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Novel Brønsted-acidic ionic liquids based on benzothiazolium cations as catalysts for esterification reactions

XIAN SI ZHOU, JIA BING LIU, WEN FENG LUO, YI WEN ZHANG and HANG SONG*

School of Chemical Engineering, Sichuan University, Chengdu 610065, P. R. China

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Abstract: Three novel Brønsted-acidic ionic liquids based on benzothiazolium cations were prepared, which served as catalysts for the synthesis of benzoic esters. All three gave good yields of the target esters in esterification reactions. Moreover, they combine the advantages of both homogeneous and heterogeneous solid catalysts in esterification reactions, which enabled them to serve as homogeneous catalysts to catalyze the reactions and be conveniently recovered by simple filtration after the reactions. They could be reused several times without noticeable decrease in efficiency.

Keywords: benzoic esters; benzothiazolium salts; catalyst; esterification; ionic liquid.

INTRODUCTION

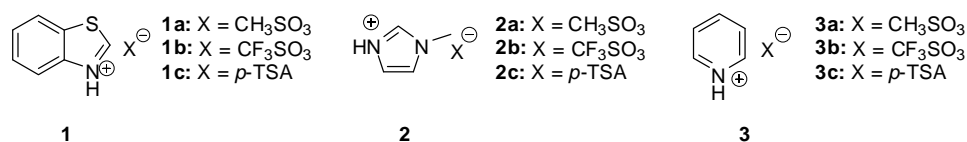
Aromatic esters are important intermediates in the chemical and pharmaceutical industries and are usually prepared in acid-catalyzed esterification reactions of alcohols with benzoic acids.¹ Inorganic acid catalysts such as H₂SO₄ and H₃PO₄, resins, supported mineral acids, heteropolyacids and zeolites have been used for esterifications.^{2–6} Although high yields could be achieved, the employment of these catalysts has some obvious drawbacks, such as the usage of organic solvents and difficulty in the recycling of the catalysts. Thus, it is necessary to develop new types of catalysts with environmentally friendly, reusable and highly efficient characteristics.

Ionic liquids (ILs), also known as molten salts or room temperature ionic liquids, have gained increasing attentions in the context of green synthesis in recent years. Owing to their negligible volatility, excellent thermal stability and structure variety, ILs are considered as environmentally benign media and catalysts for organic synthesis.^{7–10} Fisher esterification in acidic ILs was verified to be an environmentally efficient procedure for the synthesis of various esters and

* Corresponding author. E-mail: hangsong@scu.edu.cn
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had many advantages over reactions catalyzed by conventional liquid or solid acids. In recent years, parallel to the rapid development of ILs, their applications in esterification have been extensively studied. For example, catalytic amounts of Brønsted-acidic ionic liquids promoted esterification, microwave-accelerated esterification in Brønsted-acidic ionic liquids and ultrasound-assisted esterification in Brønsted-acidic ionic liquids have been reported.^{11–13} These method can reduce the reaction time, reaction temperature or diminish the consumption of ILs, but the isolation of ILs from the reaction mixture was not satisfactorily solved, due to the requirement of relatively complicated separation operations. Although polystyrene (PS)-supported ionic liquid catalysts can be recycled easily by filtration, they cannot serve as homogeneous catalysts to promote reactions.¹⁴ Davis¹⁵ and Wang *et al.*^{16,17} investigated Brønsted acidic ILs in some esterification reactions and removed the ILs by simple filtration after the reaction. The employed ILs were not conventional ILs due to their high melting points (some above 100 °C) and their solubility in the reaction mixture could be varied greatly with small-scale changes in temperature. Hence, they could serve as homogeneous catalysts to catalyze efficiently reactions at higher temperatures or as heterogeneous solid catalysts to simplify the isolation of ILs by filtration at lower temperatures. They combined the advantages of both homogeneous and heterogeneous solid catalysts. Nonetheless, the reports were still not completely satisfactory, especially for highly efficient syntheses of benzoic esters. As a result, it is very meaningful to develop new ILs as catalysts for more specific reactions.

