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Noncorrosive ionic liquids composed of [HSO_4] as esterification catalysts

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ABSTRACT

Seven Brønsted acidic ionic liquids (BAILs) composed of [HSO_4] were prepared, characterized, and used as catalysts of low dosage in various esterification reactions. Pyridinium hydrogensulfate ([Hpy][HSO_4]), 2-methylpyridine hydrogensulfate ([Hmpy][HSO_4]), and 1-methylimidazole hydrogensulfate ([Hmim][HSO_4]) are found to be nearly noncorrosive, whereas N-(4-sulfonic acid)butyl triethylammonium hydrogensulfate ([$BSEt_3N$][HSO_4]) corrodes 316L stainless steel heavily. It is illustrated that the acidity and hydrophilicity can be tuned through the variation in cations to obtain BAILs of suitable catalytic activity. [Hpy][HSO_4], as a typical noncorrosive BAIL, shows good catalytic activity in the esterification of *n*-butanol with acetic acid, primarily due to its suitable Brønsted acidity and highly hydrophilic nature to enable liquid–liquid biphasic catalysis, whereas [Hmpy][HSO_4] and [Hmim][HSO_4] require relatively large dosages to reach the equal level. The batch reaction distillation is further performed to investigate the esterification of acetic acid with *n*-butanol using [Hpy][HSO_4] as catalyst of low dosage, and is found to be a promising strategy that causes the shift of chemical equilibrium further to the product side and leads up to the completion of the reaction. The noncorrosive BAILs are also tested to be catalysts of considerable activity for the esterification of other alcohols with acids in the absence of steric hindrance. [Hpy][HSO_4] is recycled and reused seven times without significant losses of activity and quantity, showing the stability and recyclability of the noncorrosive BAILs. It is believed that the noncorrosive BAILs are prospective substitutes for corrosive mineral acids or solid resins in the catalytic distillation to overcome the corrosion of mineral acids or the difficult installation of solid catalysts in the column.

1. Introduction

Esters made from carboxylic acids are important intermediates in chemical and pharmaceutical industries, and they are mostly produced by acid-catalyzed esterification reactions [1]. Various mineral acids, such as H_2SO_4, HF, and H_3PO_4 have been widely used as catalysts in the production of esters. However, these acids are extremely corrosive and contaminative, leading to the difficulties in separating and recycling these catalysts. They must have to be neutralized at the end of the reaction. To overcome the above-mentioned problems, the use of heterogeneous catalysts such as resins [2,3], heteropolyacids [4–6], and molecular sieves [7,8] has attracted much attention. However, these catalysts also have their disadvantages such as easy deactivation, high mass transfer resistance, and especially difficult installation in a reactive distillation column, which limits their practical applications.

In view of both the advantages and disadvantages of homogeneous and heterogeneous catalysts, Brønsted acidic ionic liquids (BAILs), regarded as green reaction media, have been introduced very successfully into the area of catalysts. BAILs have several unique properties such as negligible volatility, excellent thermal stability, remarkable solubility, structural variety, and effortless reusability [9,10]. Thus, acid-catalyzed esterification reactions based on ionic liquids have received more attention [11–16]. In 2001, Deng et al. [11] reported their pioneering work on the esterification of carboxylic acids with alcohols in the presence of acidic chloroaluminate ionic liquids as catalyst. With the use of ionic liquids, especially BAILs, as catalysts, the esterification system is homogeneous at the early stage of the reaction, and often forms a liquid–liquid biphase at the end [12]. Consequently, high conversion and selectivity are obtained, and ionic liquids can be recycled and reused by decanting simply the produced ester that exists mainly in the upper phase of the resulting mixture. However, these results are not entirely satisfactory because of the high cost and complex preparation of BAILs [13,14], and the high concentration of BAILs (e.g., 100–300% (w/w) based on the mass of carboxylic acids) required for the reaction to be of high conversion [15]. Particularly, many BAILs beared with an alkyl sulfonic acid of extremely strong acidity can still cause serious equipment corrosion [12–14]. For these reasons, kinetically efficient and noncorrosive BAILs as

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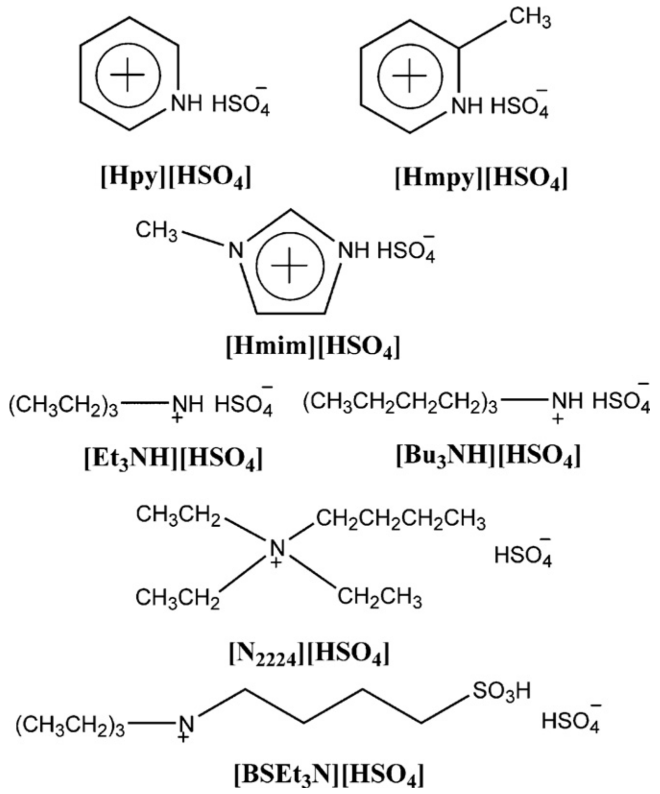

Fig. 1. Structure of seven Brønsted acidic ionic liquids.

catalyst for the esterification is still absent and therefore highly conceived.

