Available online at www.sciencedirect.com

ScienceDirect

Journal of Molecular Catalysis A: Chemical 279 (2008) 159–164

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

A green approach for the synthesis of long chain aliphatic acid esters at room temperature

Xinzhong Li [a,b], Wumanjiang Eli [b,*]

[a] *Graduate School of Chinese Academy of Sciences, Beijing 100049, China*
[b] *Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, Urumqi 830011, China*

Abstract

Fischer esterification of long chain aliphatic acids with methanol and ethanol could be promoted by two novel Brønsted acidic ionic liquids that bear an aromatic sulfonic acid group on the imidazolium or pyridinium cation. The reactions carried out smoothly at room temperature with good to excellent isolated yields (85–99%) under solvent-free conditions in the presence of 10 mol% ionic liquids. These ionic liquids could be recovered easily and recycled three times without any significant loss in catalytic activity.

Keywords: Brønsted acid; Ionic liquid; Fischer esterification; Sulfonic acid group

1. Introduction

Long chain aliphatic esters are important chemical products and intermediates [1]. There are many routes [2] available for their preparation, the simpler and most widely employed method is the Fisher esterification. However, the conventional Fisher esterification suffers from problems associated with the generation of side reactions (such as oxidation, etherification), corrosion of equipments, tedious purification procedures, long reaction times and discharge large volumes of acidic wastes. In addition to these problems, this industrially important process also suffers from using volatile organic solvents. Facing the ecological and economic increasing challenge, there is an urgent need to develop an environmentally benign, simple and highly efficient method for the synthesis of long chain aliphatic esters. Recently functional ionic liquids have crossed the barrier of solvent and entered very successfully into the area of catalyst [3,4]. For example, Brønsted acidic ionic liquids (BAILs), which contain Brønsted acid functionalized component in the cation or anion, which can take dual role in organic reactions as solvents and catalysts. Many typical acid-catalyzed organic reactions have been carried out successfully in them [5–10]. Among these reactions Fischer esterifications are hot topic [11–17]. Compared with conventional homogeneous and heterogeneous acid catalysts these published reports of esterifications using BAILs demonstrated the advantages include: reaction can carried out under solvent-free condition, the product ester can be separated by easy decantation and BAILs can be recycled. However, these reports [11–17] have not been entirely satisfactory with drawbacks such as the higher amount of BAILs (20–300 mol%), relatively long reaction time (2.5–48 h) and reactions carried out under hearting or reflux conditions, use of an excess of acid or alcohol. Aim to develop novel BAILs as catalysts for esterifications and realize the green synthesis of long chain aliphatic esters, herein we wish to report the first study on the application of two novel BAILs based on sulfonic acid group served as catalyst for Fisher esterification of long chain aliphatic acids with alcohols (Scheme 1). The use of two novel BAILs in the present work has circumvented all the above mentioned limitations, this reaction system carried out smoothly at room temperature with good to excellent isolated yields (85–99%) under solvent-free conditions without the need for any added catalyst. The recycled BAILs can be reused three times without significant loss of catalytic activity.

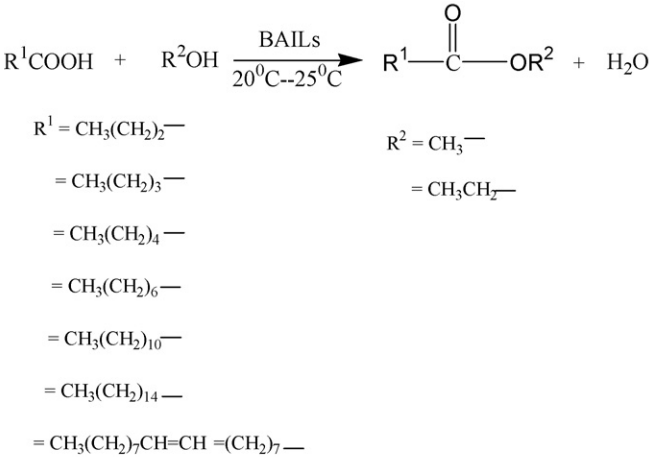
2. Experimental

Melting points were measured using Gallen Kamp melting point apparatus and are uncorrected. IR spectra were recorded

---

* Corresponding author at: Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, Urumqi 830011, China.
Tel.: +86 991 7882137; fax: +86 991 7882137.
E-mail address: BAILS_wl@126.com (W. Eli).