Over the last two decades, pyridinium or *N*-methylimidazolium ionic liquids have been widely reported and applied to many organic reactions. However, research on the synthesis and applications of benzothiazolium-containing ILs was lacking until the year of 2010 when Munawar *et al.* first reported the synthesis and characterization of a series of benzothiazolium-containing ILs.¹⁸ Thus, there is an urgent need for research into new ionic liquids. Prompted by these findings and due to our interest in the synthesis of new ILs based on benzothiazolium cations with the above-mentioned properties, in this paper we wish to complement the research findings of Munawar by reporting three novel ILs based on benzothiazolium cations (Scheme 1) and their catalytic activity for the synthesis of benzoic esters as novel catalysts (compound **1c** was described as protonated benzothiazole in previous literature).¹⁹



Scheme 1. Structures of the ionic liquids used in this study.

EXPERIMENTAL

Chemicals and instruments

All chemicals (AR) were commercially available and used without further purification. The melting points were determined on an XRC-1 melting point apparatus (Sichuan University Instrument Factory, P. R. China). The ^1H - and ^{13}C -nuclear magnetic resonance (NMR) spectra were recorded on an AV-400 spectrometer (Bruker Corporation, Germany) in $\text{DMSO-}d_6$ with tetramethylsilane (TMS) as an internal standard. The electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a ZQ 4000 mass spectrometer (Waters Corporation, USA). The UV-Vis spectra were recorded on a UV-2450 spectrophotometer (Shimadzu, Japan) in methanol. The concentrations of the products were determined by high performance liquid chromatography (HPLC) using an LC-20AT HPLC instrument (Shimadzu, Japan) with a C18 column (3.9 mm \times 150 mm, 5 μm) using an internal standard.

Preparation of the ionic liquids

The ionic liquids with *N*-methylimidazolium or pyridinium cations, **2a-c** and **3a-c** (Scheme 1), were synthesized according to literature procedures.²⁰⁻²⁴ The preparation of the novel benzothiazolinm cations-based ionic liquids (ILs **1a-c**) was as follows: benzothiazole (100 mmol) was placed in a round-bottom flask equipped with a magnetic stirrer and dissolved in 50 mL ethanol. The solution was cooled to 0-5 °C in an ice bath and 20 mL of an ethanolic solution of methanesulfonic acid (trifluoromethanesulfonic acid or *p*-toluenesulfonic acid) (110 mmol) was added dropwise way over a period of 0.5 h. The reaction mixture was stirred for a further 4 h at room temperature. The ethanol was removed under vacuum affording crude IL as a white solid, which was washed with diethyl ether (3 \times 10 mL). The crude ionic liquid was purified by recrystallization from hot ethanol to give colorless flake crystals in quantitative yield. The ILs were dried at 80 °C under high vacuum for 12 h and then characterized by ^1H -NMR, ^{13}C -NMR and ESI-mass spectroscopy.

Procedure for the esterification reactions

A typical procedure for the esterification reactions is as follows. Benzoic acid (50 mmol, 6.1 g), *n*-butanol (150 mmol, 11.1 g) and IL **1a** (25 mmol, 5.8 g) were added to a 50 mL round-bottom flask equipped with a reflux condenser. The mixture was magnetically stirred for 8 h in an oil bath at 110 °C. After the reaction, the reaction mixture was cooled to room temperature whereby a liquid-solid system formed and then the ionic liquid **1a** precipitated. The IL was collected by filtration and reused after removal of water under vacuum at 80 °C for 4-5 h. The filtrate containing the target ester was analyzed by HPLC. When there was no phase separation of the reaction mixture, the following procedure was employed for ester isolation. The reaction mixture was diluted with water (10 mL) and extracted with diethyl ether (3 \times 10 mL). The combined ether extracts were dried over anhydrous MgSO_4 , and then analyzed by HPLC.

