

# Brønsted acidic ionic liquids: A green, efficient and reusable catalyst system and reaction medium for Fischer esterification

Trissa Joseph, Suman Sahoo, S.B. Halligudi\*

*Catalysis Division, National Chemical Laboratory, Pune 411008, India*

Received 19 February 2005; received in revised form 7 March 2005; accepted 7 March 2005

Available online 11 April 2005

## Abstract

Brønsted acidic ionic liquid containing nitrogen-based organic cations 1-methylimidazole and 1-butyl-3-methylimidazolium and inorganic anions of the type  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  and  $\text{PTSA}^-$  has been synthesized in good yields and used as a catalysts and reaction medium for Fischer esterification of alcohols with acids. These were characterized using FTIR and NMR spectroscopy. Ionic liquids as catalyst afforded good alcohol conversion and excellent ester selectivity. Fischer esterification of acetic acid with benzyl alcohol with different Brønsted acidic ionic liquids was carried out. Maximum substrate conversion 100% and product selectivity 100% was observed on using  $[\text{BMIM}]^+\text{PTSA}^-$  as catalyst over a period of 2 h. The ester was easily separated from the reaction mixture and the ionic liquid was reused four times after removing water. No significant loss in catalytic activity was observed on recycling.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Ionic liquid; Fischer esterification; Acids; Alcohol and reaction medium

## 1. Introduction

Room temperature ionic liquids (RTILs) have attracted great research interest due to the potential commercial and environmental advantages they offer over existing liquids. RTILs are comprised of ions that allow them to potentially behave in a very different manner to conventional molecular liquids when they are used as solvents [1–3]. Esterification of alcohols by carboxylic acids is an important reaction in both laboratory work and in organic industry [4]. Esters ranging from aliphatic to aromatic are generally used as plasticizers, solvents, perfumes, and flavor chemicals and also as precursors for pharmaceuticals, agrochemicals and fine chemicals [5].

Esterification is conventionally carried out by using homogeneous catalysts such as sulfuric acid and *p*-toluene sulfonic acid [6,7] suffer from the problem of side reactions, corrosion of the equipment and require tedious isolation of products and removal of large volumes of salt waste during

neutralization of homogeneous acid. The extensive demand for cleaner environment is forcing chemical industry to use less hazardous materials. To overcome these disadvantages efforts have been made to the development of heterogeneous catalysts systems. Esterification has been carried out previously using different heterogeneous acid catalysts such as resins [8,9], supported mineral acid [10] heteropoly acids [11,12], and zeolites [13] by different groups. However these catalysts due to their corrosive nature, high cost and unstable nature could not be used in production centers. Another approach to environment friendly reactions is to minimize the use of volatile organic solvents (VOC's) in reactions and their subsequent workup.

Ionic liquids are emerging as a green reaction media (catalyst + solvent). The use of ionic liquids as reaction medium may offer a convenient solution to both the solvent emission and catalytic recycling problem [1,14–16]. Currently reports are available in the open literature on esterification of alcohols and olefins using ionic liquids [17–20]. Esterification of benzyl alcohol with acetic acid using H- $\beta$  and H-Y gave selectivity for ester in the range of 75–100% [21]. In this work we have used Brønsted acidic ionic liquid with

\* Corresponding author. Tel.: +91 205 893 300; fax: +91 205 893 761.

E-mail address: [halligudi@cata.ncl.res.in](mailto:halligudi@cata.ncl.res.in) (S.B. Halligudi).

different inorganic anions of the type  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  and  $\text{PTSA}^-$  and used for the esterification of benzyl alcohol with acetic acid. The role of the ionic liquid will be to provide a medium for the catalyst and solubility for starting materials and products. Such combination of catalyst with medium has been found to be a viable alternative approach towards modern synthetic chemistry especially when considering the growing environmental demands being placed on chemical processes. The advantage of using RTIL for esterification is the ease with the ester can be separated out from the reaction medium by simple decantation as they are insoluble in most of the RTILs and there is no need to remove the water formed in the reaction as it remains in the RTIL. The RTIL can be reused after removing the water.

