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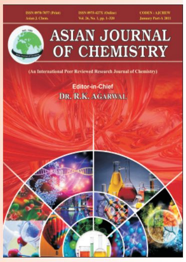

Solubility of Alkali Lignin in Dilute Solutions of [BMIm]Cl at Room Temperature†

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Dissolution of the alkali lignin by using ionic liquids will make the post treatment process become environment friendly. This paper designed an experiment to dissolve alkali lignin powder in a sequence of [BMIm]Cl dilute aqueous solutions at room-temperature and characterization by ultraviolet spectrometry. The results are as follows: (1) Both water and [BMIm]Cl can dissolve alkali lignin and [BMIm]Cl makes aqueous solution grow the structure selectivity. (2) The relationship between the dissolving amount of alkali lignin and the concentration of [BMIm]Cl solutions is not linear and the inflection point is nearby 0.002 g/L. (3) The solubility of alkali lignin in [BMIm]Cl dilute solutions at room-temperature is influenced by [BMIm]Cl concentration and dissolving time and can be fitted by using exponent equation. The key coefficient τ_i in fitting equation has differential exponent related to the [BMIm]Cl concentration.

Keywords: Alkali lignin, Ionic liquid, Dissolve, [BMIm]Cl.

INTRODUCTION

Nature has enormous reserves of lignin. Lignin can be found worldwide and as the sole renewable aromatic resource of natural raw materials[1]. Alkali lignin (or soda lignin) can mainly be obtained from alkali pulping black liquor, as the byproduct in the cellulose separation process of paper-making industry. It can be classified by making progress into kraft lignin, sulfide lignin, *etc*.[2].

Lignin is hardly soluble in water or common solvents and its organic functional groups have low reactivity. Transforming lignin into liquid and activating it may be made its application fields expanded. Currently the dominant liquefaction methods of lignin are developed as direct ways and indirect ways[2].

A new vision was raised in the research of biomass resources recently, complete-lignocellulose-dissolution system, which is a kind of special solvent system with having hydrogen-bond-disrupting ability, including two complete dissolution systems, organic solvents and ionic liquids (ILs)[3].

Until 2002, study first shown that some imidazolium-based ionic liquids could dissolve cellulose efficiently at low temperature (≤ 100 ºC)[4]. Since then, more interesting results have been reported during the past few years[5-9]. Accordingly, the dissolution of lignin-rich wood in ionic liquids has been studied[10]. It was found that wood chips could be partially dissolved in some ionic liquids, such as [Bmim]Cl. Wood sawdust sample was easier to be dissolved in ionic liquids and its solubility was 8 % in [Bmim]Cl. Rayne and Mazza[11] pointed out that dissolution in [Bmim]Cl on large scale had practical limitation due to the hygroscopic nature of [Bmim]Cl.

Owing to the high hygroscopicity, the utilization of [BMIm]Cl was limited when it was exposed to the air. This paper try to dissolve [BMIm]Cl as a solubilizing agent into low-concentration aqueous solutions firstly, then study the solubility of alkali lignin in these solutions at room-temperature.

EXPERIMENTAL

All reagents were used as received in this study except for special illumination. 1-butyl-3-methylimidazolium chloride ([BMIm]Cl, purity > 99 %) was purchased from Shanghai Cheng Jie Chemical Co., Ltd. Alkali lignin (ALG), which was ultrafiltration from black liquor supplied from a paper-making plant in Suzhou(Anhui Province, China) and was milled and sieved to get a powder with particle sizes of 40-60 mesh after air dried. Its ultimate analysis and proximate analysis are shown in Table-1 and were measured according to NY/T 1881-2010 Densified biofuel - test methods. Deionized water was prepared in laboratory.

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TABLE-L
ULTIMATE ANALYSIS AND PROXIMATE ANALYSIS OF ALKALI LIGNIN SAMPLE

Ultimate analysis (wt. %)					Proximate analysis (wt. %)			
C	H	O	N	S	Moisture	Ash	Volatiles	Fixed C
61.54	5.01	30.40	1.80	1.25	5.31	3.52	76.61	14.56

Preparation of [BMIm]Cl dilute solution: 2.5 mL [BMIm]Cl sucked at 70 ºC (relative density is 1.04) was added in a 500 mL volumetric flask. Deionized water was added later to made the aqueous solution concentration at 0.005 g/L as constant volume. Then a series of [BMIm]Cl dilute solutions from 0.0001 to 0.004 g/L were prepared by dilution on graded ratio.