UV-Vis acidity determination

The Brønsted acidity of the ILs was evaluated by determination of the Hammett acidity function using UV-Vis spectroscopy. In the present case, the ILs and the indicator 4-nitroaniline were dissolved in methanol at concentrations of 20 and 0.1 mmol L⁻¹, respectively.

RESULTS AND DISCUSSION

Spectral data of the novel ILs 1a–c

Benzothiazolium methanesulfonate (1a). Yield: 95 %, m.p. 105–107 °C. ¹H-NMR (400 MHz, DMSO-*d*₆, δ / ppm): 2.62 (3H, *s*), 7.53 (1H, *t*, *J* = 7.2 Hz), 7.59 (1H, *t*, *J* = 7.2 Hz), 8.14 (1H, *d*, *J* = 8 Hz), 8.21 (1H, *d*, *J* = 8 Hz), 9.49 (1H, *s*). ¹³C-NMR (100 MHz, DMSO-*d*₆, δ / ppm): 39.58, 122.53, 122.76, 125.53, 126.25, 133.40, 152.42, 156.38. ESI-MS (*m/z* (+)): 137.2, (*m/z* (-)): 95.0.

Benzothiazolium trifluoromethanesulfonate (1b). Yield: 90 %; m.p. 128–130 °C. ¹H-NMR (400 MHz, DMSO-*d*₆, δ / ppm): 7.54 (1H, *t*, *J* = 7.2 Hz), 7.60 (1H, *t*, *J* = 7.2 Hz), 8.14 (1H, *d*, *J* = 8 Hz), 8.22 (1H, *d*, *J* = 8 Hz), 9.49 (1H, *s*). ¹³C-NMR (100 MHz, DMSO-*d*₆, δ / ppm): 119.05, 122.53, 122.74, 125.55, 126.27, 133.39, 152.36, 156.38. ESI-MS (*m/z* (+)): 136.4, (*m/z* (-)): 148.9.

Benzothiazolium p-toluenesulfonate (1c). Yield: 95 %, m.p. 120–122 °C. ¹H-NMR (400 MHz, DMSO-*d*₆, δ / ppm): 2.31 (3H, *s*), 7.19 (2H, *d*, *J* = 8 Hz), 7.52 (1H, *t*, *J* = 7.2 Hz), 7.56 (2H, *d*, *J* = 8.0 Hz), 7.59 (1H, *t*, *J* = 7.2 Hz), 8.13 (1H, *d*, *J* = 8.0 Hz), 8.21 (1H, *d*, *J* = 8.0 Hz), 9.52 (1H, *s*). ¹³C-NMR (100 MHz, DMSO-*d*₆, δ / ppm): 20.75, 122.57, 122.69, 125.50, 125.57, 126.31, 128.34, 128.34, 133.38, 138.54, 138.54, 144.26, 152.23, 156.54; ESI-MS (*m/z* (+)): 136.8, (*m/z* (-)): 170.9.

Acidities of the novel ILs

An efficient approach to evaluate the acidity of a Brønsted acidic ionic liquid is the Hammett method.²⁵ Hammett acidity function (*H*₀) is usually determined by UV–Vis spectrophotometry, wherein a basic indicator is used to trap the dissociated proton.²⁶ With increasing acidity of the acidic ionic liquid, the concentration of the unprotonated form of the basic indicator decreases, whereas the protonated form of the indicator could not be observed because of its small absorbance and its location; so the [I]/[IH⁺] ratio could be determined from the measured absorbance differences after addition of Brønsted acidic ionic liquid, and then the Hammett acidity function could be calculated from the following equation:^{27,28}

$$H_0 = \text{p}K(\text{I})_{\text{aq}} + \log ([\text{I}]/[\text{IH}^+])$$

where *pK*(I)_{aq} is the *pK*_a value of the indicator, [I] and [IH⁺] are, respectively, the molar concentrations of the unprotonated and protonated forms of the indicator.²⁹

The results obtained are shown in Fig 1. The absorbance of the unprotonated form of the indicator with three ionic liquids decreased as follows: benzothiazolium *p*-toluenesulfonate (**1c**) > benzothiazolium methanesulfonate (**1a**) > benzothiazolium trifluoromethanesulfonate (**1b**). The Hammett function was calculated and the obtained values are listed in Table I. It is clearly shown that the acidity order of the novel ILs is benzothiazolium trifluoromethanesulfonate (**1b**) > benzothiazolium methanesulfonate (**1a**) > benzothiazolium *p*-toluenesulfonate (**1c**).

