



Short Communication

Influence of organic solvent on the separation of an ionic liquid from a lignin–ionic liquid mixture



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HIGHLIGHTS

- This provides basic information ascertaining promising solvents for the recovery.
- Some organic solvents are effective to recovery ionic liquid and obtain lignin.
- The effective order is isopropanol > ethanol > acetonitrile > ally alcohol > methanol.

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ABSTRACT

Sixteen solvents added in lignin–ionic liquid mixture provide four types of solubility characteristics. The distinct characteristics can be classified by considering solubility parameters including E_T Scale, Kamlet–Taft parameters and solubility parameters. Group 1 solvent shows promising solvents for lignin–ionic liquid separation, contributing full dissolution of ionic liquid with lignin precipitation. Isopropanol, the most potential solvent has solubility properties as following normalized molar electronic transition energies (E_T^N) = 0.57, hydrogen-bond acidity (α) = 0.76 and Hildebrand solubility parameter (δ_T) = 23.58. This study examines potential solvents for ionic recovery, provides simple method of separation and leads to the feasibility of using ionic liquids in industrial applications.

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1. Introduction

Ionic liquids have been widely used as promising solvents for the biomass pretreatment process. They have shown to be excellent solvents for lignin extraction and carbohydrate dissolution to decrease its crystallinity (Weerachanchai et al., 2012b). In addition, they have several advantages among conventional processes; such as, requiring mild conditions, low toxicity and no destructive effects on the fermentable sugar content (Weerachanchai and Lee, 2013; Weerachanchai et al., 2012b). However, the high cost of ionic liquids limits their application on an industrial scale. Therefore, their recyclability or reuse for several consequent batches of pretreatment is required. Nevertheless, drastic degradations of ionic liquids to attain lower lignin extraction and sugar conversion were marked after they were reused for a number of recycles. The major cause is a lignin accumulation in the ionic liquid during the biomass pretreatment time after time. Previous researchers had investigated the approaches to recover the ionic liquid from ionic liquid–lignin solutions. It has

known that lignin can be separated from black liquor derived from pulping process by precipitating with mineral acids such as sulfuric acid, hydrochloric acid, etc. (García et al., 2009; Liu et al., 2011). A previous research (Tan et al., 2009) had recovered lignin from the ionic liquid by acidifying the lignin and ionic liquid solution with 1 M HCl to pH 2 at room temperature. It was found that an extraction yield exceeding 93% was obtained and the regenerated ionic liquid showed certain structure and properties. The lignin was also able to be separated from water–ionic liquid by some organic solvents with forming a two liquid-phase system (Xin et al., 2012). Tetrahydrofuran (THF) was the most promising solvent among other solvents, the partition coefficients increased with increasing water amount and decreasing pH of solution. In addition, extraction of lignin from an aqueous–ionic liquid mixture was attained by conversion of lignin and sugars in solution with catalysts of CrCl_3 and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ into furfural resin and humin (Yu et al., 2012). It was found that with catalyzing by $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ at a high temperature ($\geq 170^\circ\text{C}$), almost all the lignin and sugars were converted to humin. However, there are various restrictions derived from those processes; for example, a complicated process and reaction, low efficiency of recovery and/or existence of a remaining catalyst in the ionic

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liquid. This would restrain the use of ionic liquid for industrial applications.

A powerful and simple approach to recover ionic liquid as well as to separate lignin from accumulated lignin–ionic liquid mixture in order to use it as a valuable chemical feedstock has been attempted in this study. From preliminary study, it was found that different organic solvents present distinct solubility characteristics within a lignin–ionic liquid mixture. As observed, some organic solvents possess a potential behavior to separate the ionic liquid from the lignin–ionic liquid mixture by dissolving the ionic liquid into a solvent with lignin precipitation. Therefore, this has tempted to understand the solubility behaviors of organic solvents in the mixture in order to investigate a promising solvent for ionic liquid–lignin recovery. Three kinds of solubility factors including Kamlet–Taft parameters, E_T Scale and solubility parameters were considered to evaluate the potential solvent. Furthermore, the separation of lignin–ionic liquid by some potential solvents was performed in lab scale to study the effect of solvent type and amount on effectiveness of lignin–ionic liquid separation.

2. Methods

1-Ethyl-3-methylimidazolium acetate (EMIM-AC, $\geq 90\%$), alkali lignin and organic solvents were acquired from Sigma–Aldrich. The mixture of lignin and ionic liquid (100 mg of alkali lignin in 2 ml of EMIM-AC) was prepared to be used as a model solution of accumulated lignin and used ionic liquid. Several kinds of organic solvents (3 ml) were added into the lignin–ionic liquid mixture to study their solubility characteristics. The effect of the solubility properties of organic solvents (Kamlet–Taft parameters, E_T Scale and solubility parameters) on solubility characteristics of organic solvent and mixture was examined.

In addition, some potential solvents derived from the study were used to study effect of solvent type and amount on lignin–ionic liquid separation. The mixture of alkali lignin (200 mg) and EMIM-AC (2 ml) was separated by a known amount of selected solvents (5–100 ml) at room temperature (25 °C). The solution was mixed and stirred to extract the ionic liquid into the solvent phase and the lignin pulp was precipitated after centrifuging. Lignin content in the supernatant liquid was used to detect the solvent effectiveness on lignin–ionic liquid separation. It was analyzed by UV–vis spectrophotometer (Varian, Cary 4000) using a calibration curve of the known concentrations of alkali lignin.