1381-1169/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2007.08.032



Scheme 1. Fisher esterification reaction in Brønsted acidic ionic liquids.

by a Perkin–Elmer FT-IR 240-c spectrophotometer using KBr optics. ^{1}H NMR (400 MHz) and ^{13}H NMR (100MHz) spectra were recorded on VARIAN INOVO-400 spectrometer in D_2O with DSS as internal standard. The compositions of the ester products were analyzed by GC (HP-6890). Density was measured using an Anton Paar vibrating tube density meters DMA-4500. Viscosity was measured using a NDJ-5S Digital Viscometer (Shanghai Nirun Intelligent Technology Co., Ltd., China). Pyridine purified by distillation before use, and the other chemicals (AR grade) were commercially available and used without further purification.

2.1. General procedure of preparation and characterization of ionic liquid **2a**

N-Methylimidazole (30 mmol) was dissolved in toluene (25 mL) under stirring. Equal mole amount of benzyl chloride was added dropwise over a period of 30 min at 0–5 °C. Continued the stirring at this temperature for 24 h then were heated to 65–70 °C for 24 h. Upon completion of the reaction, the solvent was evaporated under vacuum. The residual was washed with ethyl acetate (3× 30 mL) and then dried under vacuum at 70 °C for 8 h to afford **1a** as off-white viscous oil liquid in the yield of 95%.

2.1.1. Preparation of **2a** via Route 1

1a (2.3 g, 10.6 mmol) was added slowly in concentrated H_2SO_4 (5 g, 97%) at −5 to 0 °C under stirring. Continued the stirring at this temperature for 8 h, then heated to 60–65 °C for 4 h (reaction progress was monitored by TLC). Upon completion, the reaction mixture was dried under high vacuum at 70 °C for 4.5–6.5 h. The residue was purified by flash column chromatography using silica gel (methanol:ethyl acetate = 95:5). **2a** was obtained as off-white oil liquid in 88% yield.

2.1.2. Preparation of **2a** via Route 2

A mixture of **3a** (was prepared as method reported in literature [13]) (11.5 g, 40.5 mmol) and 15 mL anhydrous dichloromethane was added dropwise into chlorosulfonic acid (5 g, 42.5 mmol) at 0–5 °C over a period of 1.5 h under stirring. Continued the stirring at this temperature for 8 h, then heated to 60–65 °C for 4 h (reaction progress was monitored by TLC). Upon completion, dichloromethane was evaporated with a rotary evaporator. The reaction mixture was dried under high vacuum at 70 °C for 4.5–6.5 h. The residue was purified by flash column chromatography using silica gel (methanol:ethyl acetate = 95:5). **2a** was obtained as off-white oil liquid in 89.7% yield.

1a: IR (KBr) $\nu = 3032$, 2853, 2110, 1645, 1568, 1456, 1161, 1086, 866, 725 cm^{-1}. ^{1}H NMR $\delta = 8.74$ (d, 1H), 7.41–7.51 (m, 7H), 5.38 (s, 2H), 3.88 (s, 3H).

2a: density (g/cm^3, 25 °C): 1.41; viscosity (cP, 28 °C): 213 IR (KBr) $\nu = 3420$, 3158, 2960, 1700, 1458, 1256, 1059, 883, 781, 721, 673, 588 cm^{-1}. ^{1}H NMR $\delta = 8.64$ (s, 1H), 7.23–7.57 (m, 6H), 5.31 (s, 2H), 3.80 (s, 3H), ^{13}C NMR $\delta = 146.7$, 138.56, 137.42, 130.21, 129.54, 125.28, 123.04, 52.27, 29.24.

