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Chinese Chemical Letters 23 (2012) 1031–1034

CHINESE CHEMICAL LETTERS

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Convenient synthesis and application of novel bi-SO_3H-functionalized ionic liquids based on piperazinium

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Received 15 May 2012
Available online 18 July 2012

Abstract

In this article, series of novel bi-SO_3H-functionalized ILs were synthesized using simple, efficient and economic procedure. Hammett method had been used to determine the acidity order of these ionic liquids, and the acidities of bi-SO_3H-functionalized ILs were stronger than that of traditional single-SO_3H-functionalized ILs. Their catalytic activities in the synthesis of *N*-(3-phenyl)-3-oxo-1-(phenylpropyl)acetamide were investigated and they were consistent with their acidities.

Keywords: Novel bi-SO_3H-functionalized ionic liquids; Synthesis; Acidity characterization; Hammett function; Catalytic activity

One of the main principles of green chemistry is to develop cost-effective and environmentally benign catalytic systems which have become one of the main themes of contemporary synthetic chemistry. Ionic liquids (ILs) have been considered as eco-friendly alternatives to volatile organic media because of their negligible vapor pressure and nonflammable nature [1,2]. Although IL was initially introduced as an alternative green reaction medium, today it has marched far beyond showing its significant role in controlling the reaction as a catalyst. ILs are composed of distinct cations and anions that are capable of facilely tuning, whereby they can be designed for task-specific applications through smart choice of the respective cation and/or anion. The introduction of specific functionality has led to the identification of functionalized ILs (FILs, or taskspecific ILs, TSILs) [3,4]. Among different kinds of FILs, SO_3H-functionalized ILs have been intensively studied [5,6]. They were used as solvent-catalyst for several organic reactions such as esterifications, Aldol condensation, Pinacole reaction, Biginelli reaction and so on. The use of such TSILs as catalysts is an area of current investigations and as aforementioned, these TSILs may further expand the application of ionic liquids in chemistry.

One of significant challenges that stand in the way of development and commercialization of TSILs is high cost [7]. Herein, we reported the synthesis of novel bi-SO_3H-functionalized ILs available from cheap raw materials and simple preparation procedure (Scheme 1). We also investigated their acidities and catalytic activities comparing with traditional SO_3H-functionalized ILs.

The precursor of ILs $(PS)_2Pi$, $(BS)_2Pi$ and ILs were synthesized as follows: 1,4-bis (3-sulfopropyl) piperazinium ($(PS)_2Pi$): The mixture of piperazine (0.86 g, 0.01 mol), 1,3-propane sulfonate (3.05 g, 0.025 mol), and water (10 mL)

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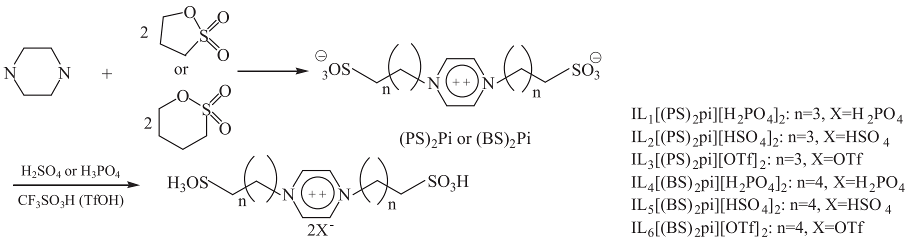
1001-8417/\$ – see front matter
http://dx.doi.org/10.1016/j.cclet.2012.06.043



Scheme 1. Synthesis route of bi-SO_3H-functionalized ILs used in this paper.

was refluxed (5 min) and then chilled. The product crystallizes out from NaOH of pH 4 in the cold, then washed with distilled water three times and dried at 100 °C for 3 h, giving $(PS)_2Pi$ as white powder.

1,4-Bis (4-sulfobutyl) piperazinium ($(BS)_2Pi$) was synthesized following the same procedure of $(BS)_2Pi$.