3. Results and discussion

3.1. Solubility characteristics of lignin–ionic liquid solution dissolved in different solvents

Table 1 shows the solubility characteristics of the lignin–ionic liquid solution in different solvents compared with three types of solubility properties of different solvents (E_T scale, Kamlet–Taft parameters and solubility parameters). The sixteen organic solvents dissolved in the mixture of lignin–ionic liquid provide four kinds of solubility behaviors. Group 1 is a characteristic of full dissolution with lignin precipitation consisting of acetonitrile, acetic acid, ally alcohol, dichloromethane, dimethyl sulfoxide, ethanol, iso-propanol and methanol. Water shows full dissolution without lignin precipitation defined as Group 2 and pyridine creates a cloudy solution and lignin–ionic liquid phase defined as Group 3. Finally, a characteristic of a clear solution and lignin–ionic liquid phase is defined in Group 4, including acetone, benzene, diethyl ether, ethyl acetate, hexane and triethylamine. From this work, it is possible to separate lignin from lignin–ionic liquid solution by using solvents of Group 1.

Fig. 1 indicates that molar electronic transition energies, $E_T(30)$ and normalized E_T^N , which are widely used as the an empirical scale of solvent polarity (Reichardt, 1994), can differentiate the solubility behaviors. The promising solvents for lignin–ionic liquid separation, Group 1 has the $E_T(30)$ and E_T^N in the range of 40.70–55.40 and 0.31–0.76, respectively. On the other hand, Group 2 contributes a higher value at 63.10 (1.0) and Group 3 and Group 4 offer lower values 40.50 (0.3) and 31.0–42.20 (0.01–0.35), respectively. Considering the Kamlet–Taft parameters, interaction capacities of solvents are expressed as dipolarity/polarization (π^*), hydrogen-bond acidity (α) and hydrogen-bond basicity (β) (Mäki-Arvela et al., 2010; Mora-Pale et al., 2011). It is observed that dipolarity/polarization (π^*) and hydrogen-bond basicity (β) are not able to distinguish the solubility characteristics, while hydrogen-bond acidity (α) could be a critical key to determine proper the solvent for lignin–ionic liquid separation (Table 1). The full dissolution with lignin precipitation is attained with solvents possessing the hydrogen-bond acidity (α) varying in wide range of 0.13–1.12 (except in the case of dimethyl sulfoxide, $\alpha = 0$), whereas, the hydrogen-bond acidity (α) of solvents in Groups 2 and 3–4 show very high and low values at 1.17 and 0–0.08, respectively (Table 1 and Fig. 2). Furthermore, the degree of interaction among organic sol-

Table 1
Solubility characteristics of lignin–ionic liquid solution dissolved in different solvents and solubility properties of different solvents.

Solubility characteristics	Solvents	E_T scale (Stenutz, 2013)		Kamlet–Taft parameters (Kamlet et al., 1983; Stenutz, 2013)				Solubility parameters (Grulke, 2005)			
		$E_T(30)$	E_T^N	α	β	π^*	$\beta-\alpha$	δ_d	δ_p	δ_h	δ_T
1. Fully dissolution with lignin precipitation	Acetonitrile	45.60	0.46	0.19	0.40	0.75	0.21	15.80	18.00	6.10	24.72
	Acetic acid	55.20	0.76	1.12	0.45	0.64	−0.67	14.50	8.00	13.50	21.37
	Ally alcohol	52.10	0.66	0.84	0.90	0.52	0.06	16.20	10.80	16.80	25.72
	Dichloromethane	40.70	0.31	0.13	0.10	0.82	−0.03	18.20	6.30	6.10	20.20
	Dimethyl sulfoxide	45.10	0.44	0.00	0.76	1.00	0.76	18.40	16.40	10.20	26.68
	Ethanol	51.90	0.65	0.86	0.75	0.54	−0.11	15.80	8.80	19.40	26.52
	Iso-propanol	49.20	0.57	0.76	0.84	0.48	0.08	15.80	6.10	16.40	23.58
	Methanol	55.40	0.76	0.98	0.66	0.60	−0.32	15.10	12.30	22.30	29.61
2. Fully dissolution without lignin precipitation	Water	63.10	1.00	1.17	0.47	1.09	−0.70	15.50	16.20	42.40	47.96
3. Cloudy solution and lignin–ionic liquid phase	Pyridine	40.50	0.30	0.00	0.64	0.87	0.64	19.00	8.80	5.90	21.75
4. Clear solution and lignin–ionic liquid phase	Acetone	42.20	0.35	0.08	0.43	0.71	0.35	15.50	10.40	7.00	19.94
	Benzene	34.30	0.11	0.00	0.10	0.59	0.10	18.40	0.00	2.00	18.51
	Diethyl ether	34.50	0.12	0.00	0.47	0.27	0.47	14.50	2.90	5.10	15.64
	Ethyl acetate	38.10	0.23	0.00	0.45	0.55	0.45	15.80	5.30	7.20	18.15
	Hexane	31.00	0.01	0.00	0.00	0.04	0.00	14.90	0.00	0.00	14.90
	Triethylamine	32.10	0.04	0.00	0.71	0.14	0.71	–	–	–	15.10

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