HSO₃-functionalized Brønsted acidic ionic liquids promote esterification of aromatic acid

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Esterification of aromatic acid can be promoted via HSO₃-functionalized Brønsted acidic ionic liquids (ILs). Under the optimum conditions, using 1-(3-sulfonic acid) propyl-3-methylimidazolium hydrogen sulfate ([MimC₃SO₃H][HSO₄]) and 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate ([MimC₄SO₃H][HSO₄]) as dual solvent-catalysts, the conversion of esterification of aromatic acid was determined to be more than 90%, indicating that HSO₃-functionalized ILs show much better catalytic ability than those of non-functionalized ionic liquids. The separation of desired product was easily performed by extraction with diethyl ether and these HSO₃-functionalized ILs could be reused 7 times after vacuum drying. Our data represent an environmentally friendly method for the preparation of aromatic esters.

aromatic esters, esterification, aromatic acids, alcohols, ionic liquids

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Aromatic esters are important intermediates in chemical industries, and also important components of many spices [1]. Up to now, a number of approaches for preparing aromatic esters have been introduced [2,3]. The traditional esterifications usually proceed using mineral acids, e.g. sulphuric acid, hydrochloric acid, orthophosphoric acid, Lewis acids, and metal salts, which are supported on solid supports. However, the esterifications carried out in conventional organic solvents suffer from several drawbacks, such as the final neutralization of the homogeneous acid catalyst, or difficulty in separation of the metal catalyst supported on solid support, or the by-reaction of susceptible groups presented in structures. Moreover, the removal of adsorbed products from catalysts is quite difficult and requires large excess of volatile organic solvents. Therefore, the development of new methods for preparing esters continues to be the subject of intensive investigations [4], and it is necessary to develop an environmentally benign method for their synthesis.

Room temperature ionic liquids (ILs) have been the sub-

ject of considerable current interest as environmentally benign reaction media in organic synthesis [5–10]. Their advantages include wide liquid range, good thermal and chemical stability, high ionic conductivity, negligible vapor pressure, and the potential for recycling. The potential of ILs as green “designer solvents and/or catalysts” has become a practical target for reducing waste and hazards by eliminating traditional volatile organic solvents and corrosive catalysts. Esterifications of aliphatic acids have been studied broadly in ILs media. Forbes and co-workers [11] have reported a new approach for esterifications in Brønsted acidic ILs. Although those catalytic systems show good conversion and selectivity, they suffer from a large amount of ILs and high temperature (>110°C). In parallel with these uses, a new class of reagents designed as task specific ionic liquids (TSILs) have been developed, whose derivatives combine an ionic liquid-type part with an attached extra function designed for the specific property [12–14]. Up to now, Brønsted acidic TSILs containing pyridinium [15], acyclic trialkanylammonium [16] and benzimidazolium cation [17] have been designed and used as catalyst and

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media in esterification. We know that imidazolium-based ILs is one of the most common ILs. In 2004, “greener” halogen-free imidazolium-based ILs that involve sulfate anions have been demonstrated to be efficient and reusable catalyst systems for esterification of aliphatic acid [4].

Encouraged by these results, and as an extension of our previous works [18–20], this paper presented a highly efficient method for the synthesis of aromatic esters by the esterification of aromatic acid with alcohols using HSO₃-functionalized Brønsted acidic ILs as dual solvent-catalysts under mild reaction conditions. Separation of desired product was easily performed by extraction with diethyl ether. The system could be recycled seven times with only a small decrease in activity. The use of ILs significantly enhanced the reactivity and recyclable efficiency of esterification.

1 Experimental

1.1 Chemicals

Starting materials and solvents were purchased from commonly commercial sources and were used without additional purification. Column chromatography was carried out on silica gel (300–400 mesh). ¹H NMR spectra were recorded at 400 MHz, using tetramethylsilane (TMS) as internal standard. Mass spectroscopy data of the product of the esterification was collected on MS-EI. Melting points were measured on X-4 melting-point device.

1-Butyl-3-methylimidazoliumchloride [bmim][Cl], 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), and [PEGmim]X series of ILs were prepared according to the procedure reported previously in [21], and the preparations of the three Brønsted acidic ILs were similar to those used in [2].

