

Preparation and characterization of a novel benzimidazolium brønsted acidic ionic liquid and its application in esterifications

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Abstract. A novel brønsted acidic ionic liquid 1-butylbenzimidazolium tetrafluoroborate ([Hbbim]BF₄) based on the benzimidazolium cation was synthesized and characterized. This new ionic liquid was successfully used as a suitable catalyst for the esterifications of carboxylic acids with aliphatic alcohols.

Keywords. Ionic liquids; benzimidazole; esterifications.

1. Introduction

Ionic liquids (ILs), also known as molten salts with melting point under 100 or 150°C¹, have attracted an increasing attention in the context of green synthesis in recent years. Although ionic liquids were initially introduced as an alternative green media because they are room temperature molten salts that are nonvolatile, thermally stable, recyclable, and easy to handle,^{2–7} they have marched far beyond showing their significant catalytic activities for many reactions.^{8–11} Since the first successful use of ionic liquid, dialkylimidazolium chloroaluminate, as a catalyst in Friedel–Crafts acylations was reported in 1986,¹² a number of ionic liquids with unique properties have been developed and applied to catalyse many types of reactions.¹³ However, just as conventional organic solvents, not all ionic liquids are appropriate for a particular reaction, and a single ionic liquid will not always be the best for every reaction.¹⁴ It continues to be worthwhile to synthesize novel ionic liquids for particular chemical processes even though a large number of these new compounds are already known.

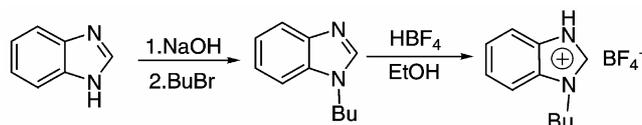
Recently, Dai *et al* reported the synthesis of a novel brønsted acidic ionic liquid based on benzimidazolium cation, 1-ethylbenzimidazolium tetrafluoroborate ([Hebim]BF₄) and found that it was an efficient medium for the preparation of aryl esters.¹⁵ In this paper, we describe fully the preparation and characterization of another benzimidazolium

ionic liquid, [Hbbim]BF₄ and study its application in the esterifications of several carboxylic acids with aliphatic alcohols (scheme 1).

2. Experimental

2.1 Materials and reagents

All chemicals (AR grade) were commercially available and used without further purification unless otherwise stated. Infrared spectra on KBr pellets were recorded on a Bruker EQUINOX-55 FT-IR spectrophotometer in the range 4000–400 cm⁻¹. Elemental analyses were determined with a Perkin-Elmer model 240C instrument. ¹HNMR spectra in propanone-*d*₆ solution using a Varian INOVA-400 spectrometer; proton chemical shifts were recorded relative to an internal TMS standard. The differential scanning calorimetry (DSC) experiment and the thermal stability of each ionic liquid was performed using Q1000DSC+LNCS+FACS Q600SDT at a heating rate 5°Cmin⁻¹ with nitrogen as the purge gas. Esterification reaction progress was monitored by GC-MS (AligentGC: 6890N, MS:5793N).



Scheme 1. The synthetic process of ionic liquid.

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2.2 Synthesis of ionic liquid [Hbbim]BF₄

2.2a 1-butyl benzimidazole ([bbim]): The synthesis process was carried out according to the previous literature.¹⁶ A mixture of 11.8 g (0.1 mol) of benzimidazole, 30 ml of 50% sodium hydroxide and 8.7 ml (0.11 mol) of 1-bromobutane were placed in a three-necked flask, which was provided with a mechanical stirrer, reflux condenser, and the thermometer. The reaction mixture was stirred for 3 min. When the mixture solidified, the temperature of the water bath was raised to 30–40°C and the content became liquid. After 2 min an exothermic effect was observed, and the temperature of the reaction mixture was maintained at 30–40°C for 10 min. The organic layer was extracted with CHCl₃ (3 × 30 ml), washed with water and dried with anhydrous sodium sulfate. The solvent was evaporated in vacuum, and the oil obtained was purified by distillation.

2.2b 1-butylbenzimidazolium tetrafluoroborate ([Hbbim]BF₄): Tetrafluoroboric acid (40% solution in water) was added drop-wise to a pre-cooled (0–5°C) ethanol solution of equivalent bbim in a three-necked flask with a mechanical stirrer. The mixture was maintained at that temperature and stirred for an additional period of 3 h. Ethanol and water was removed under vacuum in a rotary evaporator. The viscous residue was dehydrated at 80°C in a vacuum oven for 2 h. The dehydrated residue solidified on cooling to a colourless crystalline solid. Yield: 13.1 g (100%), m.p. 82–84°C. IR, ν (KBr): 3338, 3148, 3028, 2962, 2872, 1616, 1551, 1498, 1450, 1382, 1319, 1057, 754 cm⁻¹. ¹HNMR (400 Hz, CD₃COCD₃-d₆), δ : 9.60 (s, 1H, im-H), 8.11–8.13 (m, 1H, Ar-H), 8.00–8.02 (m, 1H, Ar-H), 7.71–7.76 (m, 2H, Ar-H), 4.73 (t, *J* (H, H) = 7.2 Hz, 2H, N-CH₂), 2.07–2.13 (m, 2H), 1.44–1.54 (m, 2H), 0.98 (t, *J* (H, H) = 7.4 Hz, 3H). Elemental analysis calcd. (%) for C₁₁H₁₅N₂BF₄ (262.05) C, 50.42; H, 5.77; N, 10.69. Found C, 50.47; H, 5.84; N, 10.75.

