

Research Article

Basicity Characterization of Imidazolyl Ionic Liquids and Their Application for Biomass Dissolution

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Received 11 September 2017; Revised 7 November 2017; Accepted 6 December 2017; Published 30 January 2018

Academic Editor: Bhaskar Kulkarni

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Alkalinity determination is of crucial significance for the applications of basic ionic liquids with imidazolyl. In this work, the ionization constant pK_b value and acid function H_- values of ionic liquids synthesized were calculated by pH method and UV spectrum-Hammett method. The dissolution ratio of biomass in these ionic liquids was measured at different temperatures. Finally, the relationship between the alkalinity and structure of these ionic liquids was discussed, and the relationship between the alkalinity of ionic liquid and the dissolution mechanism biomass was also discussed. The results show that the basicity of carboxylate ionic liquids is determined mainly by their anions, whereas cations take some finely tuned roles. Furthermore, cations and anions are equally important and are involved in dissolution mechanisms.

1. Introduction

Since the discovery of air- and water-stable ionic liquids (ILs) by Wilkes in 1992 [1], the research and development (R&D) of ILs have attracted the keen interest of both scientists and engineers [2–4]. Ionic liquids (ILs), generally defined as organic salts that melt below 100°C, have been closely studied because they are designable, thermally stable, nonvolatile, and capable of dissolving even polymeric compounds [5–7]. Such properties have led to an explosion in their applications as green, designable solvents for a variety of processes linked to green chemistry and clean technology [8–10]. The introduction of the specific functional group in ionic liquid anions or cations is to form functional ILs [11, 12]. Functionalized ILs can be divided into chiral ionic liquids, acidic ionic liquids, basic ionic liquids, reagents, and catalysts supported by ionic liquids and so on [13–15].

Among them, the basic ionic liquid is a kind of important functional ionic liquid in recent development [16, 17]. Basic ionic liquids not only have the physical properties and advantages of conventional ILs but also have the advantages of inorganic bases, such as stable performance in water and air,

being easy to separate, reuse, and adjust, being noncorrosive, being nonvolatile, and can be mixed with many organic solvents. It can not only be used as a solvent in the reaction medium but also can be used as a catalyst. At present, it has played an important role in various fields such as catalysis, adsorption, and separation [18–20]. Recently, cellulose reprecipitated after being dissolved in ILs could show enhanced enzymatic hydrolysis because of a decrease in its crystallinity [21]. Given that ILs can dissolve not only cellulose but also biomass [22], many researchers have extended this IL-assisted method of cellulose pretreatment to various lignocellulosic biomasses [23–25]. Some of them have demonstrated an IL-assisted fractionation of carbohydrate and lignin from lignocellulosic biomass for enhancing enzymatic hydrolysis of carbohydrate and/or utilizing lignin as feedstock for value-added products. However, the acid-base properties of ILs, which are decided by the anions and cations, are also closely related to the dissolution of biomass. Started from the study of basic ionic liquids, the alkalinity characterization methods of basic ionic liquids were studied to lay the foundation for the biomass treatment in this work.

The characterization of acid and basic strength is an important aspect of the study of acid and alkali substances, which has theoretical and guiding for the development of these substances [26, 27]. However, there are few reports on the study of the alkalinity characterization of basic ionic liquids. It is an urgent need to develop and perfect the alkaline characterization method of basic ionic liquids and deepen the study on the relationship between the basic strength of ionic liquids and their structures. The difference of anions and cations in ionic liquids is also the key to the dissolution ratio. In this work, a series of basic ionic liquid were synthesized and characterized. The ionization constant pK_b value and acid function H_- values of a series of basic ionic liquids were determined by pH method and UV spectrum-Hammett method. The relationship between the basicity and structure of these ionic liquids was discussed. Finally, the dissolution ratio of biomass in these ILs was determined at different temperatures, and the effects of anionic and cationic structure on biomass dissolution ratio were examined.