1.2 Procedure for esterification of aromatic acid

Alcohol (1.2 mmol), aromatic acid (1.0 mol), and 1-(3-sulfonic acid)-propyl-3-methylimidazolium hydrogen sulfate [MimC₃SO₃H][HSO₄] (IL7) (4 g) were added in a round-bottom flask with a reflux condenser. The reaction mixture was stirred for indicated time with the oil bath at indicated temperature. After the reaction the solution was cooled to room temperature and the ester was extracted with anhydrous diethyl ether (4×15 mL). The combined diethyl ether phase was concentrated. Further purification of the product was achieved by flash chromatography on a silica gel column. The residue was treated under vacuum at 70°C for 1 h to remove water and subjected to a second run with the same substrates without further addition of IL in the cycle.

1.3 Ethyl benzoate (C₆H₅COOCH₂^bCH₃^a, T3-1)

Colorless liquid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.39

(t, 3H, H^a), 4.37 (q, 2H, H^b), 7.41–8.06 (m, 5H, PhH). MS (EI): *m/z* (%): 150 (100) [M⁺], 121 (72), 105 (75), 77 (57).

1.4 Butyl benzoate (C₆H₅COOCH₂^dCH₂^cCH₂^bCH₃^a, T3-2)

Colorless liquid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.95 (t, 3H, H^a), 1.50 (m, 2H, H^b), 1.75 (m, 2H, H^c), 4.35 (m, 2H, H^d), 7.37–8.12 (m, 5H, PhH). MS (EI): *m/z* (%): 150 (100) [M⁺], 121 (72), 105 (75), 77 (57).

1.5 *n*-Butyl-2-nitrobenzoate (*o*-O₂N-C₆H₅COOCH₂^dCH₂^cCH₂^bCH₃^a, T3-3)

Pale yellow liquid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.96 (t, 3H, H^a), 1.47 (m, 2H, H^b), 1.71 (m, 2H, H^c), 4.34 (t, 2H, H^d), 7.63–7.70 (m, 2H, ArH, 4-H, 5-H), 7.75 (d, 1H, ArH, 6-H), 7.89 (d, 1H, ArH, 3-H). MS (EI): *m/z* (%): 223 (100) [M⁺], 224(12), 177(70), 149(35), 105(60).

1.6 *n*-Butyl-3-nitrobenzoate (*m*-O₂N-C₆H₅COOCH₂^dCH₂^cCH₂^bCH₃^a, T3-4)

Pale yellow liquid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.01 (t, 3H, H^a), 1.50 (m, 2H, H^b), 1.80 (m, 2H, H^c), 4.40 (t, 2H, H^d), 7.68 (t, 1H, ArH, 5-H), 8.37–8.44 (m, 2H, ArH, 4-H, 6-H), 8.85 (s, 1H, ArH, 2-H). MS (EI): *m/z* (%): 223 (100) [M⁺], 224(10), 177(66), 149(47), 105(50).

1.7 *n*-Butyl-4-nitrobenzoate (*p*-O₂N-C₆H₅COOCH₂^dCH₂^cCH₂^bCH₃^a, T3-5)

White solid, m.p. 35–36°C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.96 (t, 3H, H^a), 1.46 (m, 2H, H^b), 1.73 (m, 2H, H^c), 4.30 (t, 2H, H^d), 6.90 (d, 2H, ArH, 2-H, 6-H, *J*=6.5 Hz), 7.94 (d, 2H, ArH, 3-H, 5-H, *J*=6.5 Hz). MS (EI): *m/z* (%): 223 (100) [M⁺], 224(11), 177(65), 149(40), 105(45).

1.8 3,4-Dinitro-*n*-butylbenzoate (3,4-(O₂N)₂-C₆H₅COOCH₂^dCH₂^cCH₂^bCH₃^a, T3-6)

Pale yellow liquid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.02 (t, 3H, H^a), 1.51 (m, 2H, H^b), 1.83 (m, 2H, H^c), 4.47 (t, 2H, H^d), 9.16 (d, 2H, ArH, 5-H, 6-H, *J*=1.5 Hz), 9.23 (s, 1H, ArH, 2-H). MS (EI): *m/z* (%): 268(100) [M⁺], 269(13), 223 (100), 224(12), 177(68), 149(52), 105(48).

1.9 *m*-Chloro-*n*-butylbenzoate (*m*-Cl-C₆H₅COOCH₂^dCH₂^cCH₂^bCH₃^a, T3-7)

Colorless liquid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.98 (t, 3H, H^a), 1.48 (m, 2H, H^b), 1.75 (m, 2H, H^c), 4.33 (t, 2H, H^d), 7.38 (m, 1H, ArH, 5-H), 7.52 (d, 1H, ArH, 4-H), 7.92 (d, 1H, ArH, 6-H), 8.01 (s, 1H, ArH, 2-H). MS (EI): *m/z* (%): 212 (100) [M⁺], 214(32), 177(80), 149(35), 105(67).