1,4-Bis (3-sulfopropyl) piperazinium bis (hydrogen sulfate), 1,4-bis (3-sulfopropyl) piperazinium bis (hydrogen sulfate), 1,4-bis(3-sulfopropyl) piperazinium bis (trifluoromethanesulfonate): Under vigorous stirring, amount of $(PS)_2Pi$ (0.01 mol) was dissolved in water and 0.02 mol sulfuric acid, phosphoric acid or trifluoromethanesulfonic acid was dropped slowly at room temperature. After the dropping was finished, the system was slowly heated up to 90 °C and stirred for 2 h, then the water was removed under vacuum at 70 °C for 3 h, giving $[(PS)_2Pi][HSO_4]_2$, $[(PS)_2Pi][H_2PO_4]_2$ and $[(PS)_2Pi][OTf]_2$ as white powder.

1,4-Bis (4-sulfobutyl) piperazinium bis (hydrogen sulfate) ($[(BS)_2Pi][HSO_4]_2$), 1,4-bis (4-sulfobutyl) piperazinium bis (hydrogen sulfate) ($[(BS)_2Pi][H_2PO_4]_2$) and 1,4-bis(4-sulfobutyl) piperazinium bis (trifluoromethanesulfonate) ($[(BS)_2Pi][OTf]_2$) were synthesized following the same procedure of $[(PS)_2Pi][HSO_4]_2$, $[(PS)_2Pi][H_2PO_4]_2$ and $[(PS)_2Pi][OTf]_2$.

The six bi-SO_3H-functionalized ILs were characterized by IR and ^1H NMR [8].

A measurement of the acidic scale of these bi-SO_3H-functionalized ILs was conducted on an Agilent B453 UV-vis spectrophotometer with a basic indicator crystal violet. Hammett function, H_0, which could be regarded as the relative acidity of the ILs, was calculated by using Eq. (1) [9].

$$H_0 = pK(I)_{aq} + \log([I]/[IH^+]) \tag{1}$$

When an acidic IL was added, the absorbance of the unprotonated form of the indicator decreased. As shown in Fig. 1 the absorbance of the unprotonated form of the indicator on nine acidic ILs decreased as follows: $[PSpy][H_2PO_4] > [(BS)_2pi][H_2PO_4]_2 > [PSpy][HSO_4] > [(PS)_2pi][H_2PO_4]_2 > [(PS)_2pi][HSO_4]_2 > [PSpy][OTf] > [(BS)_2pi][HSO_4]_2 > [(BS)_2pi][OTf]_2 > [(PS)_2pi][OTf]_2$. Ultimately, we obtained the acidity order of the seven ILs

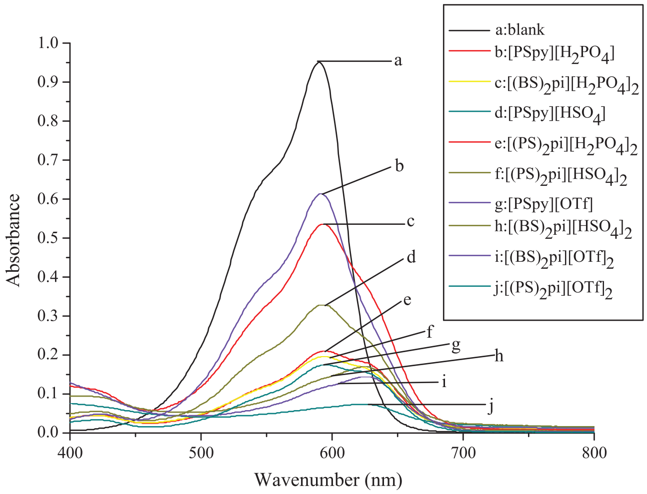


Fig. 1. Absorbance spectra of crystal violet for various SO_3H-functionalized ILs in distilled water.

Table 1
Calculation and comparison of H_0 values of different SO_3H-functionalized ILs in distilled water (20 °C).

Ionic liquid	A_{max}	[I] (%)	$[IH^+]$ (%)	H_0
Blank	0.9516	100	0	
$[(PS)_2pi][H_2PO_4]_2$	0.2073	21.80	78.20	0.2452
$[(PS)_2pi][HSO_4]_2$	0.1888	19.80	80.20	0.1925
$[(PS)_2pi][OTf]_2$	0.07382	8.00	92.20	−0.2616
$[(BS)_2pi][H_2PO_4]_2$	0.54	56.75	43.25	0.9170
$[(BS)_2pi][HSO_4]_2$	0.166	17.44	82.56	0.1248
$[(BS)_2pi][OTf]_2$	0.1366	14.35	85.64	0.0240
$[PSpy][H_2PO_4]$	0.6320	66.40	33.60	1.0958
$[PSpy][HSO_4]$	0.3533	37.10	62.90	0.5707
[PSpy][OTf]	0.1939	20.40	79.60	0.2087

Indicator: crystal violet (5 mg/L, $pk_a = 0.8$), IL (25 mmol/L).