Elemental analysis calcd. (%) for $C_{11}H_{14}N_2O_7S_2$ (350.36): C 37.71, H 4.03, N 8.00; found: C 38.13, H 3.95, N 8.12.

3a was obtained as off-white oil liquid with yield of 98.6% density (g/cm^3, 25 °C): 1.36; viscosity (Pa s, 28 °C) 3.63 IR (KBr) $\nu = 3108$, 2970, 2857, 2325, 2100, 1642, 1500, 1446, 1210, 872, 745, 710 cm^{-1}. ^{1}H NMR are same as **1a**.

2.2. General procedure of preparation and characterization of ionic liquid **2b**

Pyridine (5 g, 62.7 mmol) was dissolved in toluene (25 mL) and cooled to 0–5 °C, equal mole amount of $PhCH_2Cl$ added slowly over a period of 30 min. Continued the reaction overnight at 0–5 °C. After reaction for 24 h at room temperature, the reaction mixture was heated to 65–70 °C for 24 h. The workup procedure is the same as **1a**. Afford to the target compound **1b** in 92% yield.

2.2.1. Preparation of **2b** via Route 1

2b was prepared by the similar procedures in **2a** except that **1b** was added into H_2SO_4 (97%) in small portions at −5 to 0 °C. Addition of the total amount of the **1b** took about 1 h, **2b** was obtained as yellowish oil liquid in 85% yield.

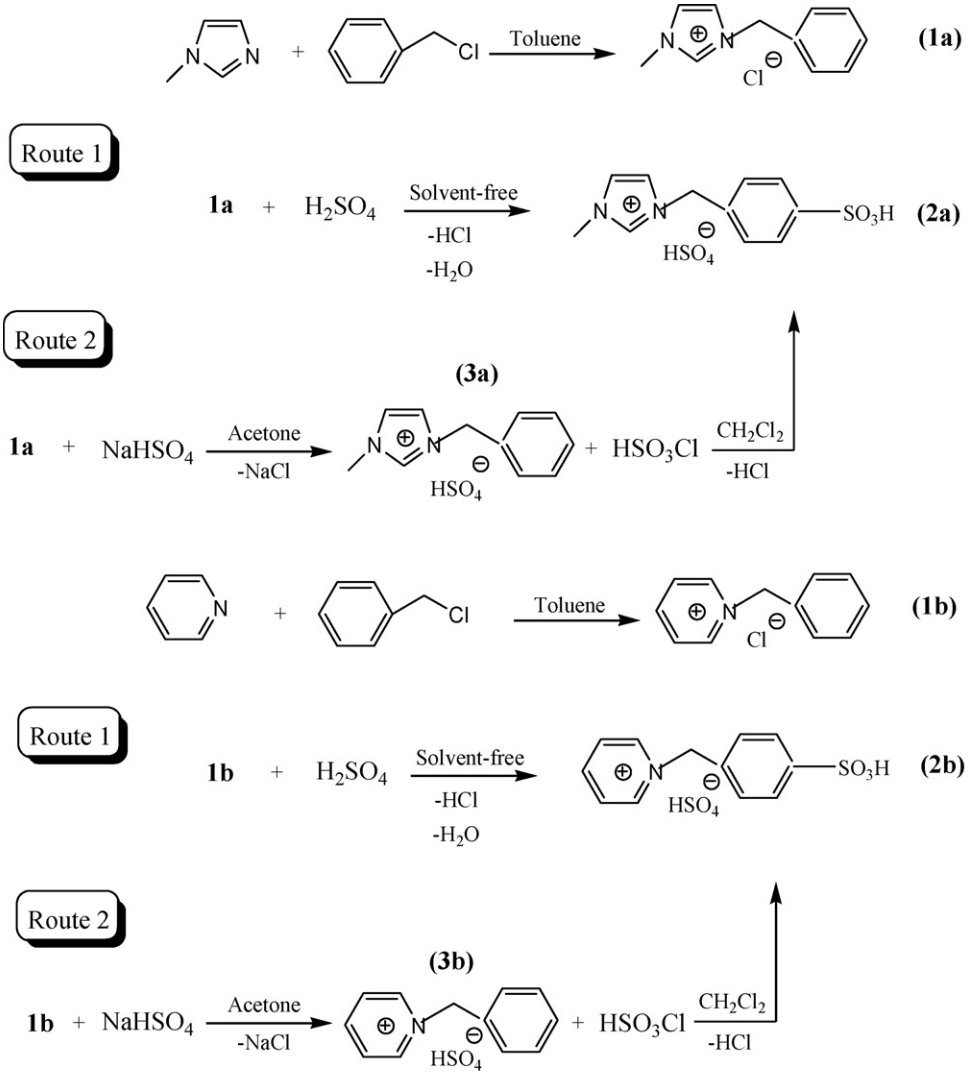
2.2.2. Preparation of **2b** via Route 2