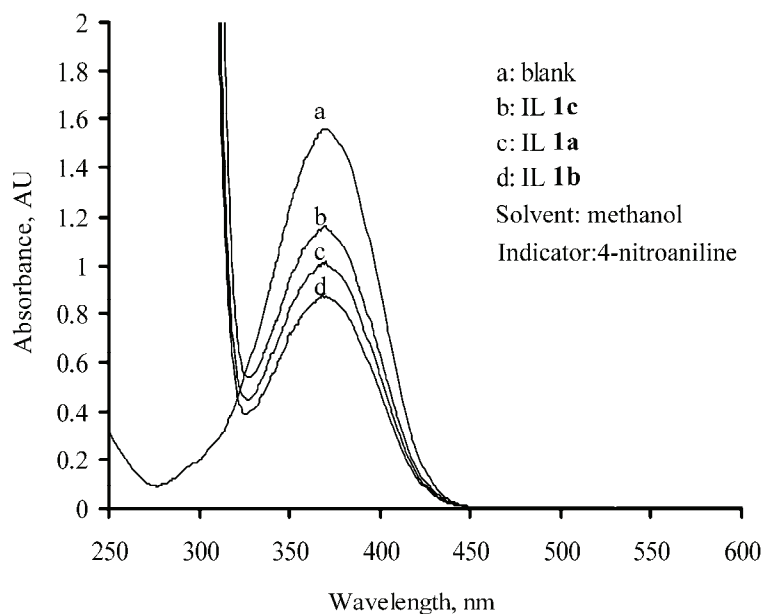


Fig. 1. Absorption spectra of 4-nitroaniline with the novel ionic liquids (20 mmol/L) in methanol.

TABLE I. Calculation and comparison of the Hammett acidity functions (H_0) of the novel ILs in methanol ($H_0 = pK(I)_{aq} + \log ([I]/[IH^+])$); indicator: 4-nitroaniline ($pK_a = 0.99$)

Ionic liquid	Absorbance	[I] / %	[IH ⁺] / %	H_0
Blank	1.5568	100	0	–
1a	1.0159	65.26	34.74	1.26
1b	0.8776	56.37	43.63	1.10
1c	1.1602	74.52	25.47	1.46

Esterification of benzoic acid by n-butanol using various ILs

The esterification of benzoic acid and *n*-butanol was chosen as a model reaction. The reaction was initially performed without a catalyst. The result (Table II, entry 1) showed that the esterification reaction was not realized and no product was obtained. This indicated that a catalyst for this reaction could be necessary. The catalytic performance of the ILs **1a–c** for the esterification of benzoic acid by *n*-butanol was investigated (Table II, entries 2–4). The ILs showed good catalytic activity and the ester yields were 93.9, 97.3 and 77.4 %, respectively. It was found that the catalytic activities of the acidic ILs in the esterification were in excellent agreement with their acidity order. ILs **1a** and **1c** formed a heterogeneous system (Fig. 2) while IL **1b** formed a homogeneous system after completion of the reaction and cooling down to room temperature. As a result, IL **1a** or **1c** could be easily separated from the reaction mixture by simple filtration. In order

