and lignin model compounds is similarly involved in or governed by hydrogen-bonding with ionic liquids ions needs further investigation.

CONCLUSIONS

In conclusion, we have demonstrated that certain ionic liquids can be used as aprotic solvents for lignin. For the $[bmim]^+$-containing ILs, the order of lignin solubility for varying anions was: $[MeSO_4] > Cl^- \sim Br^- \ggg [PF_6]^-$, indicating that the solubility of lignin was principally influenced by the nature of the anions. Ionic liquids containing large, non-coordinating anions $[PF_4]^-$ and $[BF_6]^-$ were unsuitable as a solvent for lignin. Ionic liquids [hmim][CF_3SO_3], [mmim][$MeSO_4$] and [bmim][$MeSO_4$] appear to be effective solvents for lignin. The recent studies by Lu and Ralph on dissolution and acetylation of ball-milled plant cell walls highlight the potential for alternative treatments to isolate and characterize plant biopolymers.[40] The results of our study provide an underpinning from which rational design of ionic liquid – lignin mixtures can be accomplished that will facilitate the development of innovative green chemistry for one of nature's premiere biopolymers, lignin.

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