2b was prepared by the similar procedures in **2a**, **2b** was obtained as yellowish oil liquid in 87% yield.

1b: high hygroscopic white crystal. mp 125–128 °C IR (KBr) $\nu = 3036$, 2963, 1630, 1489, 1454, 1159, 770 cm^{-1}. ^{1}H NMR $\delta = 8.95$ (d, $J = 5.2$Hz, 2H), 8.60 (m, 1H), 8.11 (m, $J = 7.2$Hz, 2H), 7.52–7.56 (m, 5H), 5.86 (s, 2H).

2b: density (g/cm^3, 25 °C): 1.44; viscosity (cP, 28 °C): 197 IR (KBr) $\nu = 4300$, 3158, 1700, 1651, 1230, 1059, 1002, 885, 779, 662 cm^{-1}. ^{1}H NMR $\delta = 8.95$ (d, $J = 5.2$ Hz, 2H), 8.64 (m, 1H), 8.15 (m, $J = 7.7$ Hz, 2H), 7.55–7.58 (d, 4H), 5.86 (s, 2H), ^{13}C NMR $\delta = 151.2$, 148.76, 139.57, 136.83, 130.25, 127.61, 124.64, 53.39. Anal. calcd. (%) for $C_{12}H_{13}N_1O_7S_2$ (347.36): C 41.49, H 3.77, N 4.03; found: C 41.79, H 3.72, N 3.87.

3b was prepared as method reported in literature [13] and was obtained as off-white oil liquid in 99% yield density (g/cm^3, 25 °C): 1.38; viscosity(Pa s, 28 °C) 2.65 IR (KBr) $\nu = 3128$,



Scheme 2. Synthetic route of Brønsted acidic ionic liquids.

2970, 2857, 2338, 1642, 1500, 1456, 1210, 882, 755, 709 cm^{-1}. ^{1}H NMR are same as **1b**.

2.3. *A typical procedure of Fischer esterification in BAILs*

The required amounts of BAILs, organic acid and alcohol were charged successively into a test tube with a magnetic stirrer and then the esterification reaction was allowed to proceed at room temperature (19–25 °C) for 3–4.5 h under vigorous stirring. Upon completion, the reaction mixture became biphasic. The upper layer contained the expected ester and can be isolated by simple decantation. The lower layer consisting of the BAILs was reused in a further run. After washing with diethyl ether (3× 7.5 mL) under vigorous stirring at ambient temperature for 1.5–2 h, the washing layer was separated by decantation, the obtained ionic liquids layer was subjected to drying under high vacuum (10^{-2} Torr) at 70 °C for 6 h to remove water, leaving behind the BAILs (recovery 97.5%) which was recycled. The combined washing layers were washed twice with NaOH solution (2M), then with H_2O, dried over $MgSO_4$ and filtered, the filtrate concentrated firstly by rotary evaporation then distilled under reduced pressure, the resulting distillate was controlled by ^{1}H NMR spectroscopy. The content of produced esters was tested by GC according to the procedures described in GB/T 17377-1998 [18] (eqv.ISO5508:1990).

Chromatographic conditions—stationary: DEGS (15%); column: wide-bore capillary column; column temperature: 165 °C; injector temperature: 215 °C; detector temperature: 215 °C; high pure N_2 press 150 kPa; H_2 press 70 kPa; air press 50 kPa; detector: FID.