2. Experimental

2.1. Materials. Trimethyl phosphate, N-methylimidazole, KOH, ethyl acetate, potassium acetate, and methanol are all analytically pure. 1-Ethyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, and 1-pentyl-3-methylimidazolium chloride were made in the laboratory. ^1H NMR (400 MHz) spectra were measured in DMSO- d_6 at room temperature. Chemical shifts (δ) were reported in ppm, with tetramethylsilane (TMS) as an internal standard. The pH was measured using a Sartorius PB-10 pH meter (Guangzhou, China). The H_- value was measured using a DR6000 UV spectrophotometer (HACH, Germany). Bromothymol blue (BTB) was analytical grade. *Eucalyptus robusta* Smith as wood materials were collected from Guangdong Paper Company, Guangzhou, China. The biomass was washed, air-dried, and then finely grounded with a grinder and sieved before use.

2.2. Synthesis and Characterization of ILs. In this study, a series of basic ionic liquids were synthesized by the method as shown in Figure 1. The carboxylic acid ionic liquids were obtained by the anion exchange reaction between acetic acid potassium salt and a series of cationic halogen compounds. Hydroxide alkaline ionic liquid was obtained by the anion exchange reaction between hydroxide potassium and a series of cationic halogen compounds.

The synthesis methods of ionic liquids were referenced as listed in [28, 29]. Ionic liquids are in the following order.

(1) [Mmim][DMP]; (2) [Emim][Ac]; (3) [Bmim][Ac]; (4) [C5mim][Ac]; (5) [Bmim][OH].

1,3-Dimethyl-imidazole Dimethyl Phosphate ([Mmim][DMP]). ^1H NMR (400 M, d_6 -DMSO): δ = 3.29 (d, 2H), 3.88 (m, 3H), 4.77 (s, 3H), 7.90 (m, 2H), 9.70 (s, 1H).

1-Ethyl-3-methylimidazolium Acetate ([Emim][Ac]). ^1H NMR (400 M, d_6 -DMSO): δ = 1.42 (t, J = 7.2 Hz, 3H), 1.62 (s, 3H), 3.91 (s, 3H), 4.25 (m, 2H), 7.96 (s, 1H), 7.86 (s, 1H), 10.12 (s, 1H).

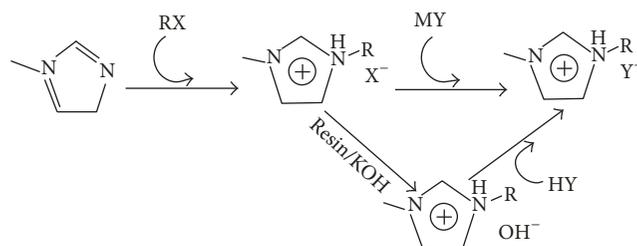


FIGURE 1: Typical preparation routes for ionic liquids (R = alkyl; X = [DMP] $^-$, Cl $^-$, Br $^-$, I $^-$; M = Na $^+$, K $^+$; Y = [AC] $^-$).

1-Butyl-3-methylimidazolium Acetate ([Bmim][Ac]). ^1H NMR (400 M, d_6 -DMSO): δ = 0.87 (t, J = 7.2 Hz, 3H), 1.22 (m, 2H), 1.53 (s, 3H), 1.74 (m, 2H), 3.84 (s, 3H), 4.16 (t, J = 7.2 Hz, 2H), 7.74 (d, J = 1.6 Hz, 1H), 7.81 (d, J = 1.6 Hz, 1H), 9.71 (s, 1H).

1-Pentyl-3-methyl Imidazolium ([C5mim][Ac]). ^1H NMR (400 M, d_6 -DMSO): δ = 5.56 (t, J = 7.2 Hz, 3H), 5.96 (m, 2H), 6.37 (s, 3H), 6.51 (m, 2H), 7.88 (s, 3H), 8.64 (s, J = 7.2 Hz, 3H), 8.99 (m, 2H), 9.34 (d, 1H), 12.58 (s, 1H), 14.61 (s, 1H).

1-Butyl-3-methylimidazolium Hydroxide ([Bmim][OH]). ^1H NMR (400 M, d_6 -DMSO): δ = 0.81 (3, J = 7.2 Hz, 3H), 1.22 (m, 2H), 1.71 (m, 2H), 3.80 (s, 3H), 4.20 (t, J = 7.2 Hz, 2H), 7.78 (d, J = 1.6 Hz, 1H), 7.86 (d, J = 1.6 Hz, 1H), 8.49 (s, 1H).