## 2. Experimental

### 2.1. Materials

All the acids and alcohols were obtained from S.D. Fine Chemicals, Ltd. (Mumbai) India and were used as received. Tetrafluoroboric acid (40%) solution in water was obtained from Loba Chemie India. 1-Methylimidazole (99%), 1-butyl-3-methylimidazolium chloride (99%), Potassium hexafluorophosphate (98%) and Sodium tetrafluoroborate (98%) were obtained from Lancaster (UK).

### 2.2. Synthesis

#### 2.2.1. Preparation of 1-methylimidazolium tetrafluoroborate ( $[\text{MIM}]^+\text{BF}_4^-$ )

Tetrafluoroboric acid (8.06 g, 0.03 mol, 40% solution in water) was slowly added to a precooled solution ( $0^\circ\text{C}$ ) of 1-methylimidazole (3 g, 0.03 mol) placed in a two-necked flask with a magnetic stirrer. The mixture was maintained at that temperature and stirred for 2 h. The resulting colorless Ionic Liquid was dried in a rotavapor for 2 h. at  $60^\circ\text{C}$  to remove water and used for esterification.

#### 2.2.2. Preparation of 1-butyl 3-methylimidazolium tetrafluoroborate ( $[\text{BMIM}]^+\text{BF}_4^-$ ) and 1-butyl 3-methylimidazolium hexafluorophosphate ( $[\text{BMIM}]^+\text{PF}_6^-$ )

1-Butyl 3-methylimidazolium chloride (1.74 g, 0.01 mol) was dissolved in 50 ml of acetone in a 100 ml round bottom

flask provided with a stirrer. Then  $\text{NaBF}_4$  (1.09 g, 0.01 mol) or  $\text{KPF}_6$  (1.84 g, 0.01 mol) was added and the solution was stirred for 24 h. at room temperature (Fig. 1). The resulting precipitate of  $\text{NaCl}$  or  $\text{KCl}$  was filtered and acetone was removed on a rotavapor to obtain a yellow colored liquid.

#### 2.2.3. Preparation of 1-butyl 3-methylimidazolium para-toluenesulfonic acid ( $[\text{BMIM}]^+\text{PTSA}^-$ )

1-Butyl 3-methylimidazolium chloride (1.74 g, 0.01 mol) was placed in a two necked flask with stirrer and was cooled to  $0^\circ\text{C}$ . Then 5 ml of water was added to it and para-toluenesulfonic acid (1.90 g, 0.01 mol) was added slowly under stirring. The mixture was stirred for 2 h. and the water was removed on a rotavapor at  $60^\circ\text{C}$  to obtain a green colored liquid.

### 2.3. Characterization procedures

The FTIR spectra of the ionic liquids were recorded on a Shimadzu (model 8201 PC) spectrophotometer using KBr plates in a frequency range  $1750\text{--}1300\text{ cm}^{-1}$  using pyridine as a probe for acidity measurement. The  $^1\text{H NMR}$  spectrum of the ionic liquids were recorded immediately after dissolution of the complex in  $\text{CDCl}_3$  with TMS as reference (200 MHz).

### 2.4. Catalytic activity studies

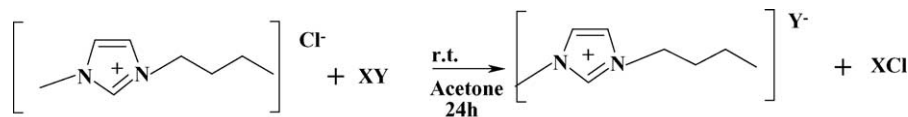
The utility of the ionic liquids was established in the esterification of aliphatic acids with alcohols. In a typical reaction benzyl alcohol (1.05 g), acetic acid (1.2 g) and 1 g of ionic liquid were taken in a 50 ml two-necked round bottom flask immersed in an oil bath and fitted with a water cooled condenser. The reactions were conducted at  $110^\circ\text{C}$ . The progress of the reactions was monitored by withdrawing the samples at different times and analyzing them by a gas chromatograph (Shimadzu 14B; FID detector; SE-52 capillary column). The identities of the products were confirmed by GC–MS (Shimadzu GC–MS QP 5000).