1.10 *m*-Methyl-*n*-butylbenzoate (*m*-Me-C₆H₅COOCH₂^d-CH₂^cCH₂^bCH₃, T3-8)

Pale yellow liquid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.98 (t, 3H, H^a), 1.48 (m, 2H, H^b), 1.75 (m, 2H, H^c), 2.39 (s, 3H, -Me), 4.32 (t, 2H, H^d), 7.26–7.85 (m, 4H, ArH). MS (EI): *m/z* (%): 192(100) [M⁺], 177(70), 149(50), 105(48).

1.11 *p*-Methyl-*n*-butylbenzoate (*p*-Me-C₆H₅COOCH₂^d-CH₂^cCH₂^bCH₃, T3-9)

Pale yellow liquid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.98 (t, 3H, H^a), 1.48 (m, 2H, H^b), 1.74 (m, 2H, H^c), 2.40 (s, 3H, -Me), 4.31 (t, 2H, H^d), 7.23 (d, 2H, ArH, 3-H, 5-H, *J*=6.0 Hz), 7.93 (d, 2H, ArH, 2-H, 6-H, *J*=6.1 Hz). MS (EI): *m/z* (%): 192(100) [M⁺], 177(69), 149(44), 105(67).

1.12 *m*-Methoxy-*n*-butylbenzoate (*p*-MeO-C₆H₅COOCH₂^dCH₂^cCH₂^bCH₃, T3-10)

Pale yellow liquid. ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.97 (t, 3H, H^a), 1.47 (m, 2H, H^b), 1.73 (m, 2H, H^c), 3.84 (s, 3H, -OMe), 4.29 (t, 2H, H^d), 6.91 (d, 2H, ArH, 3-H, 5-H, *J*=6.6 Hz), 7.99 (d, 2H, ArH, 2-H, 6-H, *J*=6.6 Hz). MS (EI): *m/z* (%): 208(100) [M⁺], 193(80), 177(70), 149(50), 105(48).

2 Results and discussion

To determine the standard conditions, the esterification of *n*-butanol and benzoic acid was chosen as the model reaction (Scheme 1), and initially equivalent *n*-butanol and benzoic acid reacted each other in 4 g ILs at 80°C for 10 h under N₂ atmosphere, in which ILs acted both solvents and catalysts. The separation of the products was easily performed by the extraction with ethyl ether.

Firstly, the effect of various ILs on the esterification was studied, as shown in Table 1. ILs consisting of 1-butyl-3-methylimidazolium cation (ILs 1–3), PEG-ILs (ILs 4–6) and four HSO₃-functional Brønsted acidic ILs (ILs 7–10) were explored. We found that both 1-butyl-3-methylimidazolium cation (Table 1, entries 1–3) and PEG-ILs could not promote the reactivity (Table 1, entries 4–6) and only poor yields were obtained. However, HSO₃-functional Brønsted acidic ILs showed excellent catalytic activities and could improve the yield of esterification (Table 1, entries 7–10), and the anion of ILs influenced the reactivity of the esterification strongly. The ILs with HSO₄[−] as anion, that is, 1-(3-sulfonic acid)-propyl-3-methylimidazolium hydrogen

sulfate [MimC₃SO₃H][HSO₄] (IL 7) and 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate [MimC₄SO₃H][HSO₄] (IL 8) significantly promoted the reactivities (Table 1, entries 7,8). However, when anion was exchanged to MePhSO₃[−] ([*p*-TSA]), 1-(3-sulfonic acid)-propyl-3-methylimidazolium *p*-toluenesulfonic acid [MimC₃SO₃H][*p*-TSA] (IL 9) and 1-(4-sulfonic acid)-butyl-3-methylimidazolium *p*-toluenesulfonic acid [MimC₄SO₃H][*p*-TSA] (IL 10) presented poor effect on the reactivity (Table 1, entries 9, 10). These results suggested that both [MimC₄SO₃H][HSO₄] and [MimC₃SO₃H][HSO₄] were superior as dual solvent-catalysts for the esterification of aromatic acid with alcohol.