2.3. Alkalinity Characterization

2.3.1. pH Value Method. Basic ionic liquids (1–4): before the experiment, the ionic liquid was dried in a vacuum for 12 h and then mixed with a certain proportion of water to get the ionic liquid concentration of 0.1, 0.01, 0.001, and 0.0001 mol·L $^{-1}$. The pH value was measured by pH meter, and [H $^+$] and [OH $^-$] were calculated. The K_b values can be obtained from formula (2). Then the pK_b values were obtained.

2.3.2. UV Spectrum-Hammett Method. Basic ionic liquids (1–5): the same concentration of bromothymol blue indicator was added to the aqueous solution of 0.1 mol·L $^{-1}$ HCl and NaOH, respectively, to determine the UV-Vis absorption in the acid and alkali solution. The alkaline ionic liquid aqueous solution was mixed with 0.1, 0.05, and 0.01 mol·L $^{-1}$. The same concentration of bromothymol blue indicator was added to the aqueous solution and the aqueous solution of the basic ionic liquid as reference to for the UV spectrum (time scanning), respectively. By comparing the UV-Vis absorbance in the alkaline aqueous solution, H_- was calculated according to function (6).

2.4. Application of Basic Ionic Liquids in the Field of Biomass Dissolution

2.4.1. Dissolution of Eucalyptus. 0.2 g of the *Eucalyptus* powder was taken for each experiment and 5 g ionic liquid was added to each sample. A microwave extraction apparatus (XH-100B, XIANGHU Microwave, Beijing, China) was

chosen to improve the efficiency of wood dissolution in ionic liquids. The pretreatment conditions were as follows: microwave power, 500 W; reaction time, 30 min; and ratio of solid to liquid, 1:25. In this paper, all ionic liquid could be recycled 6 to 8 times according to preliminary studies. The dissolution ratio of biomass at the given temperature could be calculated from (1). The dissolution ratio value of biomass in each IL was measured at the temperature range from 80°C to 120°C with 10°C intervals.

Dissolution ratio (%)

$$= \frac{\text{untreated eucalyptus powder (g)} - \text{residue}^a \text{ (g)}}{\text{untreated eucalyptus powder (g)}} \quad (1)$$

× %,

where ^aresidue is the residual wood powder after the reaction.

2.4.2. Spectroscopic Analysis (FT-IR). FT-IR spectra were recorded on a Nicolet 6700 spectrometer (Vector 33, Bruker, Karlsruhe, Germany) operating in the wavelength range of 4000–400 cm⁻¹. Each sample was coated by potassium bromide (KBr) and formed into a pellet for analysis.

3. Results and Discussion

3.1. The Principle of pH Value Method. In the aqueous solution of alkaline ionic liquids, basic anion hydrolysis equilibrium will happen, for example,



Definition of K_b is

$$K_b = \frac{[HB][OH^-]}{[B^-]} \quad (3)$$

Mass conservation is

$$C_{B^-} = [B^-] + [HB] = A^+ \quad (4)$$

Charge conservation is

$$[A^+] + [H^+] = [B^-] + [OH^-] \quad (5)$$

Get

$$C_{B^-} \times \frac{K_b}{[OH^-] + K_b} + [H^+] = [OH^-] \quad (6)$$

(The C_{B^-} approximation is equal to the concentration of the solution.)

Above all kinds of [HB], [OH⁻], [B⁻], [A⁺], [H⁺], and [OH⁻] are the molar concentration of chemical groups. The pH value was measured by pH meter; [H⁺] and [OH⁻] were calculated. The K_b values can be obtained from (6). Then the pK_b values were obtained.

3.2. pK_b Value of Alkaline Ionic Liquid. Figure 2 is the pK_b value of basic ionic liquid which is calculated by the pH. As shown in Figure 2, the basicity of ionic liquids with different anions is different. The pK_b of these ILs increase in the order: [Mmim][DMP] < [C5mim][AC] < [Bmim][Ac] < [Emim][Ac]. The pK_b mean values are 10.60, 9.58, 9.48, and 9.25. Therefore, the basicity of these ILs decreased in the order: [Emim][Ac] > [Bmim][Ac] > [C5mim][AC] > [Mmim][DMP]. This is consistent with the principle of acid and alkali; that is, the stronger the acidity, the weaker the basicity of the conjugate base. From the comparison between [DMP]⁻ and [AC]⁻, [DMP]⁻ is more difficult to dissociate in aqueous solution, and, at the same concentration, the concentration of [DMP]⁻ in aqueous solution is lower. According to (2), the concentration of free OH⁻ decreases, and the alkalinity decreases. The results were similar to those in early reported literatures and showed that the determination results of basic ionic liquids with pK_b were reliable and can be applied in the basicity forecast of ionic liquids.