to further compare the novel ILs with other pyridinium or *N*-methylimidazolium ionic liquids, six ILs (Scheme 1, **2a–c** and **3a–c**), reported in the literature, were used as catalysts for the model reaction (Table II, entries 5–10). As is shown (Table II, entries 5–7), when the reaction was promoted by *N*-methylimidazolium ILs (**2a–c**), benzoic acid could hardly react with *n*-butanol, only a trace of product was obtained, and the homogeneous reaction system made these ILs difficult to recover. Moreover, the ester yields were much lower (25.1–35.2 %) when pyridinium ILs (**3a–c**) (Table II, entries 8–10) were employed as catalysts than when benzothiazolium-based ILs were used. Taking the product yield of the reaction and the operational simplicity into consideration, benzothiazolium methanesulfonate (IL **1a**) may be preferential for the synthesis of benzoic esters.

TABLE II. Comparison of various ILs in the esterification of benzoic acid by *n*-butanol. Reaction conditions: benzoic acid, 50 mmol; *n*-butanol, 150 mmol; catalyst, 25 mmol; 110 °C for 8 h

Entry	Catalyst	IL precipitated or not (Y/N) ^a	Yield ^b , %
1	Without catalyst	–	0
2	1a	Y	93.9
3	1b	N	97.3
4	1c	Y	77.4
5	2a	N	6.1
6	2b	N	3.7
7	2c	N	Trace
8	3a	Y	33.8
9	3b	Y	35.2
10	3c	N	25.1

^aWhen the reaction mixture was cooled to room temperature; ^byields based on benzoic acid

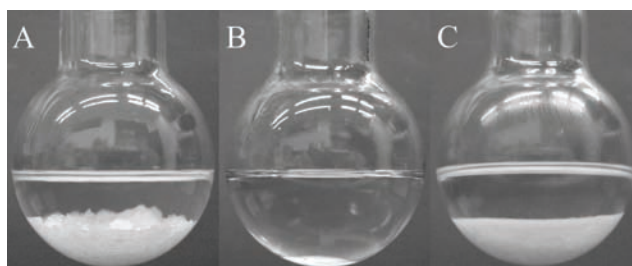


Fig. 2. Photographs of the esterification of benzoic acid with *n*-butanol over IL **1a**.

A) Heterogeneous system before reaction. The benzoic acid dissolved in *n*-butanol and the IL **1a** was at the bottom. B) Homogeneous mixture during the reaction. C) Heterogeneous system after completion of the reaction and the system had been cooled to room temperature, the IL has precipitated.

Various esterification reactions in IL **1a**

For evaluating the catalytic ability of IL **1a**, benzoic acids and several single alcohols were tried as reactants. The results of the experiments are summarized

in Table III. As is shown, under optimal conditions, the catalyst enabled good yields of all the target esters except *t*-butyl benzoate (no product was obtained, entry 8 in Table III). Yields of 70.3–97.3 % were obtained, which demonstrated that IL **1a** is an efficient catalyst for the esterification of benzoic acid with single alcohols. The reaction phenomena varied with the solubility of the catalyst in the reactants. When benzoic acid reacted with ethanol, *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol, *s*-butanol, *t*-butanol (Table III, entries 2–8), the IL dissolved in the homogeneous reaction mixture at working temperature and then the reaction medium switched from a homogeneous system to liquid–solid biphasic system when the reaction was completed and the system cooled to room temperature (Fig. 2). However, with methanol (Table III, entry 1), the esterification systems were homogeneous throughout the process. A proper explanation to this is that the solubility of the IL in alcohols varies with the polarity of the different alcohols and it decreases with decreasing alcohol polarity. The solubility of IL **1a** in the strongly polar methanol was high. However, IL **1a** has a much lower solubility in the less polar solvents (*i.e.*, ethanol, *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol, *s*-butanol and *t*-butanol) and is immiscible with the product ester at room temperature; thus, a liquid–solid biphasic system could be formed. Hence, IL **1a** could be removed by simple filtration and recycled; thus, it combines the advantages of both homogeneous catalysts and heterogeneous solid catalysts.