Therefore, our efforts were focused on noncorrosive BAILs as catalysts of low dosage for the esterification reactions. Several BAILs had been prepared via simple and atomeconomic reactions, and their catalytic behavior in various esterification reactions was investigated. The reusability of BAILs and the corrosion rate of stainless steel by BAILs were also explored. In addition, the esterification of *n*-butanol with acetic acid via batch reactive distillation was studied using noncorrosive BAILs as catalysts. The effect of water removal on the performance of esterification was also discussed, to explore the possible utility of noncorrosive BAILs in the reactive distillation column.

2. Experimental

2.1. Materials

1-Methylimidazole (purity ≥99%) was purchased from Yancheng BaiYiChem Co., Ltd. (Jiangsu, China). 2-Methylpyridine (purity ≥98%) and 1,4-butyl sultone (purity ≥99%) 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 2-methylpyridine were redistilled in vacuum before use. Triethylamine ($(C_2H_5)_3N$), tributylamine ($(C_4H_9)_3N$), pyridine, *n*-butyl bromide (C_4H_9Br), silver oxide, sulfuric acid and ethanol were of analytical grade and used without any further purification.

2.2. Preparation and characterization of ionic liquids

Seven BAILs composed of [HSO_4] anion and different cations were prepared in the paper (Fig. 1). The thermal stability (Netzsch STA 449C) and ^{1}H NMR (BRUKER DPX-300) spectrum of these BAILs were recorded, and the detailed preparation methods and characterization results are as follows.

2.2.1. Pyridinium hydrogensulfate ([Hpy][HSO_4])

Pyridine (79 g, 1 mol) was charged into a 250 mL round-bottom flask in a water bath. Sulfuric acid (98 g, 1 mol) aqueous solution was added slowly into the pyridine solution at 0 °C under stirring. The mixture was stirred for 10 h to complete the reaction. The resulting solution was then dried in vacuum at 95 °C to remove the water until the weight of the residue remained constant. The yield of [Hpy][HSO_4] was formed quantitatively and in high purity as assessed from the mass balance and ^{1}H NMR spectroscopies. Characterization results: colourless crystals; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 8.037 (d, 2H), 8.558 (t, 1H), 8.909 (d, 2H); melting point: 93 °C; crystallization point: 71 °C; and thermal decomposition point: 306 °C.

2.2.2. 2-Methylpyridine hydrogensulfate ([Hmpy][HSO_4])

The synthesis procedure was similar to that of [Hpy][HSO_4], and [Hmpy][HSO_4] was obtained in quantitative yield. Characterization results: light-yellow liquids; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 2.719 (s, 3H), 7.909 (m, 2H), 8.444 (t, 1H), 8.799 (d, 1H); melting point: 31 °C; and thermal decomposition point: 295 °C.

2.2.3. 1-Methylimidazole hydrogensulfate ([Hmim][HSO_4])

The synthesis procedure was similar to that described in the previous literature [17]. Characterization results: light-yellow liquids; ^{1}H NMR (300 MHz, D_2O-d_2, 25 °C, TMS): δ (ppm) 3.563 (s, 3H), 7.083 (s, 2H), 8.307 (s, 1H); melting point: 47 °C; and thermal decomposition point: 306 °C.

2.2.4. N-triethylammonium sulfate ([Et_3NH][HSO_4])

The preparation method was according to the literature [18]. Characterization results: Colourless crystals; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 1.17 (t, 9H), 3.08 (m, 6H), 8.89 (s, 1H); melting point: 81 °C; and thermal decomposition point: 256 °C.

2.2.5. N-tributylammonium sulfate ([Bu_3NH][HSO_4])

The preparation method was according to the literature [18]. Characterization results: colourless crystals; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 0.91 (t, 9H), 1.31 (m, 6H), 1.58 (m, 6H), 3.00 (m, 6H), 8.32 (s, 1H); melting point: 87 °C; and thermal decomposition point: 235 °C.

2.2.6. Butyltriethylammonium hydrogensulfate ([N_{2224}][HSO_4])

The preparation of [N_{2224}][HSO_4] followed a two-step procedure. Triethylbutylammonium bromide ([N_{2224}][Br]) were prepared in the first step via the alkylation of $(C_2H_5)_3N$ (35.0 g) with C_4H_9Br (47.5 g) in ethanol (100 mL) under reflux and vigorous stirring for 6 hours. The solvent and unreacted components were removed by rotary evaporation, and [N_{2224}][Br] (80 g) white solid was obtained after being dried at 60 °C under vacuum for 5 h. The objective product [N_{2224}][HSO_4] was obtained from the metathesis and neutralization reactions of [N_{2224}][Br] (59.5 g, 0.25 mol) with Ag_2O (29 g, 0.125 mol) and H_2SO_4 (24.5 g, 0.25 mol) in the mixed solvent of ethanol and water (volume fraction was 50%) for 12 h. After centrifugation and filtration, a light yellow precipitate (AgBr) was removed. The filtrate was dried in vacuum at 95 °C, leading to a light yellow paste of [N_{2224}][HSO_4] with a yield of 90% (based on the moles of triethylammonium). The concentration of the bromine ion in [N_{2224}][HSO_4] was measured by Mohr titration, and the related impurity was less than 0.02%. Characterization results: light-yellow liquids; ^{1}H NMR (300 MHZ, D_2O, 25 °C, TMS): δ (ppm) 0. 81 (t, 3H), 1.09 (t, 9H), 1.26 (m, 2H), 1.49 (m, 2H), 3.00 (m, 2H), 3.14 (q, 6H); and thermal decomposition point: 286 °C.