Table 2
Synthesis of *N*-(3-phenyl)-3-oxo-1-(phenylpropyl)acetamide using different ILs.

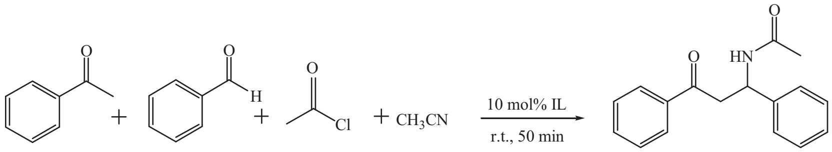
Ionic liquids	Yield (%)[a]
$[Et_3N\text{-}SO_3H]Cl$ [10]	82
$[(PS)_2pi][H_2PO_4]_2$	83
$[(PS)_2pi][HSO_4]_2$	87
$[(PS)_2pi][OTf]_2$	92
$[(BS)_2pi][H_2PO_4]_2$	77
$[(BS)_2pi][HSO_4]_2$	87
$[(BS)_2pi][OTf]_2$	90
$[PSpy][H_2PO_4]$	76
$[PSpy][HSO_4]$	80
[PSpy][OTf]	84

Reaction conditions: 5 mmol acetophenone, 5 mmol benzaldehyde, 1.5 mL acetyl chloride, 15 mL acetonitrile and 10 mol% IL as catalyst at r.t., 50 min.

[a] Isolated yield.

with the following H_0 values (Table 1): $[(PS)_2pi][OTf]_2$ (−0.2616) > $[(BS)_2pi][OTf]_2$ (0.0240) > $[(BS)_2pi][HSO_4]_2$ (0.1248) > $[(PS)_2pi][HSO_4]_2$ (0.1925) > [PSpy][OTf] (0.2087) > $[(PS)_2pi][H_2PO_4]_2$ (0.2452) > $[PSpy][HSO_4]$ (0.5707) > $[(BS)_2pi][H_2PO_4]_2$ (0.9170) > $[PSpy][H_2PO_4]$ (1.0958), suggesting that the acidities of bi-SO_3H-functionalized ILs were stronger than that of traditional single-SO_3H-functionalized ILs. The acidity of bi-SO_3H-functionalized IL depended mainly on the characteristics of anion. The acidities of IL with $[OTf]^-$ were stronger than that of the ILs with $[HSO_4]^-$ and $[H_2PO_4]^-$.

A comparative study on the catalytic activities of the novel bi-SO_3H-functionalized ILs with other ILs was carried out using the synthesis of *N*-(3-phenyl)-3-oxo-1-(phenylpropyl)acetamide, which was confirmed by IR and ^1H NMR, as a model reaction (Scheme 2 and Table 2). Zare et al. [10] reported the application of IL $[Et_3N\text{-}SO_3H]Cl$ in the synthesis of β-acetamido ketones. However, this procedure was encountered the problems of relatively long reaction time and large amount of IL. Under the same reaction condition (r.t., 50 min, 10 mol% IL), the best 92% yield of *N*-(3-phenyl)-3-oxo-1-(phenylpropyl) acetamide was achieved when the reaction was carried out in the presence of $[(PS)_2pi][OTf]_2$. While 78% yield was achieved using $[Et_3N\text{-}SO_3H]Cl$ as catalyst. Interestingly, the sequence of catalytic activity observed in the synthesis of *N*-(3-phenyl)-3-oxo-1-(phenylpropyl)acetamide was in good agreement



Scheme 2. Synthesis of *N*-(3-phenyl)-3-oxo-1-(phenylpropyl)acetamide catalyzed by IL.

Table 3
Recycling of IL $[(PS)_2pi][OTf]_2$ in the synthesis of *N*-(3-phenyl)-3-oxo-1-(phenylpropyl)acetamide.

