

# Kinetics for the Esterification Reaction of *n*-Butanol with Acetic Acid Catalyzed by Noncorrosive Brønsted Acidic Ionic Liquids

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**S** Supporting Information

**ABSTRACT:** It is very attractive that noncorrosive Brønsted acidic ionic liquids (BAILs) are used as catalysts in liquid catalyst-based reactive distillation columns, which avoids the technical difficulties raised from solid catalysts or corrosive mineral acids. The kinetics for the esterification of *n*-butanol with acetic acid using noncorrosive BAILs as catalysts was therefore studied systemically, to explore the possibility of BAIL-based catalytic distillation processes. The effects of various parameters such as temperature, catalyst loading, and molar ratio of the reactants on the kinetics were examined in detail, and a pseudohomogeneous (PH) kinetic model was used successfully to correlate the experimental data. The kinetic data are for the first time used to interpret clearly the synergistic effect resulted from the acidity and hydrophilicity of BAILs. It is also validated from the comparison of esterification kinetics between noncorrosive BAILs and Amberlyst-15 resin (a commonly used solid catalyst of strong acidity) that noncorrosive BAILs are talented and prospective substitutes for the establishment of liquid catalyst-based reactive distillation processes.

## 1. INTRODUCTION

*n*-Butyl acetate is an important intermediate in chemical and pharmaceutical industries, and it is used widely as a versatile solvent in acrylic polymers, vinyl resins, paints, and coatings to replace the toxic and teratogenic solvents such as benzene, toluene, and acetone, due to its low volatility and lower impact on the environment.<sup>1</sup> The production of *n*-butyl acetate therefore has been growing fast in the past decade due to a continual demand for solvents.

*n*-Butyl acetate is mainly produced by acid-catalyzed esterification reaction of *n*-butanol with acetic acid.<sup>2</sup> The conventional industrial production of *n*-butyl acetate through esterification is carried out in batch process using mineral acids (e.g., sulfuric acid, *p*-toluenesulfonic acid) as catalysts. However, this process faces some serious and unavoidable problems such as side reaction, corrosion of equipment, and tedious isolation of catalyst and product. To overcome the drawbacks from these corrosive homogeneous catalysts, a number of solid heterogeneous catalysts such as heteropolyacids (HPA),<sup>3</sup> molecular sieves,<sup>5</sup> and resins<sup>6,7</sup> have been studied extensively because of their obvious engineering benefits such as easy recycling, few disposal, and less corrosion. For example, Parida et al. have studied the esterification of *n*-butanol with acetic acid in the presence of HPA intercalated Zn/Al HTlc and manganese nodule leached residue as efficient catalysts, respectively.<sup>3,4</sup> Steinigeweg and Gmehling have investigated the kinetics of *n*-butanol with acetic acid in the presence of the resin Amberlyst-15 and utilized the pseudohomogeneous (PH) model to calculate the kinetic constants successfully.<sup>6</sup> Gangadwala and Mahajani have exploited further the side reaction and proposed the kinetic expression for the etherification of *n*-butanol.<sup>7</sup> All these solid acid catalysts are found to be of good catalytic performance and have been used in industrial processes extensively, especially in batch

esterification process. However, for the catalytic distillation process, the esterification reaction takes place in reactive distillation column. The catalyst particles have to be enveloped within wire gauze envelopes and fixed in the reaction zone. With the introduction of catalyst envelopes, the reactive distillation column has inevitably become more complexity and caused several serious technical problems such as hard removal of the deactivated catalyst, inconvenient regeneration of catalyst, and complex vapor–liquid contacting.<sup>8,9</sup> These issues restrain greatly the practical application in continuous catalytic distillation process and remain to be solved. For these reasons, kinetically efficient, noncorrosive, and easily recyclable liquid catalysts for the esterification in a simple reactive distillation column are therefore highly conceived and of important significance.

Brønsted acidic ionic liquids (BAILs), as green media, are thought to be promising catalysts replacing cation-exchange resins or solid acids for the esterification process. They can enable the continuous reactive distillation esterification process in a simply constructed column without difficult installation of solid catalyst. Recently, BAILs have been exploited successfully in the laboratory for many esterification reactions.<sup>10–16</sup> Cole et al. have first synthesized functionalized BAILs beared with an alkyl sulfonic acid and used these BAILs for the esterification of acetic acid with ethanol.<sup>11</sup> On the basis of Cole's work, Gui et al. have further illustrated the merits of using BAILs for esterification.<sup>13</sup> Zhang et al. have also investigated the esterification using *N*-methyl-2-pyrrolidonium methylsulfonate ([NMP][CH<sub>3</sub>SO<sub>3</sub>]) as efficient and reusable catalyst.<sup>15</sup> Huang et al. have explored

**Received:** October 14, 2010

**Accepted:** December 26, 2010

**Revised:** December 24, 2010

**Published:** January 11, 2011

the esterification catalyzed by BAILs and found that 2-pyrrolidonium hydrogensulfate ( $[\text{Hnhp}][\text{HSO}_4^-]$ ) realized the best yield of produced ester.<sup>16</sup> Despite the excellent conversions and selectivities, these results are not entirely satisfactory. For example, very high concentration (around 300% based on the mass of acetic acid) of BAILs must be required for the esterification to achieve considerable conversion.<sup>12</sup> The  $\text{SO}_3\text{H}$ -functional BAILs are also of extremely strong acidity, being similar to the nature of  $\text{H}_2\text{SO}_4$ , which can cause serious equipment corrosion.<sup>11,13,15</sup>  $[\text{Hnhp}]^+$  is found to be unstable in water and can be easily hydrolyzed to give  $\text{H}^+$ , resulting in relatively large corrosion rate.<sup>16</sup> There has been no mention of using noncorrosive BAILs as catalysts in any of these studies. In addition, these studies are only related to the catalytic activities and selectivities of various BAILs. The basic investigation on using noncorrosive BAILs as catalysts to study the intrinsic reaction kinetics is still absent. Hence, we believe that there is a need to investigate the reliable kinetics of *n*-butyl acetate production catalyzed by noncorrosive BAILs, and these results will be applicable to explore the possibility of BAIL-based reactive distillation processes and to provide optimal or important design parameters.