2.2.7. *N-(4-sulfonic acid)butyl triethylammonium sulfate ($[BSEt_3N][HSO_4]$)*

The synthesis procedure was described in the previous literature [14]. Characterization results: Colourless viscous liquid, ^{1}H NMR (300 MHz, D_2O-d_2, 25 °C, TMS): δ 1.122 (t, 9H), 1.679 (m, 4H), 2.825 (t, 2H), 3.08 (t, 2H), 3.178 (q, 6H); and thermal decomposition point: 273 °C.

2.3. *UV–vis determination of acidity*

According to the literatures [19–21], the Brønsted acidity of ionic liquids was evaluated from the determination of the Hammett functions (H_0), using an Agilent 8453 UV-visible spectroscopy. The experiments were carried out in ethanol solutions (80 mmol/L) of BAILs or H_2SO_4 (for comparison) at room temperature (25 °C). 4-Nitroaniline was used as indicator (0.06 mmol/L), and the UV–visible determination was carried out in the scale of 220–550 nm.

2.4. *Corrosion test*

A 316L austenitic stainless steel plate with 50 mm length, 20 mm width and 1 mm thickness was immersed in the esterification system containing a given BAIL catalyst for corrosion test under the following conditions: acetic acid, *n*-butanol and the BAIL being charged into a flask was stirred at 85 °C for 50 h. The treatment method of the steel immersed was according to the literature [22]. At the end of the reaction, the steel was taken out from the reaction mixture for weighing. The corrosion rate of stainless steel plate by the BAIL-containing solution was calculated from the mass loss and the exposing surface area.

2.5. *Esterification procedure*

In a typical run, acetic acid (0.25 mol), *n*-butanol (0.25 mol) were charged into a 100 mL round-bottom flask fitted with a reflux condenser. When the temperature was raised to the desired value, the BAIL catalyst was then added into the reactor. Samples were taken out from the reactor at regular intervals, and qualitative and quantitative analyses were conducted using N_2 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 temperatures of the inlet and the detector were set to be 200 °C. The results obtained via GC were also confirmed from independent titrations using standard sodium hydroxide (0.25 mol/L NaOH) solution. The analytical uncertainty of GC was less than 2%, which is well within the acceptable limits. After the reaction, the esterification system often forms a liquid–liquid biphase. The upper phase, containing mainly the desired ester, can be isolated simply by decantation, whereas the lower phase composed of ionic liquid and water can be recycled after removing the water under vacuum at 95 °C.

3. Results and discussion

3.1. *Basic properties of ionic liquids composed of $[HSO_4]$*

All BAILs were prepared with quantitative yields, and no byproduct was produced in the IL synthesis procedure. The fresh $[Hmpy][HSO_4]$ and $[Hmim][HSO_4]$ are viscous liquids at room temperature. However, they are slowly solidified at room temperature after long time setting (e.g., several weeks). This phenomenon is primarily due to the supercooling of these BAILs, and is consistent with the behavior of other BAILs [23]. $[BSEt_3N][HSO_4]$ is a colourless viscous liquid, while $[N_{2224}][HSO_4]$ is a viscous liquid of light-yellow. $[Hpy][HSO_4]$, $[Et_3NH][HSO_4]$, and $[Bu_3NH][HSO_4]$ is a stiff solid at room temperature, but they all melt bellow 95 °C. $[Hpy][HSO_4]$ and $[Hmpy][HSO_4]$ are derived from cheap pyridine. $[Et_3NH][HSO_4]$ and $[Bu_3NH][HSO_4]$ are prepared from cheap amine. Most BAILs (except $[N_{2224}][HSO_4]$ and $[BSEt_3N][HSO_4]$) have been prepared via simple and atomeconomic acid–base neutralization reactions, and the preparation is straight forward, economical and environmentally benign. All BAILs can be well dissolved in polar solvents, such as water, methanol, ethanol and DMSO, while being immiscible with weak polar solvents, such as ether and esters.

Table 1
Hammett acidity function (H_0) values of H_2SO_4 and different BAILs.

Entry	IL	$A_{\max}$	[I] (%)	$[IH^+]$ (%)	H_0
1	–	1.03	100	0	–
2	$[Hpy][HSO_4]$	0.830	80.6	19.4	1.61
3	$[Hmpy][HSO_4]$	0.903	87.7	12.3	1.84
4	$[Hmim][HSO_4]$	0.927	90	10	1.94
5	$[Et_3NH][HSO_4]$	0.963	93.4	6.6	2.14
6	$[Bu_3NH][HSO_4]$	0.971	94.2	5.8	2.20
7	$[N_{2224}][HSO_4]$	0.990	96.1	3.9	2.38
8	$[BSEt_3N][HSO_4]$	0.538	52.2	47.8	1.03
9	H_2SO_4	0.542	52.6	47.4	1.10

The Brønsted acidity is an essential property of BAILs, and Hammett function is often an effective way to evaluate the acidity of BAILs in organic solvents. It can be calculated from the following equation:

$$H_0 = \mathrm{p}K(\mathrm{I})_{\mathrm{aq}} + \log\left(\frac{[\mathrm{I}]_{\mathrm{s}}}{[\mathrm{IH}^+]_{\mathrm{s}}}\right) \tag{1}$$