Dissolution of alkali lignin in [BMIm]Cl dilute solution: Weighed 0.1 g alkali lignin on an AR1140 electronic balance (Ohaus, United States) and added the powder into a sample bottle, which was sealed after added 10 mL dilute solution prepared before. Then placed all bottles on a JH96-4 powder dissolved oscillator (Jiangyan Jianhua Medical Devices, China) and dissolved at 30 ºC in designated time. The picked alkali lignin solution sample was centrifugation on a TL80-1 medical centrifuge (Jiangyan Tianli Medical Devices, China) one minute at 4000 rpm and the supernatant was separated for the ultraviolet (UV) spectrometry.

Characterization of UV spectrum: A UV-2550 Ultraviolet and visible spectrophotometer (Shimadzu, Japan) was used with deionized water as the reference liquid. The parameters of this apparatus were setting as follow: slit width is 2.0nm, the wavelength scanning range is from 200-350 nm using high-speed scan and the absorbance detection limit is 5.0.

RESULTS AND DISCUSSION

Confirmation of the detection wavelength: Owing to the complex structure and strong intra-molecular interactions of alkali lignin, the UV spectrum detection wavelength should be confirmed to compare the absorbance of samples. Two 0.1 g alkali lignin samples were dissolved by standing or oscillation one hour in 10 mL deionized water. The detected UV spectrums are shown in Fig. 1.

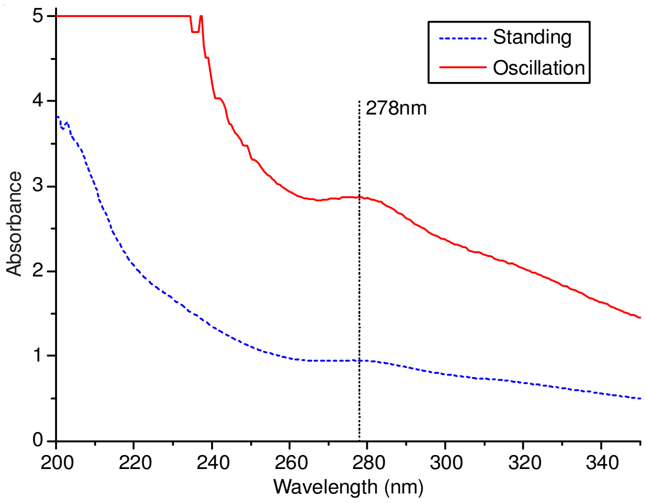

Fig. 1. UV absorption spectrums of alkali lignin samples dissolved in deionized water 1 h

Fig. 1 shows that the maximum absorption peaks both appeared at 278 nm and the peak of oscillation dissolution way is much more significant than standing way. It is the characteristic peak of benzene ring structure in lignin and the absorbance of all samples would be detected at 278 nm hereby. In addition, the peak values would be quantitative analysis because the selected absorbance of each UV spectrum is corresponding to the dissolved amount of samples.

Effects of [BMIm]Cl concentration and dissolving time to absorbance: Fig. 2(a) shows the UV spectra of alkali lignin samples dissolved in deionized water, Fig. 2(b) shows the time trend of absorbance at 278 nm the alkali lignin aqueous solutions. It is noted that the absorbance should be less than 8 within 20 h according to this trend though the detection limit had been exceeded after 300 min.

Scanned a sequence of supernatants derived from alkali lignin samples in [BMIm]Cl dilute solution, the UV spectra