Therefore, the kinetics for the esterification of *n*-butanol with acetic acid catalyzed by noncorrosive BAILs was investigated in this Article. The effects of various parameters such as kind of BAILs, catalyst loading, temperature, and initial mass ratio of reactants were explored in detail. The PH kinetic model based on the activities was also utilized for the correlation of the experimental data.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** 1-Methylimidazole (purity  $\geq 99\%$ ) was purchased from Yancheng BaiYiChem Co., Ltd. (Jiangsu, China). 1,4-Butyl sultone (purity  $\geq 99\%$ ) and tetrafluoroboric acid (40%) solution in water were obtained from Jintan Huadong Chemical Research Institute (Jiangsu, China). The ion-exchange resin Amberlyst-15 was obtained from Rohm and Haas. 1-Methylimidazole and 1,4-butyl sultone were redistilled in vacuum before used. Other reagents such as *n*-butanol, acetic acid, sulfuric acid, triethylamine, *n*-butyl bromide ( $\text{C}_4\text{H}_9\text{Br}$ ), silver oxide, and pyridine were of analytical grade and used without any further purification.

**2.2. Preparation and Characterization of BAILs.** Several BAILs composed of  $[\text{HSO}_4^-]$  anion and different cations were prepared in this Article (Figure 1). The synthesis procedure of pyridinium hydrogensulfate ( $[\text{Hpy}][\text{HSO}_4^-]$ ) was as follows: pyridine (79 g, 1 mol) was placed in a three-necked flask, immersed in a water bath. Sulfuric acid (98 g, 1 mol) solution in water was added slowly over a period of 1 h while stirring and cooling to maintain the temperature at  $0-5^\circ\text{C}$ . The mixture was stirred for 5 h to complete the reaction. Water was removed in vacuum at  $95^\circ\text{C}$  to give the product as a colorless liquid in quantitative yield.  $[\text{Hpy}][\text{HSO}_4^-]$  will soon solidify on cooling.

The synthesis procedure of butyltriethylammonium hydrogensulfate ( $[\text{N}_{2224}][\text{HSO}_4^-]$ ) followed a two-step procedure: Triethylbutylammonium bromide ( $[\text{N}_{2224}][\text{Br}^-]$ ) was prepared in the first step via the alkylation of  $(\text{C}_2\text{H}_5)_3\text{N}$  (35.0 g) with  $\text{C}_4\text{H}_9\text{Br}$  (47.5 g) in ethanol (100 mL) under reflux and vigorous stirring for 6 h. The solvent and unreacted components were removed by rotary evaporation, and  $[\text{N}_{2224}][\text{Br}^-]$  (80 g) as a white solid was obtained after being dried at  $60^\circ\text{C}$  under vacuum for 5 h. The aqueous solution of  $[\text{N}_{2224}][\text{Br}^-]$  (59.5 g, 0.25 mol),

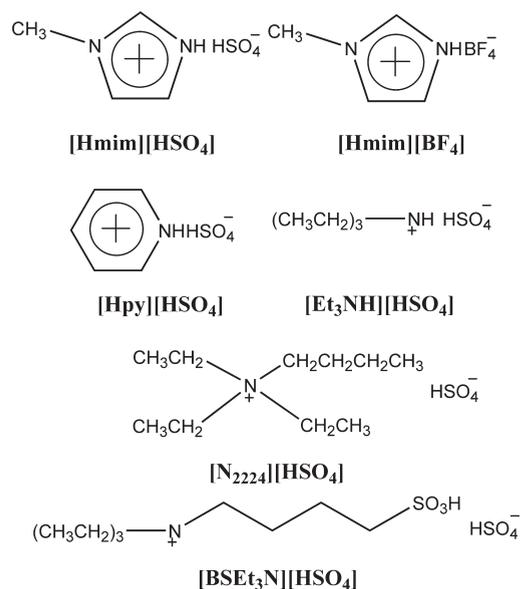


Figure 1. Structure of six Brønsted acidic ionic liquids.

Table 1. Characterization Results of BAILs

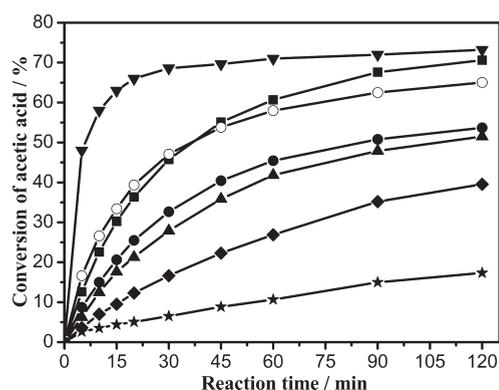
| IL  | melt point ( $^\circ\text{C}$ ) | Hammett acidity values ( $H_0$ ) | corrosion rates (mm/a) |
|---|---------------------------------|----------------------------------|------------------------|
| $[\text{Hpy}][\text{HSO}_4^-]$            | 93                              | 1.61                             | 0.021                  |
| $[\text{Hmim}][\text{HSO}_4^-]$           | 47                              | 1.94                             | 0.011                  |
| $[\text{Et}_3\text{NH}][\text{HSO}_4^-]$  | 81                              | 2.14                             | 1.30                   |
| $[\text{N}_{2224}][\text{HSO}_4^-]$       |                                 | 2.38                             |                        |
| $[\text{BSEt}_3\text{N}][\text{HSO}_4^-]$ |                                 | 1.03                             | 11.2                   |