## 3. Results and discussion

### 3.1. Characterization

#### 3.1.1. FTIR

The Lewis and Brønsted acidity of the ionic liquid has been determined using pyridine as a probe molecule by



Where  $\text{X}=\text{Na}$  or  $\text{K}$ ;  $\text{Y}=\text{BF}_4$  or  $\text{PF}_6$ , respectively

$[\text{BMIM}]^+\text{PTSA}^-$  is synthesized in presence of water instead of acetone at  $0\text{--}5^\circ\text{C}$ .

Fig. 1. Preparation of ionic liquid.

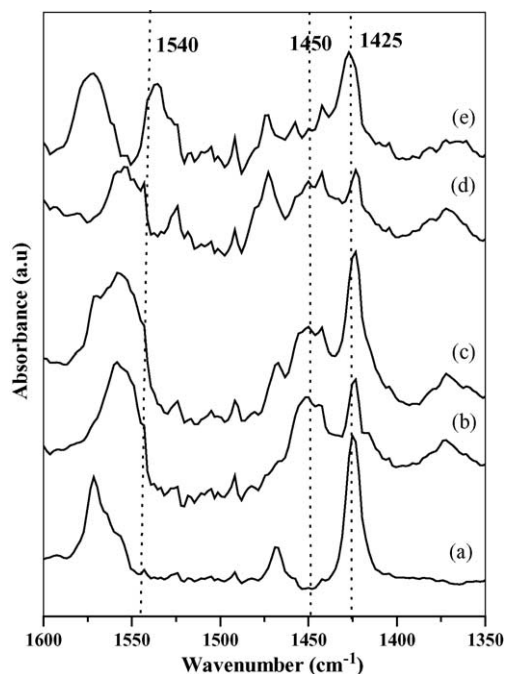


Fig. 2. FTIR spectra: (a) neat pyridine, (b) pyridine with [BMIM]<sup>+</sup>PF<sub>6</sub><sup>-</sup>, (c) pyridine with [BMIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, (d) pyridine with [BMIM]<sup>+</sup>PTSA<sup>-</sup>, (e) pyridine with [MIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup>.

monitoring the bands in the range of 1350–1600 cm<sup>-1</sup> arising from its ring vibration modes [22,23]. The FTIR spectra of neat pyridine show a band at 1425 cm<sup>-1</sup> (Fig. 2a). On mixing pyridine with ionic liquid, the spectrum of ionic liquid shows a band near 1450 cm<sup>-1</sup> indicates the coordination of pyridine to the Lewis acid sites, with an additional band near 1540 cm<sup>-1</sup> indicating the presence of Brønsted acid sites due to the formation of pyridinium ions (Fig. 2b–e).

### 3.1.2. <sup>1</sup>H NMR

The <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, TMS) spectrum of the ionic liquid [BMIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup> shows that the protons resonate in the range δ 0.88(s, 3H), 1.533(m, 2H), 1.839(m, 2H), 3.9(s, 3H), 4.062(m, 2H), 7.22(m, 2H), 9.40(s, 1H). The <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, TMS) spectrum of the ionic liquid [MIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup> shows that the protons resonate in the range δ 1.18(s, 3H), 7.1(m, 2H), 9.4(s, 1H). From the <sup>1</sup>H spectral data, it is revealed that the proton (δ 9.4), which is in between the two nitrogens in the imidazole ring, might be acidic.