Next, we employed [MimC₃SO₃H][HSO₄] (IL 7) as catalytic system to optimize how temperatures affected the esterification reaction (Table 1, entries 11–13). Reducing the temperature from 80 to 60°C had a dramatic decrease to the reaction with the yield being lowered to 72.0% (Table 1, entry 11). On the other hand, when temperature increased from 80 to 100°C, a positive effect on the esterification was exhibited and excellent yield with 90.4% was offered (Table 1, entry 12). Obviously, the increase of temperature had advantage to the reaction. However, the by-product of carbonation of reactants produced rapidly when the reaction temperature increased to 120°C (Table 1, entry 13). The best yield was obtained at 100°C.

To further optimize the reaction condition, the effect of reaction times and the mole ratio of acid to alcohol was studied and the results were presented in Table 2. Under equivalent benzoic acid and *n*-butanol (acid/alcohol 1:1), reacting for 8 h would give 87.1% product (Table 2, entry 1). Extending reaction time from 10, 12 to 14 h would improve the yield from 90.4%, 93.6% to 94.2% (Table 2, entries 2–4). Obviously, a prolongation of reaction time could lead

Table 1 Effect of IL on the esterification of *n*-butanol and benzoic acid^{a)}

Entry	IL	Yield (%) ^{b)}
1	[bmim]Cl (IL 1)	17.5
2	[bmim]PF ₆ (IL 2)	35.2
3	[bmim]BF ₄ (IL 3)	37.4
4	[PEGmim]Cl (IL 4)	6.7
5	[PEGmim][BF ₄] (IL 5)	10.3
6	[PEGmim][PF ₆] (IL 6)	9.8
7	[MimC ₃ SO ₃ H]HSO ₄ (IL 7)	86.3
8	[MimC ₄ SO ₃ H]HSO ₄ (IL 8)	82.2
9	[MimC ₃ SO ₃ H]MePhSO ₃ (IL 9)	47.3
10	[MimC ₄ SO ₃ H]MePhSO ₃ (IL 10)	45.4
11 ^{c)}	[MimC ₃ SO ₃ H]HSO ₄ (IL 7)	72.0
12 ^{d)}	[MimC ₃ SO ₃ H]HSO ₄ (IL 7)	90.4
13 ^{e)}	[MimC ₃ SO ₃ H]HSO ₄ (IL 7)	81.7

a) Reaction conditions: benzoic acid (1.0 mmol), *n*-butanol (1.0 mmol), IL (4 g), 10 h, 80°C, under N₂. b) Yields were determined by means of GC based on benzoic acid, and were average of two runs. c) Reaction was carried out at 60°C. d) Reaction was carried out at 100°C. e) Reaction was carried out at 120°C.

Scheme 1 Esterification of *n*-butanol and benzoic acid in TSIL.

Table 2 Effect of reaction time and mole ratio of acid/alcohol on the esterification of *n*-butanol and benzoic acid in [MimC₃SO₃H]HSO₄^{a)}

Entry	Time (h)	Mole ratio of acid/alcohol	Yield (%) ^{b)}
1	8	1:1	87.1
2	10	1:1	90.4
3	12	1:1	93.6
4	14	1:1	94.2
5	16	1:1	94.5
6	14	1:1.2	95.3
7	14	1:1.5	95.5
8	14	1:2	95.6

a) Reaction conditions: benzoic acid (1.0 mmol), *n*-butanol (1.0–2.0 mmol), IL (4 g), 100°C, under N₂. b) Yields were determined by means of GC based on benzoic acid, and were average of two runs.

to a big increase in yield of esterification. However, continuous prolonging to 16 h resulted only in the slight increase in yield. Considering the various factors, we indicated 14 h to be reaction time (Table 2, entry 4). In the meanwhile, the mole ratio of acid/alcohol played an important role in the reaction. When the ratio varied from 1:1 to 1:1.2, the yield would improve from 94.2% to 95.3%. Obviously, the increase of the mole ratio of acid/alcohol induced the increase in yield. However, as the further increase of alcohol, the yield only enhanced to 96.0% when the ratio of acid/alcohol increased to 1:2. As expected, the superfluous alcohol would cause the difficulty of product separation as well as the waste of reactant. So we would adopt the mole ratio of acid/alcohol with 1:1.2.