3. Results and discussion

The synthesis of **2a** and **2b** involve a two-step process (Scheme 2, Route 1). *N*-Methyllimidazole and pyridine were independently alkylated by using benzyl chloride at the first step, and the resulting quaternary halides **1a** and **1b** were finally transformed into the target compounds by using concentrated sulphuric acid as anion exchange and sulfonating agent [19–22], respectively. For the purpose of comparison, we also synthe-

Table 1
Results of Fischer esterification of aliphatic acids with methanol and ethanol in **2a** and **2b**

Entry	Acid	Alcohol	Ratio of acid/alcohol/IL (mol)	Reaction time (h)	Yield [a,b] **2a/2b**[c] (%)	Yield [a,b] **2a/2b**[d] (%)
1	*n*-Butanoic acid	Methanol	1:1:0.1	3	98/97.2	97.7/97
2	*n*-Pentanoic acid	Methanol	1:1:0.1	3	99/95.6	98.4/94.2
3	*n*-Hexanoic acid	Methanol	1:1:0.1	3	97.3/95.3	96.1/95
4	*n*-Octanoic acid	Methanol	1:1:0.1	3.5	97.1/92	97/92.4
5	*n*-Nonanic acid	Methanol	1:1:0.1	3.5	96/95	94.7/93.8
6	Dodecanoic acid	Methanol	1:1.5:0.1	4.5	93/94.2[e]	92/92.5[e]
7	Hexadecanoic acid	Methanol	1:1.5:0.1	4.5	90.4/92.5[f]	88.7/90.3[f]
8	Oleic acid	Methanol	1:1:0.1	4.5	88/94.7	86.4/91.4
9	*n*-Butanoic acid	Ethanol	1:1:0.1	3	95.4/96	93.6/95.2
10	*n*-Pentanoic acid	Ethanol	1:1:0.1	3	94/91	94/89.7
11	*n*-Hexanoic acid	Ethanol	1:1:0.1	3	97/95	95.3/94.1
12	*n*-Octanoic acid	Ethanol	1:1:0.1	3.5	95/96	95/95.2
13	*n*-Nonanic acid	Ethanol	1:1:0.1	3.5	95/97.6	93.7/95.8
14	Dodecanoic acid	Ethanol	1:1.5:0.1	4.5	87/85[e]	88/86.4[e]
15	Hexadecanoic acid	Ethanol	1:1.5:0.1	4.5	91/89.7[f]	90.3/88.2[f]
16	Oleic acid	Ethanol	1:1:0.1	4.5	86/91	84.6/90

All experiments carried out at room temperature.

[a] Yields of esters are based on isolated crude product.

[b] Purity of esters were test by GC and the content of esters no less than 95% (GC).

[c] **2a/2b** were prepared via Route 1.

[d] **2a/2b** were prepared via Route 2.

[e] Dodecanoic acid need an excess of alcohol to dissolve.

[f] Hexadecanoic acid need an excess of alcohol to dissolve.

sized **2a** and **2b** by using sodium hydrogen sulphate as anion exchange agent and using chlorosulfonic acid as sulfonating agent (Scheme 2, Route 2). Firstly, anion metathesis was carried out in dry acetone for 2 days under mechanical stirring at room temperature, the resulting **3a** and **3b** then were sulfonated by chlorosulfonic acid. The results indicate Route 2 also can give same products in satisfactory yields. **2a** and **2b** were fully characterized by ^1H NMR, ^{13}C NMR, IR spectra and elemental analyses were in conformity with their structure. In additional, using Route 2 can also obtain two novel BAILs **3a** and **3b** which bear a benzyl functionality on the imidazolium or pyridinium cation in excellent yields but they exhibited higher viscosities. The resulting water-soluble **2a** and **2b** were isolated as oil liquids with good mobility at room temperature. Their viscosities are 0.213 and 0.197 Pa s (28 °C) respectively, even less than the viscosities of [bmim]BF_4 (233 cP, 30 °C) [23] and [bmim]PF_6 (312 cP, 30 °C) [23]. The content of water in **2a**, **2b**, **3a** and **3b** were determined using Karl–Fischer titration [24] the results are as follows—**2a**: 3.1%, **2b**: 3.4%, **3a**: 3.5% and **3b**: 3.8%. Their miscibility in organic solvent was also studied, they are partially immiscible with ethyl esters, ethers, *n*-hexane, benzene, toluene and but readily soluble in methanol, ethanol and dichloromethane. In this study, the preparation of halide-free **2a**, **2b**, **3a** and **3b** are very difficult for they are completely miscible with water and cannot remove the halide ions by a washing procedure with water. The halide impurities of these ionic liquids were evaluated by using ion chromatography according to the method reported in literature [25], in our case, the contained