3.3. The Principle of Hammett Method. UV spectroscopy (Hammett method) was used to evaluate the concentration of the deprotonated acid indicator (named B⁻) in aqueous solution. By measuring the ratio of indicator [B⁻]/[HB], calculate Hammett H_- function value:

$$H_- = -\lg \frac{\alpha_{H^+} \cdot \gamma_{B^-}}{\gamma_{HB}} = pK(HB) + \lg \frac{[B^-]}{[HB]} \quad (7)$$

$$= pK(HB) + \lg \frac{A_0 - A_{a,max}}{A_{b,max} - A_0},$$

in which, $pK(HB)$ is the dissociation constant of acid indicator, and [B⁻] and [HB] are the activity of alkaline species and acidic species, respectively. H_- represents an acidic function of a negatively charged conjugate base and its conjugate acid, which indicates the ability to lose protons. The absorbance A in UV absorbance is proportional to the activity of the species, and the basic indicator species and acidic species of absorption peaks vary greatly. Therefore, the absorbance of [B⁻] and [HB] can be substituted for the acidity function of alkaline species and acid species.

3.4. H_- Value of Basic Ionic Liquid. Figure 3 summarizes the changes of UV-Vis absorption of the bromothymol blue (BTB). It can be seen from Figure 3(a) that there is a strong absorption peak at 440 nm when the BTB does not react with the base. With the increase of hydroxyl ions, BTB absorption peak at 440 nm disappeared and redshift in a new absorption peak at 640 nm and its growing strength. This peak is caused by the transfer of hydrogen from the phenolic group on the molecule. With the increasing of hydroxyl ion concentration, the intensity of absorption peak increases at 640 nm. It is unchanged when it increased to a certain extent. BTB and a large number of hydroxyl ions' interaction make hydrogen on recognition sites away, which increases the electron cloud density of the oxygen atoms on phenolic hydroxyl groups. The conjugation bond on the benzene ring result from the transfer of intramolecular charged, which leads to the new