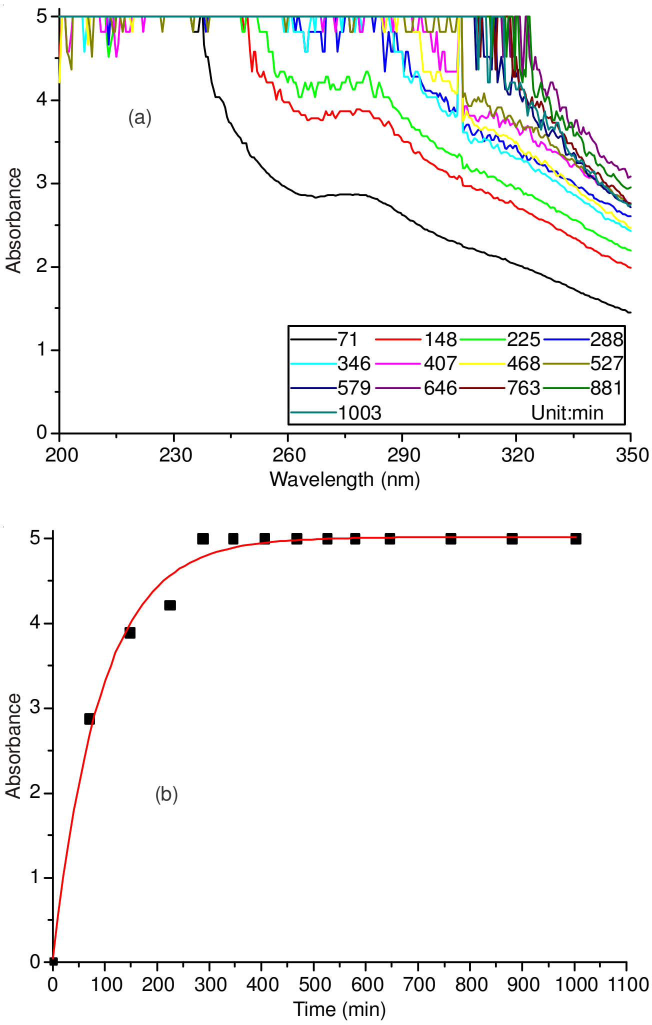

Fig. 2. Aqueous effects to alkali lignin. (a) UV absorption spectra of alkali lignin samples dissolved in deionized water, (b) Effect of time to absorbances of aqueous solution of alkali lignin at 278 nm

were obtained at the concentration of 0.0001, 0.0002, 0.0003, 0.0004, 0.0005, 0.001, 0.002, 0.003, 0.004 and 0.005 g/L. All absorbance at 278 nm wavelength were shown in Fig. 3 as data points.

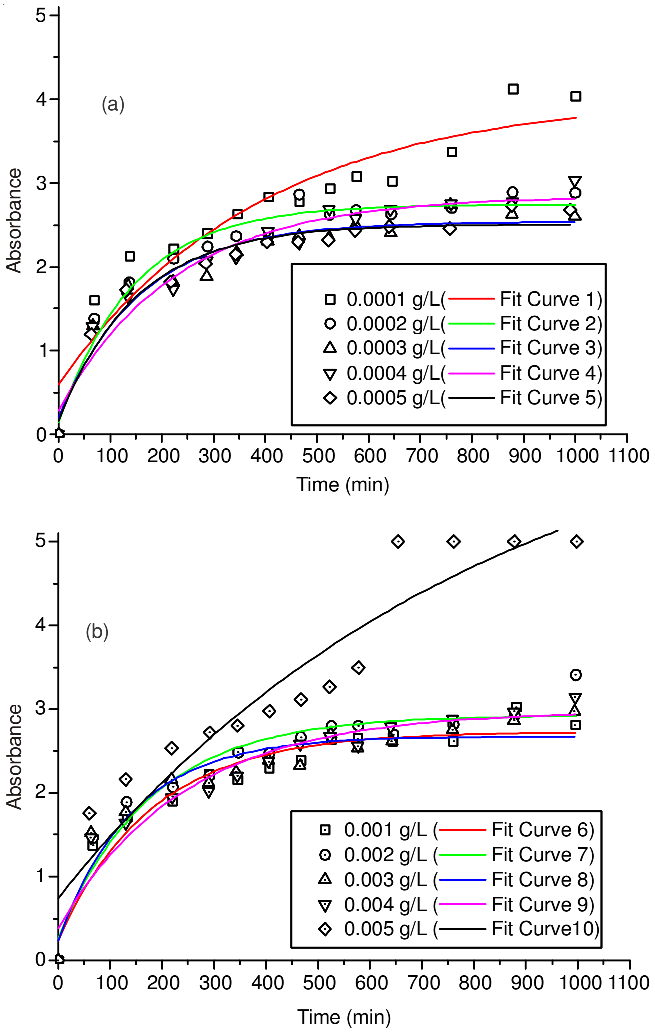

Fig. 3. Absorbance at 278 nm of alkali lignins in [BMIm]Cl dilute solution. (a) [BMIm]Cl concentration at ten-thousandth (b) [BMIm]Cl concentration at thousandth

Figs. 2 and 3 indicated that the absorbance of all solutions becomes higher with the time and the data tend towards stability after 12 h as an exponential increase. While the concentration of [BMIm]Cl aqueous solutions was lower than 0.002 g/L, the dissolved amount of alkali lignin was increasing as a result of the absorbance raising. Conversely, the alkali lignin dissolved amount was increasing with the concentration of [BMIm]Cl condensed.