Table 2
Results of Fischer esterification of aliphatic acids with methanol and ethanol in **3a** and **3b**

Entry	Acid	Alcohol	Ratio of acid/alcohol/ILs (mol)	Reaction time (h)	Yield [a,b] **3a/3b** (%)
1	*n*-Butanoic acid	Methanol	1:1:0.1	5	49.8/51.7
2	*n*-Pentanoic acid	Methanol	1:1:0.1	5	47/50.4
3	*n*-Hexanoic acid	Methanol	1:1:0.1	5	48/51.2
4	*n*-Octanoic acid	Methanol	1:1:0.1	5	27.7/31.2
5	Dodecanoic acid	Methanol	1:1.5:0.1	5	15.7/19.7
6	Hexadecanoic acid	Methanol	1:1.5:0.1	5	8.1/10.2
7	*n*-Butanoic acid	Ethanol	1:1:0.1	5	48.8/52.3
8	*n*-Pentanoic acid	Ethanol	1:1:0.1	5	48.2/48.7
9	*n*-Hexanoic acid	Ethanol	1:1:0.1	5	46.5/50.4
10	*n*-Octanoic acid	Ethanol	1:1:0.1	5	22.7/26.5
11	Dodecanoic acid	Ethanol	1:1.5:0.1	5	12.5/13.2
12	Hexadecanoic acid	Ethanol	1:1.5:0.1	5	7.6/8.4

All experiments carried out at room temperature. Hexadecanoic acid and Dodecanoic acid need an excess of alcohol to dissolve.

[a] Yields of esters are based on isolated crude product.

[b] Purity of esters were test by GC and the content of esters no less than 95% (GC).

Table 3
Reuse of **2a/2b** of the esterification of *n*-octanoic acid with methanol and ethanol

Run	Acid	Alcohol	Ratio of acid/alcohol/ILs (mol)	Reaction time (h)	Reaction temperature (°C)	Yield[a,b] **2a/2b** (%)
1	*n*-Octanoic acid	Methanol	1:1:0.1	3.5	20–25	96.1/89
2	*n*-Octanoic acid	Methanol	1:1:0.1	3.5	20–25	95/90
3	*n*-Octanoic acid	Methanol	1:1:0.1	3.5	20–25	92/91
1	*n*-Octanoic acid	Ethanol	1:1:0.1	3.5	20–25	94.2/95
2	*n*-Octanoic acid	Ethanol	1:1:0.1	3.5	20–25	92/95.3
3	*n*-Octanoic acid	Ethanol	1:1:0.1	3.5	20–25	93/95.7

[a] Yield of esters are based on isolated crude product.

[b] Purity of esters were test by GC and the content of esters no less than 95% (GC).

amounts of halide ranges from 130 to 180 ppm. We think these values may not be a problem for catalytic applications in Fischer esterification.