TABLE III. Results of the esterifications of benzoic acid (A) with various aliphatic alcohols (B) in IL **1a**. Reaction conditions: benzoic acid, 50 mmol

Entry	Alcohol	<i>t</i> / °C	τ / h	$n_A:n_B:n_{IL}$	IL precipitated or Not (Y/N) ^a	Yield ^b , %
1	Methanol	120	8	1:4:1	N	97.9
2	Ethanol	110	6	1:4:1.5	Y	97.3
3	<i>n</i> -Propanol	110	8	1:4:1	Y	96.1
4	<i>i</i> -Propanol	110	8	1:4:1	Y	70.3
5	<i>n</i> -Butanol	110	8	1:3:0.5	Y	93.9
6	<i>i</i> -Butanol	120	8	1:3:0.5	Y	90.3
7	<i>s</i> -Butanol	120	11	1:3:0.5	Y	72.6
8	<i>t</i> -Butanol	120	12	1:3:0.5	Y	Trace

^aWhen the reaction mixture was cooled to room temperature; ^byields based on benzoic acid

Reusability of the ionic liquid **1a**

To investigate the reusability of IL **1a**, a recycling experiment was performed. After the reaction of benzoic acid (50 mmol, 6.1 g), *n*-butanol (150 mmol, 11.1 g) and IL **1a** (25 mmol, 5.8 g) at 110°C for 8 h, the reaction mixture was cooled down to room temperature and IL **1a** was recovered by filtration. After treatment under vacuum at 80 °C for 4–5 h, IL **1a** was directly reused for the next run. The results (Table IV) showed that IL **1a** could be conveniently reused several times to catalyze the reaction in high product yields. The observed

slight decrease in the ester yield with the increase in reuse run may mostly be due to catalyst loss during filtration. In spite of this, the reuse performance of IL **1a** was excellent and 91.1 % yield was retained after three recycles. This indicates that the ionic liquid is recyclable and stable for these reactions.

TABLE IV. Reusability of IL **1a** in the esterification of benzoic acid by *n*-butanol. Reaction conditions: benzoic acid, 50 mmol; *n*-butanol, 150 mmol; catalyst, 25 mmol; 110°C for 8 h

Entry	Run	Yield ^a , %
1	Fresh catalyst	93.9
2	1 st cycle	93.1
3	2 nd cycle	92.0
4	3 rd cycle	91.1

^aYields based on benzoic acid

CONCLUSIONS

In summary, three novel acidic ionic liquids were successfully synthesized and used as highly efficient catalysts for esterification reactions. The catalytic procedure could produce a series of benzoic esters in high yield under mild reaction conditions. They combined the advantages of both homogeneous and heterogeneous solid catalysts in that they could be recycled by simple filtration and reused at least three times without obvious activity loss. Thus, a new, simple, efficient and eco-friendly method has been developed to synthesize a series of benzoic esters using these novel ILs.

ИЗВОД

НОВЕ ЈОНСКЕ ТЕЧНОСТИ ТИПА БРЕНСТЕД–ЛОРИЈЕВЕ КИСЕЛИНЕ СА БЕНЗОТИАЗОЛИЈУМ КАТЈОНОМ КАО КАТАЛИЗАТОРИ У РЕАКЦИЈАМА ЕСТЕРИФИКАЦИЈЕ

XIAN SI ZHOU, JIA BING LIU, WEN FENG LUO, YI WEN ZHANG и HANG SONG

School of Chemical Engineering, Sichuan University, Chengdu 610065, P. R. China

Синтетисане су три нове Бренстед–Лоријево киселине као јонске течности, које су употребљене као катализатори у синтези естара бензојеве киселине. Сва три катализатора омогућавају високе приносе у реакцијама естерификације. Осим тога, катализатори имају предности и хомогених и хетерогених катализатора у реакцијама естерификације, што омогућава да се користе као хомогени катализатори током реакције и касније изоловање филтрацијом током обраде реакција и поновно коришћење. Могу бити поново коришћене више пута без запаженог губитка ефикасности.

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