The UV absorption spectra of alkali lignins dissolved in 0.005 g/L [BMIm]Cl dilute solution is shown as Fig. 4. Compare this figure with Fig. 2a indicated that [BMIm]Cl made aqueous solution grown the structure selectivity by the smoother curves. The solubility of alkali lignin also became higher as the dissolving time goes on.

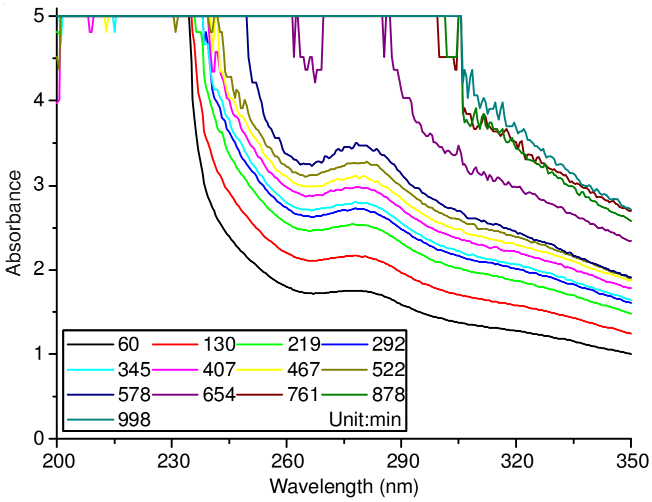

Fig. 4. UV absorption spectrums of alkali lignin samples dissolved in 0.005 g/L [BMIm]Cl aqueous solution

Four solutions of alkali lignin dissolving samples at typical concentrations of [BMIm]Cl were shown as Fig. 5. It is obvious shown that high-purity [BMIm]Cl can dissolve the alkali lignin efficiently, the mixture became a high viscosity liquid not crystallization at 30 ºC and the dissolving amount of pure [BMIm]Cl is higher than the maximum of deionized water *via* the shade of solutions after 12 h. Also it can be inferred that a critical point exist in a special concentration of [BMIm]Cl dilute solution between deionized water and pure [BMIm]Cl.

Dissolution kinetics derivation of alkali lignin in [BMIm]Cl dilute solutions: Fitting the experimental data of Fig. 3 using exponent equation $A = A_0 + K \exp(-t/\tau)$, the fitting parameters are calculated in Table-2. On account of the adjusted R-squares of exponential fitting in last column of Table-2, it

TABLE-2
FITTING COEFFICIENTS OF EXPERIMENTAL ABSORBANCE USING EXPONENTIAL EQUATION

i	[BMIm]Cl concentration x_i (g/L)	A_{0i}		K_i		τ_i		Statistics	
		Value	Error	Value	Error	Value	Error	Reduced Chi-Sqr	Adjusted R-Square
1	0	5.0176	0.0504	-4.9695	0.1464	93.8424	6.2810	0.0210	0.9893
2	0.0001	4.0384	0.4418	-3.4453	0.4201	388.0390	127.3730	0.1251	0.8816
3	0.0002	2.7464	0.0703	-2.6054	0.1550	146.3161	19.8869	0.0262	0.9571
4	0.0003	2.5388	0.0850	-2.3389	0.1734	159.7011	27.6718	0.0339	0.9341
5	0.0004	2.8480	0.1262	-2.5652	0.1818	229.7268	41.6023	0.0389	0.9383
6	0.0005	2.5097	0.0707	-2.3435	0.1488	151.8788	22.5861	0.0250	0.9512
7	0.001	2.7320	0.1018	-2.4874	0.1853	181.3086	32.5163	0.0398	0.9327
8	0.002	2.9296	0.1197	-2.6649	0.2207	178.7685	35.5895	0.0564	0.9180
9	0.003	2.6786	0.0973	-2.4427	0.2143	144.2412	29.4453	0.0511	0.9108
10	0.004	2.9807	0.1552	-2.6005	0.2088	243.8133	51.3384	0.0513	0.9226
11	0.005	7.0735	2.1873	-6.3293	2.0209	814.3812	473.9310	0.2433	0.8843