2.3 Esterifications in novel ionic liquid

Ethanol 0.46 g (0.01 mol), equivalent acetic acid 0.06 g (0.01 mol) and ionic liquids [Hbbim]BF₄ 1.31 g (0.005 mol) were added in a flask with a reflux condenser and oil-bath. The reaction mixture was stirred for 2 h with the oil bath at 80°C. Reaction progress was monitored by GC-MS. After the reaction, the ester was simply decanted from the ionic liquid, and the ionic liquid [Hbbim]BF₄ was reused after removal of water under vacuum (0.01 Torr) at 80°C for 2 h.

3. Results and discussion

3.1 Synthesis of ionic liquid

The [Hbbim]BF₄ ionic liquid was prepared by simple acid-base neutralization from the corresponding 1-butylbenzimidazole with tetrafluoroboric acid. Ethanol was used as the solvent because of the high solubility involved. The reaction was carried out in an ice bath and required little time or labour. The molecular structure of the ionic liquid was characterized via FT-IR, ¹HNMR and elemental analysis. All the data of characterization are in accordance with the expected compositions and structures.

3.2 Solubility

The solubility property of [Hbbim]BF₄ in some common solvents was studied. It was completely soluble in water, ethanol, methanol, acetonitrile and acetone and immiscible with benzene, toluene, cyclohexane, ethyl acetate and diethyl ether.

3.3 Thermal stability and DSC measurement

The thermogravimetric analysis experiment was conducted to determine the thermal stabilities of the novel ionic liquid. Although the study¹⁷ indicated that the new ionic liquid began to decompose at slightly lower temperature than that of imidazole series, it also displayed high thermal stability. The sample was stable to temperature of 210°C and showed a weight loss of 90% between 220 and 270°C. When the temperature was 290°C, the amount of residue was only 0.5%. Thus, it has potential usage as alternative to conventional organic solvents due to its special solubility and excellent thermal stability.

3.4 Esterifications in the novel ionic liquid [Hbbim]BF₄

The esterifications of several carboxylic acids with common aliphatic alcohols were carried out using the [Hbbim]BF₄ as a catalyst. Higher yields were obtained because of the good solubility of the acids and alcohols in [Hbbim]BF₄ while the esters are almost immiscible with ionic liquid. The benzimidazolium novel brønsted acidic ionic liquid which was screened as a catalyst for esterifications of carboxylic acids and aliphatic alcohols could be easily reused after

Table 1. Results of esterification for different acids and alcohols in [Hbbim]BF₄.

| Entry | Acid | Alcohol | Time (h) | T (°C) | Yield (%) |
|-------|--------------------------|----------------------------|----------|--------|-----------|
| 1 | Acetic acid | 1-butanol | 2.0 | 120 | 96 |
| 2 | Acetic acid | <i>iso</i> -butyl alcohol | 2.0 | 120 | 89 |
| 3 | Acetic acid | <i>sec</i> -butyl alcohol | 2.0 | 120 | 71 |
| 4 | Acetic acid | <i>tert</i> -butyl alcohol | 2.0 | 120 | 58 |
| 5 | Acetic acid | Ethanol | 2.0 | 80 | 96 |
| 6 | Oxalic acid ^a | 1-butanol | 8.0 | 120 | 93 |
| 7 | Benzoic acid | Ethanol | 8.0 | 80 | 86 |

^aIn the reaction of oxalic acid, no monoesterification products were detected when the molar ratio of acid to alcohols was 1 : 2

Table 2. Reuse of [Hbbim]BF₄ in the synthesis of acetic acetate.

| Run | Time (h) | T (°C) | Yield (%) |
|-----|----------|--------|-----------|
| 1 | 2.0 | 80 | 95 |
| 2 | 2.0 | 80 | 95 |
| 3 | 2.0 | 80 | 94 |
| 4 | 2.0 | 80 | 95 |
| 5 | 2.0 | 80 | 95 |
| 6 | 2.0 | 80 | 94 |

removal of water under vacuum. Its catalytic activity was still very high after 6 times reuse.

The esterification results of several different acids with alcohols were outlined in table 1. It can be found that the [Hbbim]BF₄ is of high activity for esterification, and esterification of aromatic acids gave lower yields compared with those of aliphatic acids. No by-product was detected.

The results in table 1 also suggested that the esterifications of acids with primary alcohols was satisfactory, followed by secondary alcohols. The lower yield of tertiary alcohols (Entry 4, table 1) was due to the increase in the steric interaction.

The [Hbbim]BF₄ is miscible with water and immiscible with ethers, so the esterifications proceeded smoothly for completion even without simultaneous removal of the produced water, even though esterification is a reversible reaction. The ionic liquid could be easily recycled. After reaction, the ionic liquid was simply separated and regenerated by removal of the water in vacuum. It was reused repeatedly over 6 times in the esterification of acetic acid with ethanol, and its catalytic activity was unchanged (table 2).

4. Conclusion

The esterifications of aliphatic acids in a novel brønsted ionic liquid were investigated. The results

indicated that the ionic liquid [Hbbim]BF₄ showed good catalytic activity to the esterifications and high yields were obtained under mild reaction conditions. After the reaction, the esters could be easily separated; the ionic liquids could be recycled at least 6 times without a significant decrease in catalytic performance.

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