### 3.2. Esterification

Fischer esterification of acetic acid with benzyl alcohol was carried out with different ionic liquids (Table 1). All the ionic liquids gave very good conversions and excellent product selectivity. The results on varying the anion of the ionic liquid are presented in Table 1 esterification proceeded smoothly to completion. A maximum 100% conversion and 100% product selectivity was observed on using [BMIM]<sup>+</sup>PTSA<sup>-</sup> as catalyst over a period of 2 h. [BMIM]<sup>+</sup>PF<sub>6</sub><sup>-</sup> also gave 100% conversion in 2 h but only 90% selectivity for ester was observed and the remaining 10% ether was formed (Table 1, Entry 3).

The effect of mole ratio of imidazole and BF<sub>4</sub><sup>-</sup> on the esterification of benzyl alcohol with acetic acid was studied (Table 1, Entry 1–2). It is seen that on increasing the amount of anion in the ionic liquid, the conversion increases but the selectivity remains the same. The results in Table 2 show the esterification of different alcohols with acetic acid and propionic acid using [MIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (MIM/BF<sub>4</sub><sup>-</sup>, 1:0.4) as catalyst and solvent. Conversion in the range 70–80% and 100% selectivity was observed for all the reactions over

Table 1  
Results of esterification of benzyl alcohol and acetic acid in different ionic liquids

Entry	Acid	Alcohol	Ionic liquid	Ratio <sup>a</sup>	Time (h)	% Conversion	% Selectivity
1	Acetic acid	Benzyl alcohol	[MIM] <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	1:1	4	91	100
2	Acetic acid	Benzyl alcohol	[MIM] <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	1:0.4	4	70.2	100
3	Acetic acid	Benzyl alcohol	[BMIM] <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	1:1	2	100	90 <sup>b</sup>
4	Acetic acid	Benzyl alcohol	[BMIM] <sup>+</sup> PTSA <sup>-</sup>	1:1	2	100	100
5	Acetic acid	Benzyl alcohol	[BMIM] <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	1:1	4	80	100

Reaction condition: acetic acid:benzyl alcohol, 2:1; ionic liquid = 1 g; temperature = 110 °C.

<sup>a</sup> Ratio of imidazole to anion source.

<sup>b</sup> [BMIM]<sup>+</sup>PF<sub>6</sub><sup>-</sup> gave 90% ester selectivity and 10% dibenzyl ether was formed.

Table 2  
Results of esterification of different alcohols and acids with [MIM]<sup>+</sup>BF<sub>4</sub><sup>-</sup>

Entry	Acid	Alcohol	MIM/BF <sub>4</sub>	Time (h)	% Conversion	Ester	Formula	Fragrance
1	HAc	Benzyl alcohol	1:0.4	4	70.2	Benzyl acetate	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	Peach
2	HAc	1-Octanol	1:0.4	4	70.8	Octyl acetate	CH <sub>3</sub> CO <sub>2</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	Orange
3	HAc	Isoamyl alcohol	1:0.4	6	78.7	Isoamyl acetate	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	Banana
4	PrAc	Ethanol	1:0.4	4	72	Ethyl propionate	CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Pear
5	PrAc	Isobutanol	1:0.4	6	76.2	Isobutyl propionate	CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	Rum

Reaction condition: acid:alcohol, 2:1; ionic liquid = 1 g; temperature = 110 °C; imidazole:BF<sub>4</sub><sup>-</sup> 1:0.4; HAc = acetic acid, PrAc = propionic acid.

Table 3  
Catalyst recycling of benzyl alcohol esterification using  $[\text{MIM}]^+\text{BF}_4^-$

Cycle	Ester yield (%)
Fresh	91
1st recycle	90
2nd recycle	90
3rd recycle	87
4th recycle	86

Reaction condition: acetic acid:benzyl alcohol, 2:1; ionic liquid=1 g; temperature = 110 °C.

a period of 4 h. For complete conversion, the reaction had to be carried out for longer time. Further increase in conversion was also observed on increasing the temperature to 120 °C.