where $\mathrm{p}K(\mathrm{I})_{\mathrm{aq}}$ is the $\mathrm{p}K_{\mathrm{a}}$ value of the indicator referred to an aqueous solution and can be obtained from many references. $[\mathrm{IH}^+]_{\mathrm{s}}$ and $[\mathrm{I}]_{\mathrm{s}}$ are the molar concentrations of the protonated and unprotonated forms of the indicator in the BAILs, respectively. According to Lambert–Beer's Law, the value of $[\mathrm{I}]_{\mathrm{s}}/[\mathrm{IH}^+]_{\mathrm{s}}$ can be determined and calculated from UV–visible spectrum, so that the value of H_0 can be obtained from Eq. (1). In this work, the Hammett acidity of seven BAILs and H_2SO_4 has been investigated. The maximal absorbance of unprotonated form of 4-nitroaniline is observed at 371 nm in ethanol solutions. The $\mathrm{p}K(\mathrm{I})_{\mathrm{aq}}$ value of 4-nitroaniline is 0.99, and the results are listed in Table 1. The acidity order is as follows: $[BSEt_3N][HSO_4] > H_2SO_4 > [Hpy][HSO_4] > [Hmpy][HSO_4] > [Hmim][HSO_4] > [Et_3NH][HSO_4] > [Bu_3NH][HSO_4] > [N_{2224}][HSO_4]$. It is obvious that the cationic structures of BAILs have significant influence on their Brønsted acidities, and can be explained from the theory of conjugate acid–base. For example, $[BSEt_3N][HSO_4]$ beared with an alkyl sulfonic acid exhibits the strongest acidity, and its acidity is even slightly higher than the acidity of H_2SO_4, implying that $[BSEt_3N][HSO_4]$ may be similar to the nature of H_2SO_4 (entries 8 and 9). The acidity of $[Et_3NH][HSO_4]$, $[Bu_3NH][HSO_4]$, and $[N_{2224}][HSO_4]$ is weak due to their neutral or weakly acidic cations (entries 5–7). In contrast, the cations of $[Hpy][HSO_4]$, $[Hmpy][HSO_4]$, and $[Hmim][HSO_4]$ are the conjugate acids derived from very weak alkalis of $\mathrm{p}K_{\mathrm{b}}$ values ranging from 7.05 to 8.75 at 25 °C, so that the Hammett acidity values of these BAILs are all bellow 2.0 (entries 2–4).

The corrosion of 316L stainless steel by BAILs is another important characteristic that determines their practical use in a RD column and also the economy and safety of esterification processes. A 316L austenitic stainless steel plate was immersed in the esterification system containing a given BAIL for corrosion test. The results are summarized in Table 2. It is observed that the corrosion rate of 316L stainless steel in the reactive solution containing $[Hpy][HSO_4]$, $[Hmpy][HSO_4]$, or $[Hmim][HSO_4]$ is 0.021, 0.019, and 0.011 mm/a,

Table 2
Corrosion rate of 316L stainless steel in reaction solutions of BAILs.[a]

Entry	IL	Mass loss × 10^4 (g/g h)	Corrosion rates (mm/a)
1	[Hpy][HSO_4]	0.487	0.021
2	[Hmpy][HSO_4]	0.422	0.019
3	[Hmim][HSO_4]	0.251	0.011
4	[Et_3NH][HSO_4]	14.8	1.30
5	[$BSEt_3N$][HSO_4]	128	11.2

[a] Equimolar reaction of 0.5 mol acetic acid with 0.5 mol *n*-butanol at 85 °C for 50 h in the presence of BAILs as catalysts with a dosage of 25% (w/w) (based on the mass of acetic acid).

respectively, being almost noncorrosive (Table 2, entries 1–3), and [$BSEt_3N$][HSO_4] is obviously the most corrosive catalyst because of its strongest acidity (Table 2, entry 5). It is of interest to note that [Et_3NH][HSO_4] containing solution has a corrosion rate of 1.3 mm/a and is more corrosive than [Hpy][HSO_4], [Hmpy][HSO_4], and [Hmim][HSO_4] systems, though its acidity is the weakest of them (see Table 1). It may be caused by the triethylamine resulting from the slight decomposition of [Et_3NH][HSO_4], and amine is more corrosive due to the coordination with iron ions.

3.2. *Influence of cationic structure on the catalytic performance of BAILs*

Esterification is a kind of classical acid-promoted organic reaction and is usually used to check the catalytic activity of an acid catalyst. The esterification of *n*-butanol with acetic acid in the presence of several BAILs composed of various cations was conducted with different catalyst dosages. The results are summarized in Table 3. Combined with the acidities of these BAILs from Table 1, it is obvious that the catalytic activity of BAIL approximately depends on its acidities. For example, in the presence of 5% (w/w) [$BSEt_3N$][HSO_4] at 85 °C, the conversions of acetic acid is 61.7% at 0.5 h, whereas [Hpy][HSO_4] and [Hmpy][HSO_4] catalyze the esterification reaction to have conversions of only 15.5% and 12.8%, respectively, being significantly less than that of [$BSEt_3N$][HSO_4] under identical conditions. This is primarily ascribed to the strongest acidity of [$BSEt_3N$][HSO_4] among all the catalysts investigated. The super strong acidity enables [$BSEt_3N$][HSO_4] to have the best catalytic activity. Therefore, it is demonstrated that varying the cationic structure of BAIL can tune its acidity, and the catalytic activity order of the BAIL is consistent with the acidity order.