silver oxide (29 g, 0.125 mol), and sulfuric acid (24.5 g, 0.25 mol) was then mixed and stirred in a container at room temperature for 6 h. The reaction mixture was filtered, and the solution was dried in a vacuum at  $95^\circ\text{C}$ .  $[\text{N}_{2224}][\text{HSO}_4^-]$  was obtained after the removal of water with an overall yield of 90% (on the base of triethylamine).

The preparation methods of 1-methylimidazole hydrogensulfate ( $[\text{Hmim}][\text{HSO}_4^-]$ ) and *N*-triethylammonium sulfate ( $[\text{Et}_3\text{NH}][\text{HSO}_4^-]$ ) were similar to that of  $[\text{Hpy}][\text{HSO}_4^-]$ . The synthesis procedures of 1-methylimidazolium tetrafluoroborate ( $[\text{Hmim}][\text{BF}_4^-]$ ) and *N*-(4-sulfonic acid) butyl triethylammonium sulfate ( $[\text{BSEt}_3\text{N}][\text{HSO}_4^-]$ ) were carried out according to the previous literature.<sup>12,13</sup>

The thermal analysis (Netzsch STA 449C) and  $^1\text{H}$  NMR (BRUKER DPX-300) spectrum of these BAILs were recorded. The Brønsted acidity of these BAILs (Agilent 8453 UV-visible spectroscopy) and the corrosion rate of 316 L stainless steel in the esterification system containing BAILs were also examined according to the previous references.<sup>17,18</sup> The characterization results of melt point, Brønsted acidity, and corrosion rate are summarized in Table 1. The detailed characterization procedure and data can be found in the Supporting Information.

**2.3. Apparatus and Procedure of Esterification Experiments.** The esterification reactions were carried out in a 100 mL glass stirred tank reactor immersed in a constant temperature water bath for maintaining the required reaction temperature. In a typical run, acetic acid (0.25 mol) and *n*-butanol (0.25 mol) were charged into the reactor fitted with a reflux condenser.



**Figure 2.** Equimolar reactions of *n*-butanol with acetic acid at 358.15 K using (■) [Hpy][HSO<sub>4</sub>]; (●) [Hmim][HSO<sub>4</sub>]; (▲) [Et<sub>3</sub>NH][HSO<sub>4</sub>]; (◆) [N<sub>2224</sub>][HSO<sub>4</sub>]; (★) [Hmim][BF<sub>4</sub>] with a dosage of 25% w/w (based on the mass of acetic acid), and using (▼) [BSEt<sub>3</sub>N][HSO<sub>4</sub>]; and (○) the resin Amberlyst-15 with a dosage of 10% w/w.

When the temperature was raised to the desired value, the BAIL catalyst was then added into the reactor. Samples were taken from the reactor at regular intervals and analyzed using N<sub>2</sub> as the carrier gas in a HP 6890 GC analyzer (Agilent) equipped with a FID detector and a capillary column HP-5 (50 m × 0.32 mm × 0.25 μm). The temperature of the inlet and the detector was kept at 473 K. The results obtained via GC were also confirmed from independent titrations using standard sodium hydroxide (0.25 mol/L NaOH) solution. The reliability of the titration method was confirmed with the help of analysis of standard samples containing *n*-butyl acetate to ensure that the hydrolysis of ester does not take place during the course of titration. The analytical uncertainty of GC was less than 2%, which is well within the acceptable limits.

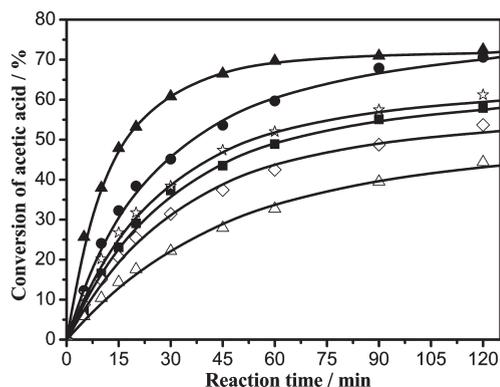
### 3. RESULTS AND DISCUSSION

**3.1. Catalyst Performance.** The esterification of *n*-butanol with acetic acid in the presence of different BAILs as catalysts was conducted for testing the reaction kinetics at 358.15 K, with an acid to alcohol molar ratio of 1:1, and catalyst loading of 25% w/w (based on the mass of acetic acid). It is shown in Figure 2 that the BAILs catalysts exhibit different catalytic activities. Combined with the acidity order of these BAILs ranked by  $H_0$  (see Table 1), it is obvious that the acidity has a great effect on the catalytic performance of the esterification. The stronger acidity the BAILs have, the higher are the catalytic activities. For example, from the kinetics curves, [N<sub>2224</sub>][HSO<sub>4</sub>] shows more efficiently catalytic performance than does [Hmim][BF<sub>4</sub>] because of the stronger acidity of hydrogen sulfate anion relative to tetrafluoroborate anion. [BSEt<sub>3</sub>N][HSO<sub>4</sub>] beared with an butyl sulfonic acid can further improve its Brønsted acidity in comparison to [N<sub>2224</sub>][HSO<sub>4</sub>]. The super strong acidity enables [BSEt<sub>3</sub>N][HSO<sub>4</sub>] to have the best catalytic activity, and this is in accordance with the general phenomena of acid catalysis for the esterification. In addition, it is seen that the conversions of acetic acid at 2 h are similar in the cases of [BSEt<sub>3</sub>N][HSO<sub>4</sub>] and [Hpy][HSO<sub>4</sub>], although their acidities are quite different. The acidities of [Hpy][HSO<sub>4</sub>], [Hmim][HSO<sub>4</sub>], and [Et<sub>3</sub>NH][HSO<sub>4</sub>] are near each other (see Table 1), but the differences in their catalytic performance increase gradually with the prolonging reaction time. Hence, we believe that the acidity of BAIL is not the only factor in determining the catalytic activity. The hydrophilicity of BAILs can