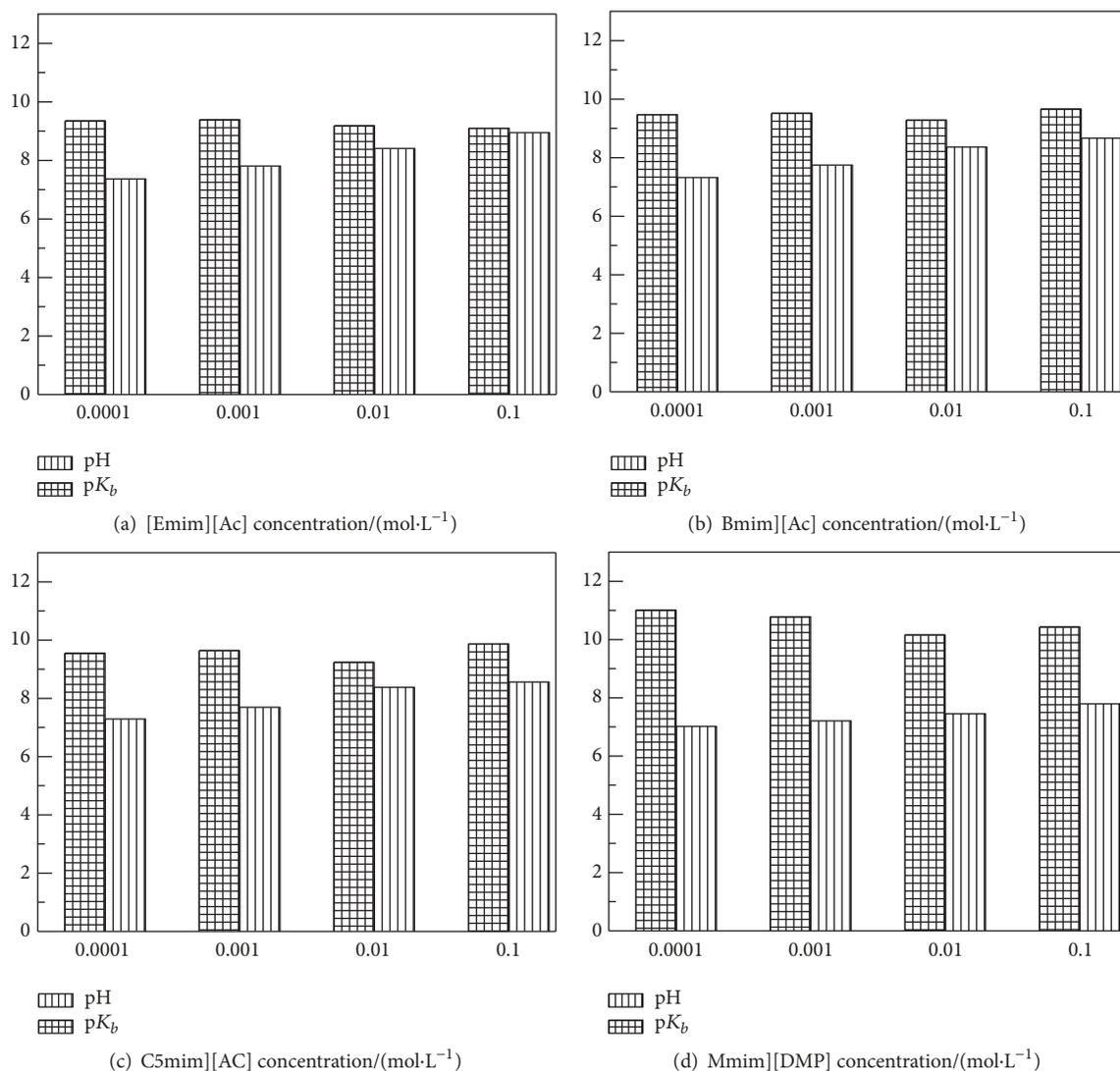


FIGURE 2: The pH and pK_b value of alkaline ionic liquid.

absorption peak appearing at 640 nm. At the same time, the color of the solution of BTB also changed from light yellow to blue. With the increasing of solution concentration of OH⁻, blue gradually deepened. There are no longer changes when the concentration reaches a certain level; the variation of the curve in Figure 3(a) is consistent with this description.

It can be seen from Figures 3(b), 3(c), and 3(d) that BTB and a large number of acetate ions' interaction make hydrogen on recognition sites away, which result from the transfer of intramolecular charge. These lead to the new absorption peak appearing at 640 nm. The absorption peak of BTB at 640 nm increases with the increasing of ionic liquid concentration. At the same concentration, the absorption peak of BTB at 640 nm decreases with the increasing of the alkyl chain. This is because an increase in the length of alkyl chain leads to the electron donating ability weakening, which increases the positive charge density of the imidazole ring. The interaction between BTB and acetate ions was increased

and the number of free acetate ions was decreased. Therefore, the stronger the alkaline of ionic liquids, the stronger the absorption peak intensity at 640 nm.

The concentration of BTB was 1.6×10^{-3} mol·L⁻¹. Dissociation constant of BTB in aqueous solution: pK(HB) = 7.3 [30]. The maximum absorption peak at 640 nm of the basic $A_{b,max} = 1.60$; acid absorption peak $A_{a,max} = 0$.

It can be seen from Table 1 that the absorption peak of BTB increases with the increasing of ionic liquid concentration. At the same concentration, the absorption peak of BTB decreases with the increasing of the alkyl chain. This is because an increase in the length of alkyl chain leads to the electron donating ability weakening, which increase the positive charge density of the imidazole ring. The interaction between BTB and acetate ions was increased and the number of free acetate ions was decreased. The effect of H on phenolic hydroxyl groups in BTB molecules is less, and the basicity weakened. And the [Bmim][OH] contains strong OH⁻ that