Initially, the esterification of *n*-pentanoic acid with methanol and ethanol in **2a** and **2b** were chosen as model reactions, under optimized reaction conditions, *n*-pentanoic acid and equal mole amount of alcohol and **2a** (10 mol%) or **2b** (10 mol%) were mixed together and reacted under stirring for 3 h at room temperature (20–25 °C). Upon completion of the reaction, the system became biphasic, the upper layer, which is the produced esters were isolated by simple decantation, the lower layer is BAILs that contain the unreacted materials, produced water and a portion of the produced esters. The BAILs were regenerated by extraction and removing water under vacuum. The results of reactions were listed in Table 1 (entry 2, entry 10). **2a** and **2b** have demonstrated excellent catalytic activity. Based on this initial result, we performed esterifications by using *n*-butanoic acid, *n*-hexanoic acid, *n*-octanoic acid, *n*-nonanic acid, dodecanoic acid, hexadecanoic acid and oleic acid as substrates. These results were listed in Table 1. As is evident, all reactions gave rise to excellent isolated yields in a relatively short reaction time. It was interesting to note that the corresponding reaction in **3a** and **3b** under same condition over a period of 5 h afforded the esters in relatively lowered yields (7.6–52%) (Table 2), thereby, highlighting the role of **2a** and **2b** in promoting these reactions. Furthermore, **2a/2b** preparation from Route 2 were also tested in the esterifications under same reaction conditions, the results were listed in Table 1, they gave essential same results as **2a/2b** preparation from Route 1.

These good results could be explained by the following facts: esterification is a reversible reaction so it is necessary to simultaneously remove the formed water in order to make complete reaction. In this case an outstanding feature of these synthesized BAILs is that they have excellent solubility in water but hardly miscible with esters, so the water formed during the reaction can easily enter into BAILs phase from the produced ester. This induces a spontaneous phase separation, which may drive the reaction toward to full conversion. In addition, these good results can also be contributed to the stronger Brønsted acidity of counter-anion HSO_4^- [12,14,16,17] and smaller viscosity of **a** than **b**. From Table 1 we also found that with the increasing of carbon chain of aliphatic acids the yields of esters are decreased, this is because of the following reasons: (1) the emulsification of ester is improved with the increasing of its carbon chain, so water become more difficult to be separated from the formed esters; (2) longer carbon chain aliphatic acids take longer time dissolved in BAILs, so in Table 1 (entries 4–8 and entries 12–16) need longer reaction times than Table 1 (entries1–3 and entries 9–11). Another interesting phenomenon we found was that the cation also had an impact on the results of esterification, **2a** gave better results for shorter carbon chain aliphatic acid than **2b**. On the contrary, **2b** gave better results for longer carbon chain aliphatic acid than **2a**. The reason is under further investigation in our laboratory.

One of the primary aims of our study was to investigate the recycling of these BAILs and this is clearly important in the context of economic feasibility and sustainable development. The recycling performance of **2a** and **2b** were investigated in the esterfication of *n*-octanoic acid with methanol and ethanol. These results were listed in Table 3. The recovered BAILs were recycled three times with only a marginal loss (1–5%) in yield. Furthermore, a small portion of producted esters in yields of 1.7–4.8% were obtained during the recovering of BAILs.

4. Conclusions

In this paper, we have designed and synthesized two novel BAILs that bear an aromatic sulfonic acid group on imidazolium and pyridinium cation by a simple and straight-foward procedures from cheap starting materials in good yields, which served as an efficient and reusable catalyst realized the green synthesis of long chain aliphatic acid esters at room temperature. This reaction system has several note-worthy features: (1) the reaction can be carried out at room temperature with shorter reaction time; (2) the produced esters can be separated by easy decantation with high yields and purity; (3) the BAILs can be reused for three times after simple treatment and (4) the BAILs are cheap, environmentally benign and safe.

Acknowledgments

The authors would like to thank Prof. Halidan, Dr. Gang Li, Bin Wen and Li Fan for their technical assistance and fruitful discussion.

References

[1] K. Wessermel, H.J. Arpe, Industrial Organic Chemistry, 3rd ed., VCH, New York, 1997, p. 289.

[2] (a) M.A. Ogliaruso, J.F. Wolfe, Esters and Their Derivatives, John Wiley and Sons, Chichester, 1991;
(b) W.H. Brown, Introduction to Organic Chemistry, Saunders College Publishing, Orlando, 1997.