also affect on the catalytic activity, and this effect is in a large part attributable to an expected Le Chatelier effect<sup>19</sup> in which the insolubility of BAIL catalyst in the reaction mixture speeds up the reaction rate. For example, in the presence of [Hpy][HSO<sub>4</sub>], the homogeneous esterification system at the early stage of the reaction becomes heterogeneous, when the reactants acetic acid and *n*-butanol are consumed and the products (ester and water) appear in large quantities. In less than 15 min, the esterification system is found to become turbid. The produced ester forms a light phase, while water and [Hpy][HSO<sub>4</sub>] are combined to be a heavy phase. The unreacted acetic acid and *n*-butanol partition between the two phases. [Hpy][HSO<sub>4</sub>] is almost insoluble with *n*-butyl acetate but miscible with water, so that the produced ester can be extruded rapidly from the heavy phase, resulting in a faster esterification rate. However, in the cases of [Hmim][HSO<sub>4</sub>] and [Et<sub>3</sub>NH][HSO<sub>4</sub>], their esterification systems require long time (about 45 min) to form a liquid–liquid biphasic, and relatively poor conversions are obtained. It may be reasoned that both of them have better solubility with reaction components than does [Hpy][HSO<sub>4</sub>]. The later two esterification systems are comparatively difficult to form phase splitting, leading to the decrease in the reaction rate. In other words, [Hpy][HSO<sub>4</sub>] of greater hydrophilicity rather than [Hmim][HSO<sub>4</sub>] and [Et<sub>3</sub>NH][HSO<sub>4</sub>] contributes to a widening gap between their catalytic performances.

The kinetic data presented in Figure 2 reveal clearly that the acidity and hydrophilicity of BAILs have a synergistic effect on the catalytic performance for the esterification. Varying the cationic structure of BAIL can lead to the slight tuning of acidity and most importantly the dramatic change in hydrophilicity. This provides a new idea for exploring the catalytic processes with the use of noncorrosive BAILs, to avoid the corrosion problem and meanwhile realize the considerable conversion. The corrosion results in Table 1, together with the kinetic data in Figure 2, provide strong evidence for this thought. Even though [BSEt<sub>3</sub>N][HSO<sub>4</sub>] enables the best catalytic performance, it has the strongest acidity to cause serious equipment corrosion. In fact, [BSEt<sub>3</sub>N][HSO<sub>4</sub>] is extremely corrosive and contaminative, similar to the nature of H<sub>2</sub>SO<sub>4</sub>. In contrast to [BSEt<sub>3</sub>N][HSO<sub>4</sub>], [Hpy][HSO<sub>4</sub>] and [Hmim][HSO<sub>4</sub>] are nearly noncorrosive and thought to be green and environmentally benign. Therefore, noncorrosive [Hpy][HSO<sub>4</sub>] and [Hmim][HSO<sub>4</sub>] were used as catalysts in the remainder of the kinetic experiments studied, and a comparison of the kinetic parameters between them and Amberlyst-15 resin was also explored in the following sections.

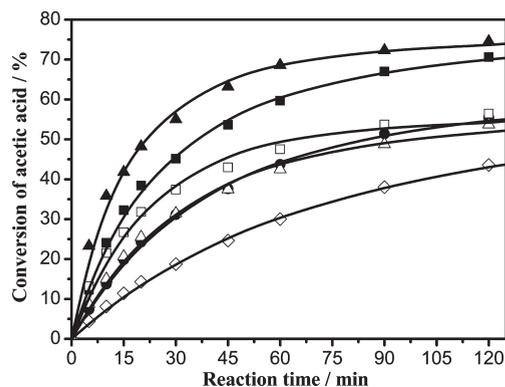
**3.2. Influencing Factors of the Esterification.** The esterification of *n*-butanol with acetic acid in the presence of the resin Amberlyst-15 was investigated for comparison. It is shown in Figure 2 that the conversion profile in the presence of 10% w/w Amberlyst-15 is almost similar to the case of 25% w/w [Hpy][HSO<sub>4</sub>] at times less than 1 h. However, after 1 h, the conversion of acetic acid in the case of 25% w/w [Hpy][HSO<sub>4</sub>] continues to reach at 71%, whereas the conversion using 10% w/w Amberlyst-15 is only 65%. This can be ascribed to the formation of the liquid–liquid biphasic. When [Hpy][HSO<sub>4</sub>] is used as catalyst for esterification, the phase splitting appears in less than 15 min and results in two effects that can facilitate the shift of the esterification reaction to the product side: one is the concentrated [Hpy][HSO<sub>4</sub>] in the heavy phase that can influence greatly the activity coefficient of each component and thus the reaction equilibrium, and the other is the ester being extruded from the heavy phase. As a result, the conversion of acetic acid in the case of 25% w/w [Hpy][HSO<sub>4</sub>] can continue to increase.