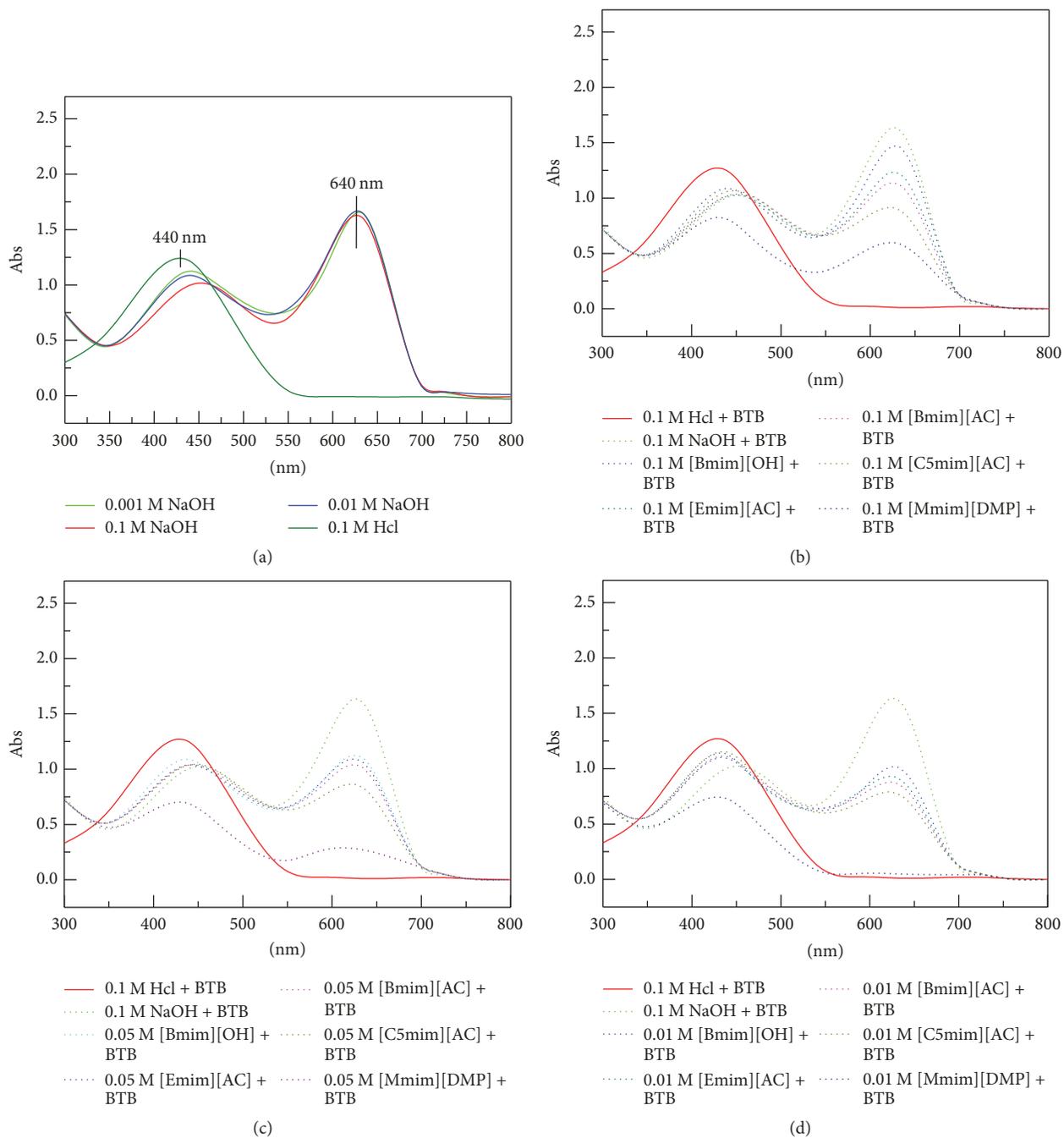


FIGURE 3: UV-Vis absorption of BTB in alkaline and acidic solutions and in different concentrations of alkaline ionic liquids. ((a) BTB in alkaline and acidic solutions; (b) BTB in 0.1 M ionic liquid; (c) BTB in 0.05 M ionic liquid; (d) BTB in 0.01 M ionic liquid.)

TABLE 1: H_{-} values in different concentrations of alkaline ionic liquids.

ILs	H_{-} in different concentrations ($\text{mol}\cdot\text{L}^{-1}$)		
	0.1	0.05	0.01
[Mmim][DMP]	7.05	6.60	5.79
[C5mim][Ac]	7.39	7.33	7.26
[Bmim][Ac]	7.66	7.53	7.30
[Emim][Ac]	7.79	7.59	7.41
[Bmim][OH]	8.29	7.64	7.52

TABLE 2: Dissolution ratio of biomass in the ILs at different temperatures.