Most of the esters were immiscible with ionic liquid, so it could be separated by decantation as it forms a separate layer at the end of the reaction. The esters that were miscible with the ionic liquid had to be separated by extraction with ether. All the ionic liquids were easily recyclable after removing water.  $[\text{MIM}]^+\text{BF}_4^-$  was recycled 4 times for the esterification of benzyl alcohol with acetic acid (Table 3). Minor loss in activity was observed after 4 recycles. Selectivity remained same for all the recycles.

#### 4. Conclusions

Esterification using catalytic amount of ionic liquids gave high substrate conversion and product selectivity. Esterification with ionic liquid as reaction medium proceeded smoothly to completion and liquid esters were conveniently decanted out from the ionic liquid. Use of such a reaction medium should be appreciated for its easy preparation, convenient separation, recycle of the catalyst, low cost and eco-friendly nature.

#### Acknowledgments

T.J. acknowledges DST for Young Scientist Fellowship. One of the authors S.S. thanks CSIR, New Delhi for granting her JRF.

#### References

- [1] T. Welton, Chem. Rev. 99 (1999) 2071.
- [2] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772.
- [3] C. Gordan, Appl. Catal. A: Gen. 222 (2001) 101.
- [4] R.C. Larock (Ed.), Comprehensive Organic Transformations, second ed., VCH, New York, 1999.
- [5] P.W. Greene, P.G.M. Wuts, Protective Groups in Organic Chemistry, Wiley, New York, 1999 (Chapter 5).
- [6] M. Mäki-Arfela, T. Salmi, M. Sundell, K. Ekman, R. Peltonen, J. Lehtonen, Appl. Catal. A: Gen. 184 (1999) 25.
- [7] M. Hino, K. Arata, Appl. Catal. A: Gen. 18 (1985) 401.
- [8] A. Heidekum, M.A. Harmer, W.F. Hoelderich, J. Catal. 181 (1999) 217.
- [9] M. Gruffaz, O. Micaelli, USP 4275228 (1981).
- [10] I.J. Dijks, H.L.F. van Ochten, C.A. van Walree, J.W. Geus, L.W. Jennesskens, J. Mol. Catal. A: Chem. 188 (2002) 209.
- [11] K. Sano, M. Nishiyama, T. Suzuki, S. Wakabayashi, K. Miyahara, USP 5189201 (1993).
- [12] K. Inoue, M. Iwasaki, K. Matsui, USP 5241106 (1993).
- [13] R.A. Crane, S.H. Brown, L. De Caul, USP 5973193 (1999).
- [14] M.J. Earle, P.B. McCormac, K.R. Seddon, Chem. Commun. (1998) 2245.
- [15] F. Liu, M.B. Abrams, R.T. Baker, W. Tumas, Chem. Commun. (2001) 5433.
- [16] E.D. Bates, R.D. Mayton, I. Ntai, J.H. Davis, J. Am. Chem. Soc. 124 (2002) 926.
- [17] D.C. Forbes, K.J. Weaver, J. Mol. Catal. A, Chem. 214 (2004) 129.
- [18] H.-P. Zhu, F. Yang, J. Tang, M.-Y. He, Green Chem. 5 (2003) 38.
- [19] Y. Gu, F. Shi, Y. Deng, J. Mol. Catal. A, Chem. 212 (2004) 71.
- [20] J. Gui, X. Cong, D. Liu, X. Zhang, Z. Hu, Z. Sun, Catal. Commun. 5 (2004) 473.
- [21] S.R. Kirumakki, N. Nagaraju, S. Narayanan, Appl. Catal. A: Gen. 272 (2004) 1.
- [22] E.P. Parry, J. Catal. 2 (1963) 371.
- [23] Y.-I. Yang, Y. Kou, Chem. Commun. (2004) 226.