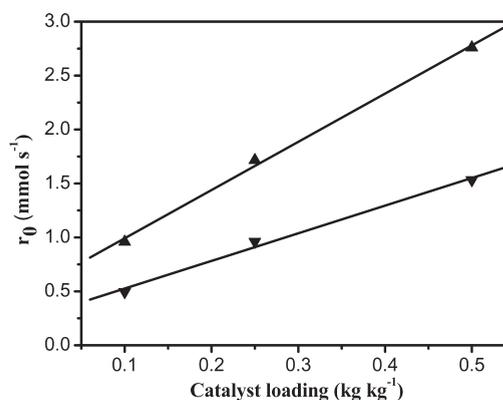
**Figure 3.** Effect of temperature on the conversion of acetic acid with time using [Hpy][HSO<sub>4</sub>] (solid symbol) and [Hmim][HSO<sub>4</sub>] (open symbol) as catalysts at (■, △) 348.15 K; (●, ◇) 358.15 K; (▲, ☆) 368.15 K, acid to alcohol molar ratio of 1:1, and catalyst loading of 25% w/w. The solid lines represent the calculated results from the PH model.

The effect of temperature ranging from 348.15 to 368.15 K on the conversion of acetic acid was investigated using [Hpy][HSO<sub>4</sub>] and [Hmim][HSO<sub>4</sub>] as catalysts. As seen from Figure 3, the conversion of acetic acid increases rapidly with the increase of reaction temperature. For example, in the case of [Hpy][HSO<sub>4</sub>], the conversion of acetic acid at 0.5 h is only about 45% at 358.15 K, whereas when the temperature is raised to 368.15 K, it reaches almost 60%. However, similar conversions of acetic acid at 2 h are obtained when the temperature is raised from 358.15 to 368.15 K. The conversion of acetic acid cannot continue to be enhanced because of the limitation of chemical reaction equilibrium. According to the expression for the constant of chemical equilibrium<sup>20</sup> ( $K_e = 3.8207e^{3581.7/RT}$ ), it is found thermodynamically that the esterification of *n*-butanol with acetic acid is slightly exothermic and the equilibrium constant decreases slowly with the increase of reaction temperature. The high reaction temperature is not positive to the esterification reaction. It is also possible that sideproduct (such as dibutyl ether) would be produced at a temperature higher than 373.15 K.<sup>7,21</sup> However, from kinetics, the increasing reaction temperature is helpful to improve the conversion of acetic acid at a short reaction time. As a result, an optimized reaction temperature should be around 100 °C for [Hpy][HSO<sub>4</sub>] to reach the best catalytic activity. In contrast, [Hmim][HSO<sub>4</sub>] shows relatively poor catalytic activity under the identical conditions, due to the weak synergistic effect of its acidity and hydrophilicity. This suggests that the esterification reaction time in the case of [Hmim][HSO<sub>4</sub>] should be prolonged appropriately so as to realize considerable conversions.

The experiments were also carried out at a temperature of 358.15 K and an acid to alcohol molar ratio of 1:1, to investigate the effect of catalyst loading varying from 10% w/w to 50% w/w (based on the mass of acetic acid). It is obvious that increasing the amount of catalyst is positive to the improvement of conversion of acetic acid (see Figure 4). The conversion of acetic acid increases rapidly with the catalyst loading ranging from 10% w/w to 25% w/w. However, only a fair change is observed in the conversions of acetic acid when the dosage is raised from 25% w/w to 50% w/w. It suggests that the further increase in the amount of catalyst is not very necessary for the conversion of reactants. This may be reasoned that the increase of catalyst loading provides more acidic active sites that are



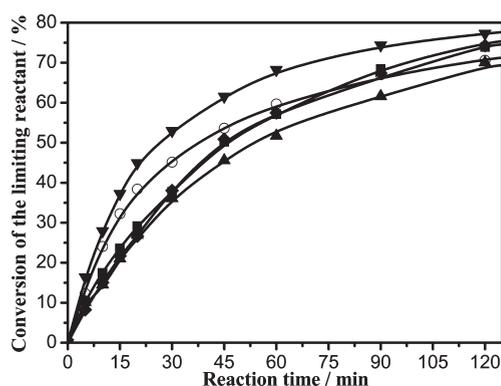
**Figure 4.** Effect of catalyst loading on the conversion of acetic acid with time using [Hpy][HSO<sub>4</sub>] (solid symbol) and [Hmim][HSO<sub>4</sub>] (open symbol) as catalysts at 358.15 K, acid to alcohol molar ratio of 1:1, and catalyst loading of (●, ◇) 10% w/w; (■, △) 25% w/w; (▲, □) 50% w/w. The solid lines represent the calculated results from the PH model.



**Figure 5.** Effect of catalyst loading on the initial reaction rate in the presence of (▲) [Hpy][HSO<sub>4</sub>] and (▼) [Hmim][HSO<sub>4</sub>] at 358.15 K and acid to alcohol molar ratio of 1:1. The solid lines represent the model regression of  $r_0$  versus  $M_{cat}$ .

helpful for the generation of active intermediates and the conversion of acetic acid. However, the conversion of acetic acid is not improved too much when there exists an excess of catalyst active sites than required by the reactant molecules. Beyond a certain catalyst loading, the conversion of acetic acid is mainly influenced by chemical reaction equilibrium. Therefore, 25% w/w catalyst loading is considered suitable and is used in most of the esterification experiments. In addition, the initial reaction rate in the presence of [Hpy][HSO<sub>4</sub>] and [Hmim][HSO<sub>4</sub>] was calculated at the starting point of the reaction ( $t = 0$ ) and proposed to be a linear function of the catalyst loading in the PH model (see next section). The initial reaction rate for both catalysts is proved to increase linearly with the increase of catalyst loading, in good agreement with the PH model (Figure 5). In contrast to the influence of catalyst loading on the conversion of acetic acid, the initial reaction rate is positively related to the catalyst loading in a whole range from 10% w/w to 50% w/w. This should be ascribed to that the initial reaction is far away from the reaction equilibrium so that more active sites available is beneficial to the initial reaction rate.