In addition, the experimental results also indicate that the variations in the cations can affect the hydrophilicity of BAILs, which is found to be another important factor that determines the catalytic activity [24,25]. For example, high conversion of acetic acid is induced in the presence of [Hpy][HSO_4] (Table 3, entries 3, 5 and 6), mainly ascribed to its greater hydrophilicity rather than [Hmpy][HSO_4] and [Hmim][HSO_4], although their Brønsted acidities are close to each other (see Table 1). This can be validated from the phenomenon of esterification in the presence of those three noncorrosive BAILs as catalysts. With the use of 25% (w/w) [Hpy][HSO_4], the esterification system is found to become heterogeneous and turbid in less than 15 min. The product of *n*-butyl acetate forms a light phase, while water and [Hpy][HSO_4] are combined to be a heavy phase. The unreacted acetic acid and *n*-butanol partition between the two phases. [Hpy][HSO_4] is miscible with water but almost insoluble in *n*-butyl acetate, so that the produced ester can be extruded rapidly from the heavy phase. As a result, the formation of a separate ester phase in a short time facilitates the shift of chemical equilibrium to the product side and improves the conversion of acetic acid. For comparison, in the cases of [Hmpy][HSO_4] and [Hmim][HSO_4], their esterification systems require long time (about 30 min for [Hmpy][HSO_4] system and 45 min for the other) to form liquid–liquid biphases. Both of them have better solubility in the reactive mixture than [Hpy][HSO_4], due to the weaker hydrophilicity of their cations. Then relatively poor conversions are obtained. Similarly, the bulk carbon chain in the cations [N_{2224}] decreases the hydrophilicity of [N_{2224}][HSO_4], resulting in poorer conversions of acetic acid than those in [Et_3NH][HSO_4] and [Bu_3NH][HSO_4] systems (Table 3, entries 7–9). Therefore, it is demonstrated that the cationic structure also determines the hydrophilicity. The catalytic activity of BAIL can be adjustable through the variation in cations to obtain the BAILs of suitable acidity and hydrophilicity, which benefits to keep the catalytic activity and reduce the corrosion.

Table 3
Results of esterification of *n*-butanol with acetic acid using different BAILs as catalysts.[a]

Entry	Catalyst	Time (h)	Conversion of acetic acid (%)			
			(i) 5% (w/w)	(ii) 10% (w/w)	(iii) 25% (w/w)	(iv) 50% (w/w)
1[b]	[$BSEt_3N$][HSO_4]	0.5	42.4	49.4	–	–
		2	53.7	63.6	–	–
2	[$BSEt_3N$][HSO_4]	0.5	61.7	68.6	74.4	–
		2	68.1	73.2	78.7	–
3	[Hpy][HSO_4]	0.5	15.5	30.4	46.4	53.8
		2	37.6	55.5	71	72.5
4[c]	[Hpy][HSO_4]	0.5	–	65.1	68.1	–
		2	–	85.3	90.9	–
5	[Hmpy][HSO_4]	0.5	12.8	24.1	37.7	48.6
		2	31.2	51.3	62.3	68.3
6	[Hmim][HSO_4]	0.5	–	19.2	32.7	40
		2	–	43.6	53.7	56.5
7	[Et_3NH][HSO_4]	0.5	–	16.8	27.9	38.6
		2	–	39.2	51.5	55.8
8	[Bu_3NH][HSO_4]	0.5	–	10.6	17.6	30.5
		2	–	30	41.2	52.3
9	[N_{2224}][HSO_4]	0.5	–	15	16.6	22.5
		2	–	30.6	39.5	44.9

No byproducts were found by GC.

[a] 0.2 mol acetic acid was refluxed with 0.2 mol *n*-butanol using BAILs as catalysts with a dosage (base on the mass of acetic acid) of (i) 5% (w/w); (ii) 10% (w/w); (iii) 25% (w/w); (iv) 50% (w/w) at 85 °C.

[b] Reaction temperature at 60 °C.

[c] Reaction temperature at 105 °C via batch reactive distillation.

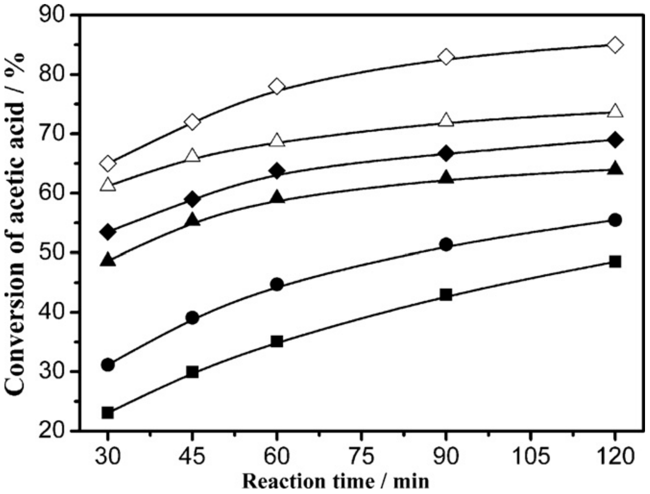

Fig. 2. Equimolar reactions of *n*-butanol with acetic acid using [Hpy][HSO_4] with a dosage of 10% (w/w) (based on the mass of acetic acid) at (■) 75 °C; (●) 85 °C; (▲) 95 °C; (◆) 105 °C. Equimolar reactions of *n*-butanol with acetic acid via batch reactive distillation using 10% (w/w) [Hpy][HSO_4] at (△) 95 °C; (◇) 105 °C.

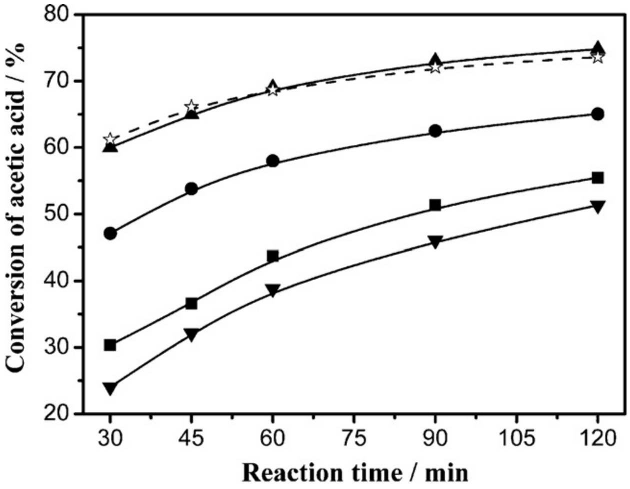

Fig. 3. Equimolar reactions of *n*-butanol with acetic acid at 85 °C using (▲) H_2SO_4, (●) the resin Amberlyst-15, (■) [Hpy][HSO_4], and (▼) [Hmpy][HSO_4] with a dosage of 10% (w/w). Equimolar reactions of *n*-butanol with acetic acid via batch reactive distillation using 10% (w/w) [Hpy][HSO_4] at (☆) 95 °C.