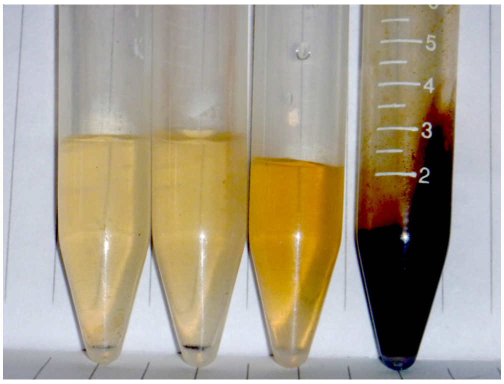

Fig. 5. Alkali lignin solutions in four [BMIm]Cl concentrations: from left to right, 0.0001 g/L, 0.001 g/L, deionized water and pure [BMIm]Cl (purity > 99 %)

can be derived that the progress of alkali lignin dissolving in [BMIm]Cl dilute solutions at room-temperature is conformed to the first order reaction in statistics.

Refer to the fitting error of each parameter, the equation coefficients τ_i, which could be called time constant, has significant influence on the absorbance (A_i) depending on the [BMIm]Cl concentration (x_i). First order differentiation was used to determinate the relationship between x_i and τ_i and the consequence is shown in Fig. 6.

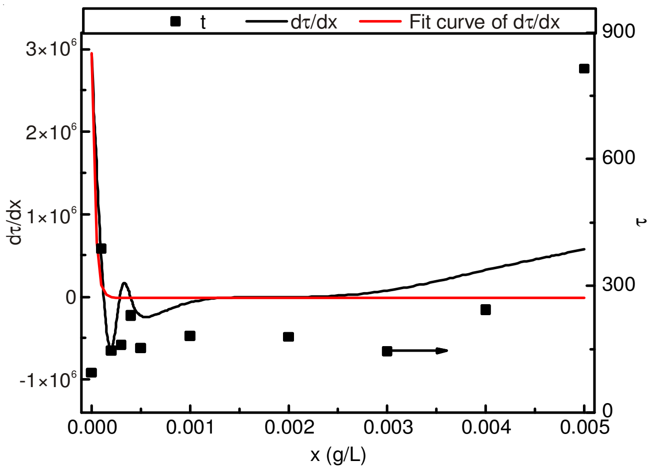

Fig. 6. Relationship between x_i and τ_i

The solutions of different [BMIm]Cl concentration has quantitative relations as differential exponent equation by fitting on Fig. 6:

$$\frac{d\tau}{dx} = -7.92143\times10^{3} + 2.95289\times10^{6}\exp(-x/3.38795\times10^{-5})$$

And the critical point as assumed earlier can be illustrated from the tangential point of two curves in Fig. 6, probably 0.002 g/L, which is deduced the effect of water hydrogen bond prior and the interaction of [BMIm]Cl afterwards.

Conclusion

The alkali lignin is a recyclable waste but a hard-to-use pollution. Dissolving the lignin using green agents will make the post treatment process become environment friendly. Ionic liquids have unparalleled advantages in green solutions since they were applied in the field of biomass resource. This paper made an experiment to dissolve alkali lignin powder in a sequence of [BMIm]Cl dilute aqueous solutions at room-temperature. Three preliminary conclusions are obtained as follows: Both water and [BMIm]Cl can dissolve alkali lignin and the final dissolving amount of pure [BMIm]Cl is higher than the maximum of deionized water. [BMIm]Cl made aqueous solution grown the structure selectivity while using for dissolve alkali lignin. The relationship between the dissolving amount of alkali lignin and the concentration of [BMIm]Cl solutions is not linear until 0.002 g/L as the inflection point. The solubility of alkali lignin in [BMIm]Cl dilute solutions at room-temperature can be fitted using exponent equation and the key coefficient τ_i has differential exponent related to the [BMIm]Cl concentration.

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