The effect of the acid to alcohol molar ratio for the esterification system was also investigated by varying the acid to alcohol molar ratio (ranging from 1:3 to 3:1). It should be noted that the



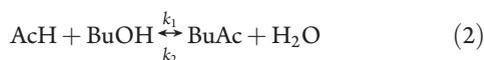
**Figure 6.** The conversion of the limiting reactant with time using [Hpy][HSO<sub>4</sub>] as catalyst at 358.15 K, catalyst loading of 25% w/w, and initial molar ratio of (■) 3:1; (▼) 2:1; (○) 1:1; (▲) 1:2; (◆) 1:3. The solid lines represent the calculated results from the PH model.

limiting reactant is acetic acid for the runs at initial acid to alcohol ratios of 1:3 and 1:2, and it is *n*-butanol for the runs at initial acid to alcohol ratios of 2:1 and 3:1. At an equimolar feed ratio of 1:1, either the acid or the alcohol can be considered to be the limiting reactant. As seen from Figure 6, higher conversions of acetic acid are obtained with the initial acid to alcohol ratio of 2:1 in comparison to the case of 1:1. However, other nonequimolar ratios of initial acid to alcohol induce poor conversions, and the reaction profiles in the cases of 3:1 and 1:3 are close to each other. It reveals that an appropriate initial excess of acid rather than alcohol around the initial ratio of 1:1 appears to be more beneficial. This may be explained by that when the homogeneous esterification system becomes turbid in less than 15 min and forms a liquid–liquid biphasic system, the slight excess of acetic acid can drive *n*-butanol into the heavy phase (containing mainly water and [Hpy][HSO<sub>4</sub>]) for a further reaction, due to its good solubility in the mixture of water, [Hpy][HSO<sub>4</sub>], and acetic acid. As a result, good conversions in the case of 2:1 are realized. However, too much acetic acid can increase the miscibility of the reaction mixture and make the esterification system difficult to form the liquid–liquid biphasic system, leading to a slight drop in the conversion of the limiting reactant. In addition, in the cases of 1:2 and 1:3, the excess *n*-butanol partitions in the light phase (ester) more than in the heavy phase due to its insolubility in water and [Hpy][HSO<sub>4</sub>]. After phase splitting occurs, an ineffective contact between *n*-butanol and acetic acid or between reactants and catalyst induces relatively poor conversions.

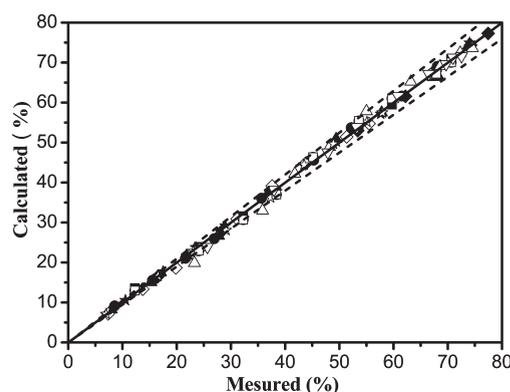
**3.3. PH Model and Kinetic Parameters.** Janowsky et al.<sup>20</sup> have studied the kinetics of the esterification of *n*-butanol with acetic acid in the presence of Lewatit SPC 108 and 118 resins as catalysts and proposed a pseudohomogeneous (PH) kinetic model for the esterification reaction. The expression for equilibrium constant (eq 1) proposed by them will be used in this work.

$$K_e = 3.8207 \exp(3.5817 \times 10^3 / RT) \quad (1)$$

The reaction equation for the esterification of *n*-butanol with acetic acid was written as



The PH model is usually applied for the system where one of the reactants or solvents was of high polarity, and it is used to interpret the experimental kinetic data for many esterification



**Figure 7.** Comparison between measured and calculated conversions of acetic acid in the presence of [Hpy][HSO<sub>4</sub>] under conditions as follows: reaction temperature of 348.15 K (☆), 358.15 K (□), 368.15 K (▽); catalyst loading of 10% w/w (◇), 25% w/w (○), 50% w/w (△); initial molar ratio of 1:1 (■), 1:2 (●), 1:3 (▲), 2:1 (◆), 3:1 (★). The dash lines represent the deviation limits of ±5%.

reactions.<sup>6,7,22,23</sup> In this work, the esterification kinetic equation of *n*-butanol with acetic acid in the presence of [Hpy][HSO<sub>4</sub>] and [Hmim][HSO<sub>4</sub>] as catalysts can be established on the basis of the PH model. For the nonideal mixing behavior of the bulk liquid phase, the activities of the components are employed to describe the kinetic model. For a homogeneously catalyzed system, the reaction rate equation for the PH model in terms of equilibrium constant is as follows:

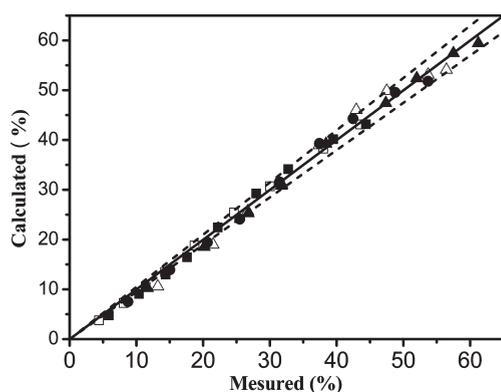
$$\begin{aligned} r &= M_{\text{cat}} (k_1 a_{\text{AcH}} a_{\text{BuOH}} - k_2 a_{\text{BuAc}} a_{\text{H}_2\text{O}}) \\ &= M_{\text{cat}} k_1 \left( a_{\text{AcH}} a_{\text{BuOH}} - \frac{1}{K_e} a_{\text{BuAc}} a_{\text{H}_2\text{O}} \right) \end{aligned} \quad (3)$$

where  $K_e = k_1/k_2$ , and  $K_e$  is the equilibrium constant.  $k_1$  and  $k_2$  are the kinetic constants for the forward and reverse reactions, respectively.  $M_{\text{cat}}$  is the catalyst loading per unit mass of acetic acid,  $\alpha_i (= \gamma_i \cdot x_i)$  is the activity of the *i*th component in the bulk liquid phase, and  $\gamma_i$  and  $x_i$  are the activity coefficient and mole fraction of the *i*th component. The NRTL model was used to determine the activity coefficients in the liquid phase, and binary interaction parameters of reaction components were obtained from DECHEMA.<sup>24</sup> The kinetic equations were integrated numerically using a fourth-order Runge–Kutta method. The parameters for the kinetics model were estimated from the minimization of the sum of residual squares (SRS) between the experimental and calculated conversions of acetic acid, which is

$$\text{SRS} = \sum_{\text{samples}} (x_{\text{expt}} - x_{\text{calc}})^2 \quad (4)$$

where SRS is the minimum sum of residual squares and  $x$  is the conversion of acetic acid. The subscripts expt and calc denote experimental and calculated values, respectively. The nonlinear least-squares method was used as the optimization method for the parameter estimation.

Experimental data are compared to the PH model values at different temperatures, catalyst loadings, and initial molar ratios of reactants, as shown in Figures 3 and 4 and 6–8, respectively. It is found that the calculated values are in a good agreement with the measured results with an averaged relative deviation (ARD) of less than 5%. The value of ARD is thought to be well within the



**Figure 8.** Comparison between measured and calculated conversions of acetic acid in the presence of [Hmim][HSO<sub>4</sub>] under conditions as follows: reaction temperature of 348.15 K (■), 358.15 K (●), 368.15 K (▲); catalyst loading of 10% w/w (□), 25% w/w (○), 50% w/w (△). The dash lines represent the deviation limits of ±5%.

acceptable limit for engineering purpose. In addition, it is interesting that the deviations between the calculated results and the experimental data increase gradually with the increase of catalyst loading (see Figures 7 and 8). This may be reasoned by that the calculation of liquid activity coefficient from the NRTL model does not include the interactions between the BAIL and reaction components in this work. In the cases of 10% w/w and 25% w/w, the interactions between the BAIL and reaction components contribute less to the activity coefficient due to the low mole fraction of BAIL in the esterification system. Good agreement is still realized between calculated values and experimental data. However, relatively large deviations are obtained at catalyst loading of 50% w/w, indicating that the interaction should not be neglected when the catalyst loading is high enough. Therefore, the PH model can give a good representation of the esterification kinetic behavior at a low catalyst loading. A more accurate description of the kinetic behavior can be obtained if the interactions between the BAIL and reaction mixture can be determined and taken into account.

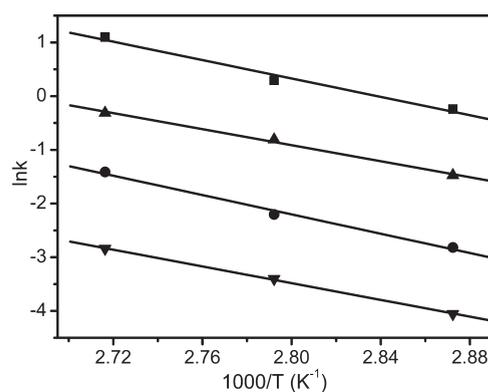
The temperature dependency of the rate constant  $k$  can be expressed by the Arrhenius equation:

$$k_i = k_i^0 e^{-E_{A,i}/RT} \quad (5)$$

Equation 5 can be rewritten as

$$\ln k_i = \ln k_i^0 - \frac{E_{A,i}}{RT} \quad (6)$$

By plotting  $\ln k_i$  versus  $1/T$ , straight lines with the slope of  $-E_{A,i}/R$  can be obtained from eq 6 and are shown in Figure 9. The values of the pre-exponential factor ( $k_1^0, k_2^0$ ) and activation energy ( $E_{A,1}, E_{A,2}$ ) are given in Table 2. For comparison, the kinetic parameters for Amberlyst-15 resin catalytic systems measured by Gangadwala<sup>7</sup> are also listed. The results show that the value of the activation energy of [Hmim][HSO<sub>4</sub>] is close to that in the case of Amberlyst-15 resin. However, the pre-exponential factors of forward reaction for these two catalysts are quite different. In contrast, all the kinetic parameters for [Hpy][HSO<sub>4</sub>] and Amberlyst-15 resin catalytic systems are near each other. The kinetic data as investigated in the previous section also indicate that [Hpy][HSO<sub>4</sub>] and Amberlyst-15 resin are of similar catalytic performance and are more efficient than [Hmim][HSO<sub>4</sub>]. Therefore, it is demonstrated that catalytic



**Figure 9.** Arrhenius plot for the esterification of *n*-butanol with acetic acid using [Hpy][HSO<sub>4</sub>] and [Hmim][HSO<sub>4</sub>] as catalysts. (■)  $k_1^0$  of forward reaction and (●)  $k_2^0$  of reverse reaction for [Hpy][HSO<sub>4</sub>]; (▲)  $k_1^0$  of forward reaction and (▼)  $k_2^0$  of reverse reaction for [Hmim][HSO<sub>4</sub>]. The solid lines represent the regression of  $\ln k$  versus  $1000/T$ .