3.3. Influence of other parameters on the catalytic performance of BAILs

The effects of catalyst concentration, reaction time, and reaction temperature on the conversion of acetic acid were also investigated. It is observed that the conversion of acetic acid increases rapidly in the presence of BAILs with dosages ranging from 10% (w/w) to 50% (w/w) (Table 3, entries 5–9). With the increasing reaction time, the conversion of acetic acid in the case of 25% (w/w) [Hpy][HSO_4] also has a great improvement (from 46.4% at 0.5 h to 71% at 2 h). In comparison to the catalytic activity of 25% (w/w) [Hpy][HSO_4], [Hmpy][HSO_4] and [Hmim][HSO_4] only with a dosage of 50% (w/w) can reach the equal level (Table 3, entries 3, 5 and 6). Therefore, high concentration of BAILs and reaction time can improve the catalytic performance. [Hpy][HSO_4], [Hmpy][HSO_4], [Hmim][HSO_4], and [$BSEt_3N$][HSO_4] can all induce comfortable conversions of acetic acid at 2 h, even though the catalyst loadings required for the three noncorrosive BAILs are larger than [$BSEt_3N$][HSO_4] system. In addition, the effect of temperature on the performance of esterification was also studied in the presence of 10% (w/w) [Hpy][HSO_4] as catalyst. It is shown in Fig. 2 that the increase of reaction temperature is beneficial to the conversion of acetic acid. For example, the conversion of acetic acid at 0.5 h is less than 20% at 75 °C. When the temperature is raised to 95 °C, it reaches about 50%. However, increasing the temperature to 105 °C, the conversion of acetic acid at 0.5 h is only 55%. The improvement of conversion is limited because of the limitation of chemical equilibrium [3]. In addition, sideproduct (such as dibutyl ether) would be probably produced, while the temperature is higher than 110 °C [26]. The overhigh reaction temperature is not positive to the esterification reaction. Therefore, an optimized reaction temperature would not exceed 105 °C.

For comparison, we had investigated the esterification of *n*-butanol with acetic acid in the presence of Amberlyst-15 resin and H_2SO_4 with a dosage of 10% (w/w). As seen from Fig. 3, H_2SO_4 and Amberlyst-15 resin show more efficiently catalytic performances than [Hpy][HSO_4] and [Hmpy][HSO_4] under identical conditions. The strong acidity enables H_2SO_4 and Amberlyst-15 resin to induce remarkable conversions, and this is in accordance with the general phenomena of acid catalysis for the esterification. In addition, the catalytic performance of noncorrosive BAILs with that of Amberlyst-15 resin at different dosages was also compared and shown in Fig. 4. It is of interest to note that the conversion profiles in the presence of 25% (w/w) [Hpy][HSO_4] and 50% (w/w) [Hmpy][HSO_4] are almost near to the case of 10% (w/w) Amberlyst-15 at times less than 1 h. After 1 h, the conversions in the presence of 25% (w/w) [Hpy][HSO_4] and 50% (w/w) [Hmpy][HSO_4] are found to be continuously enhanced and are higher than that of 10% (w/w) Amberlyst-15. Therefore, it is believed that the difference in catalytic performances of these three catalysts is mainly owing to the formation of liquid–liquid biphase in the esterification system containing BAILs. The chemical equilibrium in the esterification is favorably shifted to the product side and the conversion of acetic acid can continue to be enhanced under two effects from phase splitting: one is the concentrated BAILs in the heavy phase that can influence greatly the activity of each component, and the other is the ester being extruded from the heavy phase. In addition, increasing the amount of Amberlyst-15 to 15% (w/w), the conversion of acetic acid at 2 h is still lower than that in the case of 25% (w/w) [Hpy][HSO_4] or 50% (w/w) [Hmpy][HSO_4], even though the catalytic performance of the former is superior to the latter at time less than 1.5 h (see Fig. 4). This provides strong evidence for the explanation mentioned above.

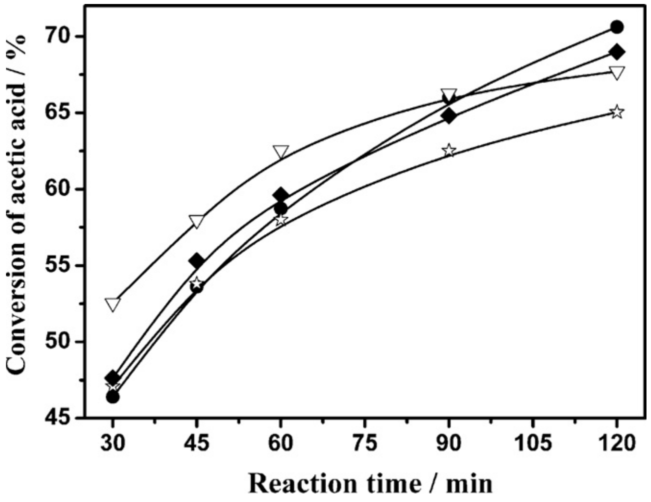

Fig. 4. Equimolar reactions of *n*-butanol with acetic acid at 85 °C using (●) 25% (w/w) [Hpy][HSO_4], using (◆) 50% (w/w) [Hmpy][HSO_4], and using the resin Amberlyst-15 with a dosage of (☆) 10% (w/w); (▽) 15% (w/w).