[3] (a) J.A. Boon, J.A. Levinsky, J.L. Pflug, J.S. Wilkes, J. Org. Chem. 51 (1986) 480;
(b) R. Sheldon, Chem. Commun. (2001) 2399;
(c) J.R. Harjani, S.J. Nara, M.M. Salunkhe, Tetrahedron Lett. 43 (2002) 1127;
(d) V. Namboodiri, R.S. Varma, Chem. Commun. (2002) 342;
(e) W. Sun, C.G. Xia, H.W. Wang, Tetrahedron Lett. 44 (2003) 2409;
(f) T. Akaiyama, A. Suzuki, K. Fuchibe, Syn. Lett. (2005) 1024.

[4] (a) D. Zhao, M. Wu, Y. Kou, E. Min, Catal. Today 74 (2002) 157;
(b) H. Olivier-Bourbigou, L. Magna, J. Mol. Catal A: Chem. 182–183 (2002) 419;
(c) T. Welton, Coord. Chem. Rev. 248 (2004) 2459;
(d) N. Jain, A. Kumar, S. Chauhan, S.M.S. Chauhan, Tetrahedron 61 (2005) 1015;
(e) P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley–VCH, Weinheim, 2002.

[5] P. Wasserscheid, M. Sesing, W. Korth, Green Chem. 4 (2002) 134.

[6] K. Qiao, C. Yokoyama, Chem. Lett. 33 (2004) 472.

[7] K. Qiao, C. Yokoyama, Chem. Lett. 33 (2004) 808.

[8] D. Li, F. Shi, J. Peng, S. Guo, Y. Deng, J. Org. Chem. 69 (2004) 3582.

[9] D. Li, F. Shi, S. Guo, Y. Deng, Tetrahedron Lett. 45 (2004) 265.

[10] V. Singh, S. Kaur, V. Sapehiyia, J. Singh, G.L. Kad, Catal. Commun. 6 (2005) 57.

[11] A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weaver, D.C. Forbes, J.H. Davis, J. Am. Chem. Soc. 124 (2002) 5962.

[12] J. Fraga-Dubreuil, K. Bourahla, M. Rahmouni, J.P. Bazureau, J. Hamelin, Catal. Commun. 3 (2002) 185.

[13] A. Arfan, J.P. Bazureau, Org. Process Res. Dev. 9 (2005) 743.

[14] J.Z. Gui, X.H. Cong, D. Liu, X.T. Zhang, Z.D. Hu, Z.L. Sun, Catal. Commun. 5 (2004) 473.

[15] Y.L. Gu, J. Mol. Catal. A: Chem. 71 (2004) 212.

[16] H.B. Xing, T. Wang, Z.H. Zhou, Y.Y. Dai, Ind. Eng. Chem. Res. 44 (2005) 4147.

[17] D. Fang, X.L. Zhou, Z.W. Ye, Z.L. Liu, Ind. Eng. Chem. Res. 45 (2006) 7982.

[18] Animal and vegetable fats and oils-analysis by gas chromatography of methyl ester of fatty acids, GB/T 17377-1998 (eqv ISO5508:1990) National Standard of China, 1998.

[19] A. Spryskov, J. Gen. Chem. USSR 30 (1960) 2433.

[20] H. Cerfontain, Mechanistic Aspects in Aromatic Sulfonation and Desulfonation, Wiley, New York, 1968.

[21] M.B. Smith, J. March, March's Advanced Organic chemistry, 5th ed., John Wiley & Sons, 2001, p. 689.

[22] M.R. Grimmet, Imidazole and Benzimidazole Synthesis, Academic Press, 1997, p. 247.

[23] R. Hagiwara, Y. Ito, J. Fluorine Chem. 105 (2000) 221–227.

[24] J. Mendam, R.C. Dennery, J.D. Barnes, M. Thomas, Vodel's Textbook of Quantitative Chemical Analysis, 6th ed., Prentice Hall, Harlow, 2000.

[25] C. Villagrán, M. Deetlefs, W.R. Pitner, C. Hardacre, Anal. Chem. 76 (2004) 2118–2123.