Entry	IL	Dissolution ratio (%)				
		80°C	90°C	100°C	110°C	120°C
(1)	[Mmim][DMP]	24.34	28.85	33.42	38.85	40.33
(2)	[C5mim][Ac]	28.62	37.03	40.62	42.35	44.83
(3)	[Bmim][Ac]	31.54	38.22	44.34	48.19	50.23
(4)	[Emim][Ac]	36.36	45.24	49.33	50.24	52.12
(5)	[Bmim][OH]	27.53	34.80	36.78	37.66	37.05

TABLE 3: Band assignments for FTIR spectra.

Band (cm^{-1})	Assignment
3200–3500	O–H vibrations
1730	C=O stretching vibration
1591	Aromatic skeletal vibration breathing with C=C stretching
1503	Aromatic skeletal vibration
1260	asymmetric bending in CH_3
1251	C–O vibration in the syringyl ring
1050	C–O stretching vibration in cellulose/hemicellulose
890	C–H deformation vibration in cellulose

are difficult to ionize in water, which made its basicity stronger. The basicity of these ILs decreased in the order: [Bmim][OH] > [Emim][Ac] > [Bmim][Ac] > [C5mim][Ac] > [Mmim][DMP].

3.5. Dissolution of Eucalyptus Powder

3.5.1. Anionic and Cationic Structure Dependence of Dissolution Ratio. Table 2 summarizes the relationship between the dissolution ratio of *Eucalyptus* and the basic ionic liquids. It is evident from Table 2 that both cation and anion influence biomass dissolution ratio. From 80 to 90°C, the dissolution efficiency of *Eucalyptus* in imidazolium acetate ionic liquids is significantly higher than imidazolium phosphate ionic liquids. Larger anion size results in a reduction of dissolution; hence it contributes to low ability of H-bonds formation. Within limit, with the increasing of alkalinity of the acetate ionic liquid, the dissolution ratio is increasing. It proved that smaller alkyl-side chain on cations boosts up the dissolution ratio. It is interesting that the maximum dissolution ratio of [Bmim][OH] treated is lower than that of other ionic liquid. Its dissolution ratio should be greater. It may be the [Bmim][OH] is unstable. The introduction of hydroxyl groups and the temperature increasing lead to the breakage of the imidazole ring. All these can lead to the decrease of the dissolution ratio.

3.5.2. FT-IR Analysis of Treated and Untreated Wood Materials. FT-IR analyses of the *Eucalyptus* residue after its extraction by basic ionic liquids with imidazolyl are presented in Figure 4. The FT-IR spectra for the presence of hydroxyl, carbonyl, and carboxyl functional groups, respectively, were analyzed according to literature in Table 3. All these basic ionic liquids were able to dissolve significant amounts of the refined *Eucalyptus*, even though they have been previously

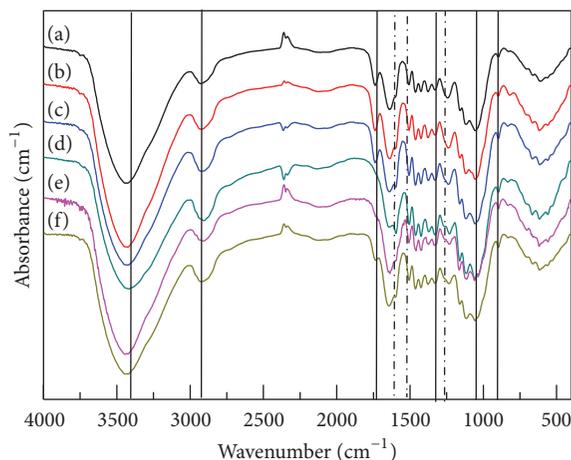


FIGURE 4: FT-IR spectra of the insoluble *Eucalyptus* fraction after treatment with different basic ionic liquids ((a) untreated; (b) [Mmim][DMP]; (c) [C5mim][Ac]; (d) [Bmim][Ac]; (e) [Emim][Ac]; (f) [Bmim][OH]).

observed to enable significant dissolution of polysaccharides in lignocellulosic composites [23]. However, replacing the phosphate with various carboxylate anions, namely, acetate, caused the dissolution efficiency to increase significantly. The band at 1730 cm^{-1} in the original *Eucalyptus* (Figure 4(a)) comes from a C=O stretching vibration in acetyl groups of hemicellulose. After BEING treated by [Bmim][Ac] and [Emim][Ac], this band disappears, indicating that some hemicellulose was lost in the washing step. But when treated by other ionic liquids, the peak is still here, just changing the intensity of the peak.