To further understand the scope and limitations of the esterification in [MimC₃SO₃H]HSO₄, a variety of aromatic acids and alcohols were applied to the reaction and the results were presented in Table 3. We could see that the esterification

Table 3 Esterification of aromatic acid with alcohol in [MimC₃SO₃H]HSO₄^{a)}

Entry	Aromatic acid	Alcohol	Product	Yield (%) ^{b)}
1 ^{c)}		C ₂ H ₅ OH		91.4
2		CH ₃ (CH ₂) ₃ OH		95.0
3		CH ₃ (CH ₂) ₃ OH		96.2
4		CH ₃ (CH ₂) ₃ OH		87.7
5		CH ₃ (CH ₂) ₃ OH		89.3
6		CH ₃ (CH ₂) ₃ OH		83.2
7		CH ₃ (CH ₂) ₃ OH		92.6
8		CH ₃ (CH ₂) ₃ OH		95.8
9		CH ₃ (CH ₂) ₃ OH		96.5
10		CH ₃ (CH ₂) ₃ OH		97.7

a) Reaction conditions: benzoic acid (1.0 mmol), 1-butanol (1.2 mmol), IL (4 g), 14 h, 100°C, under N₂. b) Yields of esters were based on isolated crude product. c) Reaction was carried out at 85°C.

between different alcohols and different aromatic acids furnished the products in high yields in HSO_3 -functionalized Brønsted acidic ILs catalytic system. Due to the lower boil, $\text{CH}_3\text{CH}_2\text{OH}$ as alcohol species need lower temperature with only 85°C , which gave 91.4% when it reacted with benzoic acid. As the extension of chain of aliphatic alcohols, the high yields were obtained and $\text{CH}_3(\text{CH}_2)_3\text{OH}$ offered 95.0% (Table 3, entries 1, 2).

On the other hand, a variety of aromatic acids were applied to the esterification with $\text{CH}_3(\text{CH}_2)_3\text{OH}$, as shown in Table 3. It was worth noting that the catalytic system was tolerance to a broad range of functional groups, such as NO_2 , Cl, Me and OMe, and the property of withdrawing and donating electron of the groups would affect the activities. From the results we could see that the electron-deficient aromatic acid showed the less reactivity and moderate yields were obtained (Table 3, entries 3–7). For example, *m*-nitro-benzoic acid, *p*-nitro-benzoic acid and *m*-chloro-benzoic acid gave fewer yields (Table 3, entries 4, 5, 7). Furthermore, benzoic acid with more withdrawing electron groups exhibited poorer activities, and *p,m*-dinitro-benzoic acid (Table 3, entry 6) gave lower yield than benzoic acid with only one $-\text{NO}_2$ substituent (Table 3, entries 4, 5). However, *o*-nitro-benzoic acid gave higher yield with 96.2% (Table 3, entry 4). The reason can be explained by field effect, which activates the hydroxyl in carboxyl and induces to the acceleration of the reaction. On the other hand, the electron-rich aromatic acids, showed the excellent reactivity with high yields (Table 3, entries 8–10). *p*-Methylbenzoic acid afforded the desired product in 96.5% (Table 3, entry 9), while *p*-methoxybenzoic acid improved to 97.7% (Table 3, entry 10). Moreover, the substituent position could result in the different reactivities. *Meta*-position group decreased the yield for the more sterically hindered, while the *para*-substituent benzoic acids gave preferable reactivities (Table 3, entries 4 and 5, 8 and 9).

The reusability of the catalytic system was tested in the esterification of *n*-butanol with benzoic acid in $[\text{Mim}-\text{C}_3\text{SO}_3\text{H}]\text{HSO}_4$ at 100°C for 14 h. Since the IL was insoluble in diethyl ether and soluble in water, the products were easily isolated by simple extraction with diethyl ether. The rest of the IL was treated under vacuum at 70°C for 1 h to remove water and reuse in the recycle without further addition of IL. As was shown in Figure 1, the catalytic activity of the esterification was still very high after 7 times recycle of IL, which indicated that the IL as dual solvent-catalyst for the synthesis of aromatic esters was recyclable. It also could be seen that the conversion of the product was slightly decreased from 1st run to 7th run, which may be ascribed to the deactivation of IL.

3 Conclusions

The HSO_3 -functionalized Brønsted acidic ILs were proved

Figure 1 Recycling of esterification of *n*-butanol and benzoic acid in TSIL. Reaction conditions: benzoic acid (1.0 mmol), *n*-butanol (1.2 mmol), IL (4 g), 14 h, 100°C , under N_2 . Yields of esters were based on isolated crude product.

to be an excellent dual solvent-catalyst reaction media for the syntheses of aromatic esters with various aromatic acids and methanol, ethanol, and butanol, and it showed better catalytic than non-functionalized ILs. Utilization of IL results in the easy isolation of the product as well as catalyst recycling. The approach avoids the use of disadvantageous catalysts and volatile organic solvents, representing an environmentally friendly and effective method.

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