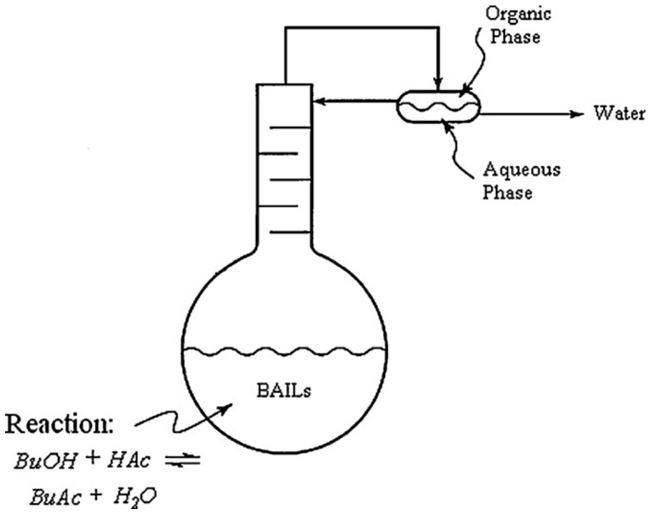

Fig. 5. Schematic of a batch reaction distillation in the presence of BAILs.

3.4. Influence of water removal on the catalytic performance of [Hpy][HSO_4]

It is well known that the esterification reaction of *n*-butanol with acetic acid is reversible, and the reactants cannot be completely converted because of the limitation of chemical equilibrium [3]. Several attempts have been made to shift the equilibrium to the product side in the past. For example, a large excess of alcohol is often taken to improve the performance of reaction. The water generated in the esterification reaction has to be continuously removed by azeotroping or by use of a dehydrative agent. As the most effective tool to achieve such objective, reactive distillation has been attracted much attention in recent years [2,27–30]. It can remove product(s) simultaneously during the course of the reaction and facilitate the improvement of reactant conversion. The schematic of a batch reactive distillation system is given in Fig. 5. During the esterification process, the reactants were consumed quantitatively and the reactive azeotrope was distilled into the decanter. After condensation, the distillate was separated into two phases: organic phase contained mainly butanol, butyl acetate and water, while aqueous phase was mainly water. Then, water was removed out and organic phase was recycled to the reaction vessel.

As seen from Figs. 2 and 3, when [Hpy][HSO_4] is used as catalyst at 95 °C, the batch reactive distillation induces the conversion of acetic acid at 0.5 h to be 61%, whereas the conversion at 0.5 h without water removal is only 48%. The esterification is found to have a great improvement using the reactive distillation strategy. In addition, it is also shown in Fig. 3 that the catalytic performance of 10% (w/w) [Hpy][HSO_4] via batch reactive distillation at 95 °C are almost equal to that of 10% (w/w) H_2SO_4 without water removal at 85 °C. In the presence of 25% (w/w) [Hpy][HSO_4], the conversion of acetic acid at 2 h via batch reactive distillation can even reach around 91% (see Table 3, entry 4). It is therefore demonstrated that a combination of reactive distillation with a noncorrosive BAIL as catalyst of low dosage is effective to drive the reaction equilibrium further to the product side and lead up to the completion of esterification. This is equivalent to say that the noncorrosive [Hpy][HSO_4] in combination with the reactive distillation has an improved catalytic performance comparable to that of H_2SO_4 without water removal. Noncorrosive BAILs-based reactive distillation processes can thus avoid the corrosion problem raised from H_2SO_4 and meanwhile realize the considerable conversion. It is also exciting to use noncorrosive BAILs to replace solid catalysts in the reactive distillation processes, to overcome the technical difficulties [29] such as difficult installation of solid catalysts in the column, serious mass transfer resistance and high pressure drop, though it needs a separation step to recycle the BAIL catalyst.

3.5. Esterification of other alcohols with acids in the presence of noncorrosive BAILs

The esterification of other alcohols with acids in the presence of noncorrosive [Hpy][HSO_4], [Hmpy][HSO_4], and [Hmim][HSO_4] was also studied, and the results are shown in Table 4. It is obvious that [Hpy][HSO_4], [Hmpy][HSO_4] and [Hmim][HSO_4] perform well in the catalytic reactions of acetic acid with other alcohols, such as methanol, ethanol, *n*-propanol and isobutanol (entries 1–4, 12 and 15). [Hpy][HSO_4] plays better catalytic performances than [Hmpy][HSO_4] and [Hmim][HSO_4], owing to its cationic structure. Considerable conversions are also obtained in the esterification of other acids with alcohols catalyzed by [Hpy][HSO_4] (entries 6, 9, 12–15 and 19). However, [Hmim][HSO_4] is of poor activity in the

Table 4
Results of esterification for various alcohols with acids in the presence of [Hpy][HSO_4], [Hmpy][HSO_4], and [Hmim][HSO_4].[a]