The characteristic peaks of lignin at $1591/1503\text{ cm}^{-1}$ (C=C stretching vibration), 1260 cm^{-1} (asymmetric bending in

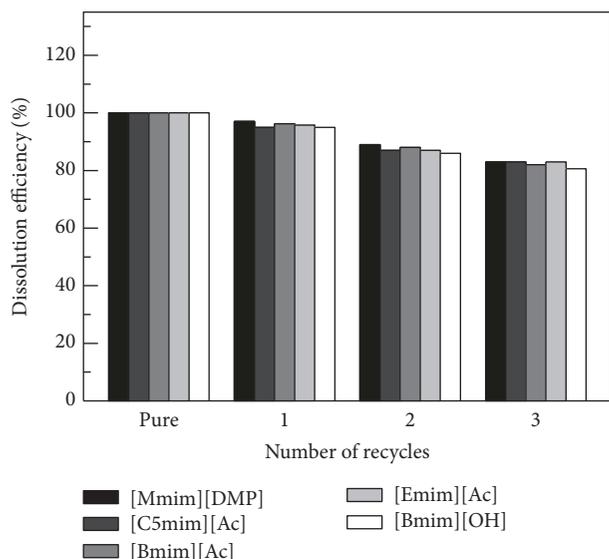


FIGURE 5: The dissolution efficiency of biomass in pure and recycled ILs.

CH_3), and 1251 cm^{-1} (C–O vibration in the syringyl ring) remained in the IL-treated sample but with lower intensity when compared with those from the untreated sample. This decrease in intensity is due to partial removal of lignin during IL treatment. It is interesting that both anions and cations affect the dissolution, as illustrated by the changes in the intensity of the peak. The absorbance bands at 1050 and 890 cm^{-1} , corresponding to C–O stretching vibration in cellulose/hemicellulose and C–H deformation vibration in cellulose, respectively, were more resolved in ILs treated materials, indicating that the ILs treated materials are richer in carbohydrates. These results are consistent with the results obtained from the dissolution rate.

3.5.3. Effect of Solvent Recycling. The recyclability of the solvent without losing its extraction efficiency is essential to achieve economical and environmentally friendly biomass processing. To demonstrate this, the recovered solvent was subjected to rotary vacuum evaporation for 6 h at 70°C . The recovered mass of the ILs after recycling was found to be more than 95% (Figure 5), which indicated these basic ionic liquids as a potentially good recyclable solvent. The reduction in dissolution efficiencies may be due to the water content of the solvent. The recovery efficiency of [Bmim][OH] is the lowest due to the water content of the solvent and it is extremely unstable.

4. Conclusions

(1) Five basic ionic liquids were synthesized and characterized, and their $\text{p}K_b$ value and H_- values were determined by pH method and UV spectrum-Hammett method. The results show that $\text{p}K_b$ values and H_- values can identify sorting the alkalinity strength of basic ionic liquids effectively.

(2) The relationship between the structure of imidazolyl ionic liquid and its alkalinity was investigated; the alkalinity was related not only to the length of alkyl chain in imidazole ring but also to the dissociation activity of anions; the results also show that the Hammett method can be applicable in a variety of solvents to be expected as a routine method for the alkalinity characterization of ionic liquids.

(3) The smaller size of aromatic heterocyclic cation and smaller alkyl-side chain boost up the biomass dissolution. As a whole, both cation and anion influence biomass dissolution and are equally important and are involved in dissolution mechanism. In addition, the stronger basicity of the ionic liquid does not necessarily mean the higher dissolution ratio.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors are grateful for the support of the National Key Research and Development Plan (Grant no. 2017YFB0307901), the National Natural Science Foundation of China (Grant no. 21476091), and the Science and Technology Planning Project of Guangdong Province (Grant no. 2015A020215009). The authors also appreciate the financial support from Science and Technology Planning Project of Foshan in Guangdong Province (Grant no. 2015AG10011).

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