**Table 2.** Kinetic Parameters for the Pseudo-homogeneous Model

| catalyst                  | $k_j^0$ (kmol/min, $\times 10^3$ ) |         | $E_{A,j}$ (kJ/mol) |         |
|---------------------------|------------------------------------|---------|--------------------|---------|
|                           | $j = 1$                            | $j = 2$ | $j = 1$            | $j = 2$ |
| [Hpy][HSO <sub>4</sub> ]  | 173.4                              | 46.86   | 71.04              | 74.80   |
| [Hmim][HSO <sub>4</sub> ] | 2.25                               | 0.4386  | 61.96              | 64.74   |
| Amberlyst-15              | 202.8 <sup>7</sup>                 |         | 70.66 <sup>7</sup> |         |

activities are mainly influenced by the pre-exponential factors of forward reaction, when the reaction energy barriers (activation energy) are quite similar. The comparison of esterification kinetics between [Hpy][HSO<sub>4</sub>] and Amberlyst-15 resin also indicates that [Hpy][HSO<sub>4</sub>] being noncorrosive BAILs is a talented and prospective substitute as catalyst for the esterification. Its kinetics data based on the PH model can be incorporated conveniently into the technology aided engineering and commercial software Aspen Plus<sup>6,25</sup> so as to realize the process simulation and provide an optimal setup of various operating parameters (e.g., numbers of reactive and nonreactive stages, number and location of feed positions). These simulation results will therefore be applicable to explore the possibility of BAILs-based catalytic distillation esterification processes.

## 4. CONCLUSIONS

The reaction kinetics of *n*-butyl acetate production using noncorrosive BAILs as catalysts was investigated, and the PH model was utilized successfully for the correlation of the experimental data. The reaction kinetic was for the first time used to interpret clearly the synergistic effect resulted from the acidity and hydrophilicity of BAILs. [Hpy][HSO<sub>4</sub>], as the typical noncorrosive BAILs, is found to enable the formation of the liquid–liquid biphasic system that facilitates the reaction kinetics and therefore accelerates the conversion of acetic acid. The conversion of acetic acid can be improved effectively with the increase of reaction temperature or catalyst loading in the presence of [Hpy][HSO<sub>4</sub>] and [Hmim][HSO<sub>4</sub>]. However, the high temperature and catalyst loading are not very necessary due to the limitation of chemical reaction equilibrium. The initial reaction rate is also found to increase linearly with catalyst loading. An

appropriate initial excess of acid rather than alcohol around the initial molar ratio of 1:1 appears to be more beneficial. It is also validated from the comparison of esterification kinetics between noncorrosive BAILs and Amberlyst-15 resin that noncorrosive BAILs are talented and prospective substitutes for the establishment of liquid catalyst-based reactive distillation processes.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ ACKNOWLEDGMENT

We are grateful to the National Natural Science Foundation of China (no. 20776065) and the Natural Science Foundation of Jiangsu (no. BK2009242 and no. BK2008023) for financial support.

## ■ NOMENCLATURE

$\alpha_i$ =activity of the *i*th component in the liquid phase  
 $E_{a,1}$ =activation energy for the forward reaction, kJ/mol  
 $E_{a,2}$ =activation energy for the reverse reaction, kJ/mol  
 $k$ =reaction rate constant, kmol/min  
 $k_1^0$ =pre-exponential factor for the forward reaction, kmol/min  
 $k_2^0$ =pre-exponential factor for the reverse reaction, kmol/min  
 $k_1$ =forward reaction rate constant, kmol/min  
 $k_2$ =reverse reaction rate constant, kmol/min  
 $K_c$ =equilibrium constant of esterification  
 $M_{cat}$ =the catalyst mass based on the mass of AcH, kg/kg  
 $R$ =gas constant, J/(mol·K)  
 $SRS$ =the sum of residual squares  
 $T$ =temperature, K  
 $w/w$ =weight of catalyst/weight of acetic acid, kg/kg  
 $x_i$ =mole fraction of the *i*th component in the liquid phase  
 $x_{calc}$ =calculated conversion  
 $x_{expt}$ =experimental conversion

### Greek Letters

$\gamma$ =the activity coefficient of the component

### List of Abbreviations

[BSEt<sub>3</sub>N][HSO<sub>4</sub>]=*N*-(4-sulfonic acid) butyl triethylammonium sulfate  
 [Et<sub>3</sub>NH][HSO<sub>4</sub>]=*N*-triethylammonium sulfate  
 [Hpy][HSO<sub>4</sub>]=pyridinium hydrogensulfate  
 [Hmim][BF<sub>4</sub>]=1-methylimidazolium tetrafluoroborate  
 [Hmim][HSO<sub>4</sub>]=1-methylimidazole hydrogensulfate  
 [N<sub>2224</sub>][HSO<sub>4</sub>]=butyltriethylammonium hydrogensulfate  
 PH=pseudohomogeneous

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#### ■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on January 11, 2011, with an error in the unit designation of the first column of Table 2. The corrected version was reposted on January 21, 2011.