Entry	Alcohol	Acid	IL	*T* (°C)	Conversion of acid at 0.5 h (%)	Conversion of acid at 2 h (%)
1	Methanol	Acetic acid	[Hpy][HSO_4]	60	51.8	62.8
2	Methanol	Acetic acid	[Hmpy][HSO_4]	60	34.6	55.2
3	Ethanol	Acetic acid	[Hpy][HSO_4]	70	32.5	61.4
4	Ethanol	Acetic acid	[Hmpy][HSO_4]	70	24.6	48.5
5	Ethanol	Acetic acid	[Hmim][HSO_4]	70	15	37.3
6	Ethanol	*n*-Propanoic acid	[Hpy][HSO_4]	85	31.8	54.4
7	Ethanol	*n*-Propanoic acid	[Hmpy][HSO_4]	85	28.2	53.2
8	Ethanol	*n*-Propanoic acid	[Hmim][HSO_4]	85	–	39.3
9	Ethanol	*n*-Butyric acid	[Hpy][HSO_4]	85	41.9	59.5
10	2-Propanol	Acetic acid	[Hpy][HSO_4]	85	–	36.2
11	2-Propanol	Acetic acid	[Hmim][HSO_4]	85	–	30
12	*n*-Propanol	Acetic acid	[Hpy][HSO_4]	85	30	70
13	*n*-Propanol	*n*-Propanoic acid	[Hpy][HSO_4]	85	30.7	53.7
14	*n*-Propanol	*n*-Butyric acid	[Hpy][HSO_4]	85	37	56.9
15	isoButanol	Acetic acid	[Hpy][HSO_4]	85	–	62.4
16	isoButanol	Acetic acid	[Hmim][HSO_4]	85	–	39.4
17	2-Butanol	Acetic acid	[Hpy][HSO_4]	85	–	41.2
18	*n*-Butanol	Acetic acid	[Hpy][HSO_4]	85	46.4	71
19	*n*-Butanol	*n*-Propanoic acid	[Hpy][HSO_4]	85	48.7	66.3
20	*n*-Butanol	*n*-Propanoic acid	[Hmim][HSO_4]	85	–	38.1
21	*n*-Butanol	*n*-Butyric acid	[Hpy][HSO_4]	85	–	43.6
22	*n*-Butanol	*n*-Butyric acid	[Hmim][HSO_4]	85	–	29

[a] Equimolar reaction of acid with alcohol using BAILs as catalysts with a dosage of 25% (w/w) (based on the mass of acid). No byproducts were found by GC.

Table 5
Recycling of [Hpy][HSO_4] for the esterification of *n*-butanol with acetic acid.[a]

Run	Conversion of acid at 0.5 h (%)	Conversion of acid at 2 h (%)	Weight of IL at each recycle step (g)	Cumulative recovery of IL (%)
1	46.4	71	3.75	100
2	47.6	69	3.71	99
3	48	71.5	3.64	97.1
4	47.1	72	3.6	96
5	49	71.5	3.59	95.7
6	45.5	70	3.57	95.2
7	46	69.7	3.53	94.13

[a] Equimolar reaction of *n*-butanol with acetic acid at 85 °C using [Hpy][HSO_4] as catalyst with a dosage of 25% (w/w) (base on the mass of acetic acid). No byproducts were found by GC.

esterification reactions of entries 5, 8, 20 and 22. It is reasoned that [Hmim][HSO_4] can be partially miscible in the desired esters and the esterification system requires long time to form liquid–liquid biphase, whereas [Hpy][HSO_4] of more hydrophilicity induces fast phase splitting and thus high conversions. In addition, low conversions are obtained and resulted from the steric effect of 2-propanol, isobutanol and 2-butanol in the esterification reactions (entries 10, 11, 16 and 17). Similarly, the conversion of acetic acid decreases gradually in the order of *n*-butanol > isobutanol > 2-butanol, due to their different steric effects (entries 15, 17 and 18). The conversion of an acid is also reduced with the growth of carbon chain length of carboxylic acid in the presence of [Hpy][HSO_4] (entries 18, 19 and 21), ascribed to the effect of steric hindrance of bulk carbon chain which can inhibit the diffusion of the reactants.

3.6. Recycling of [Hpy][HSO_4]

As the most suitable ionic liquid among these noncorrosive BAILs, the reusability of [Hpy][HSO_4] was checked. [Hpy][HSO_4] can be easily separated by decantation and regenerated by vaporization in vacuum at 95 °C. A period of 12 h is adopted in our experiments for the regeneration of [Hpy][HSO_4] to ensure that there are no other chemical residues in the sample to affect the calculation of catalyst recovery. The data in Table 5 show that the catalyst [Hpy][HSO_4] for the esterification is stable enough to be recycled. Seven cycles have been successively completed and no obvious change is observed on the recovered catalytic activity and quantity. The slight decrease in the conversion of acetic acid should be ascribed to the slight loss of [Hpy][HSO_4] due to the transferring of samples during the regeneration.

4. Conclusions

Seven BAILs composed of [HSO_4] have been synthesized, and five of them have been prepared via simple and atom-economic acid–base neutralization reactions. It is pointed out from the corrosion tests that [$BSEt_3N$][HSO_4] is extremely corrosive and contaminative being similar to the nature of H_2SO_4, whereas [Hpy][HSO_4], [Hmpy][HSO_4], and [Hmim][HSO_4] are nearly noncorrosive. Even though corrosive [$BSEt_3N$][HSO_4] of a low dosage are found to have the best activities, the noncorrosive BAILs shows also high catalytic activity in the esterification of acetic acid with *n*-butanol and other alcohols such as methanol, ethanol, *n*-propanol and isobutanol, primarily due to its suitable Brønsted acidity and highly hydrophilic nature to enable liquid–liquid biphasic catalysis. Batch reaction distillation was further done to examine the esterification using [Hpy][HSO_4] as catalyst, and a comparison of catalytic performance was made among the BAILs, H_2SO_4 and solid resin. It is concluded that the noncorrosive BAILs in the reactive distillation experiments show enough catalytic activity to lead to the completion of esterification. Noncorrosive BAILs are therefore suggested to replace corrosive mineral acids or solid resins in the reactive distillation processes to avoid the technical difficulties from corrosion or installation of solid catalysts in the column. Since the noncorrosive BAILs prepared atom-economically are green liquid catalysts of low cost and high recyclability, it is believed that noncorrosive BAIL-based catalytic distillation may have potential applications in the near future.

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