Recycling times	Yield (%)[a]
1	92
2	91
3	91
4	90
5	90
6	88

Reaction conditions: 5 mmol acetophenone, 5 mmol benzaldehyde, 1.5 mL acetyl chloride, 15 mL acetonitrile and 10 mol% $[(PS)_2pi][OTf]_2$ as catalyst at r.t., 50 min.

[a] Isolated yield.

with the acidity order determined by the Hammett method. Therefore, $[(PS)_2pi][OTf]_2$ was chosen as the model catalyst to investigate the reusability of bi-SO_3H-functionalized ILs. As shown in Table 3, $[(PS)_2pi][OTf]_2$ could be reused six times without obvious loss of catalytic activity. This indicated that the $[(PS)_2pi][OTf]_2$ was a high efficient and recyclable catalyst.

In summary, a new group of bi-SO_3H-functionalized ILs was synthesized from cheap raw materials and simple preparation procedure. Their acidities and catalytic activities were investigated. Compared with traditional single-SO_3H-functionalized ILs, bi-SO_3H-functionalized ILs showed stronger acidities and better catalytic activities in the synthesis of *N*-(3-phenyl)-3-oxo-1-(phenylpropyl)acetamide.

Acknowledgments

The authors gratefully acknowledge the National Natural Science Foundation of China (Nos. 21003049, 21073064) and the Fundamental Research Funds for the Central Universities for financial support.

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[8] $[(PS)_2Pi][HSO_4]2$: Mp. (oC): 273–274. IR (KBr, ν/cm^{-1}): 3481, 3033, 2787, 1450, 1208, 1163, 1039, 643, 544. ^{1}H NMR (500 MHz, D_2O) δ: 2.10 (m, 4H), 2.90 (t, 4H, $J = 7.0$ Hz), 3.33 (t, 4H, $J = 7.5$ Hz), 3.60 (s, 8H). $[(PS)_2Pi][H_2PO_4]_2$: Mp (oC): 278–281. IR (KBr, ν/cm^{-1}): 3345, 3029, 2741, 1479, 1215, 1182, 1031, 633, 541. ^{1}H NMR (500 MHz, D_2O) δ: 2.09 (m, 4H), 2.87 (t, 4H, $J = 7.0$ Hz), 3.32 (t, 4H, $J = 7.5$ Hz), 3.53 (s, 8H). $[(PS)_2Pi][OTf]_2$: Mp (oC): 189–190. IR (KBr, ν/cm^{-1}): 3455, 3018, 2707, 1480, 1248, 1161, 1027, 643, 590. ^{1}H NMR (500 MHz, D_2O) δ: 2.07 (m, 4H), 2.85 (t, 4H, $J = 7.0$ Hz), 3.30 (t, 4H, $J = 7.6$ Hz), 3.78 (s, 8H). $[(BS)_2Pi][HSO_4]_2$: Mp (oC): 107–108. IR (KBr, ν/cm^{-1}): 3427, 3128, 2689, 1633, 1458, 1236, 1163, 1052, 1021, 596, 540. ^{1}H NMR (500 MHz, D_2O) δ: 1.75 (m, 4H), 1.84 (m, 4H, $J = 7.2$ Hz), 2.87 (t, 4H, $J = 7.7$ Hz), 3.25 (t, 4H), 3.85 (s, 8H). $[(BS)_2Pi][H_2PO_4]_2$: Mp (oC): 225–227. IR (KBr, ν/cm^{-1}): 3421, 3027, 2951, 2689, 2486, 1643, 1473, 1236, 1166, 1027, 594, 553. ^{1}H NMR (500 MHz, D_2O) δ: 1.86 (m, 4H), 1.95 (m, 4H), 2.99 (t, 4H, $J = 7.2$ Hz), 3.37 (t, 4H, $J = 7.6$ Hz), 3.73 (s, 8H). $[(BS)_2Pi][OTf]_2$: Mp (oC): 106–107. IR (KBr, ν/cm^{-1}): 3400, 3003, 2698, 2501, 1631, 1477, 1384, 1295, 1169, 1033, 633, 584, 532. ^{1}H NMR (500 MHz, D_2O) δ: 1.78 (m, 4H), 1.89 (m, 4H), 2.92 (t, 4H, $J = 7.4$ Hz), 3.31 (t, 4H, $J = 7.7$ Hz), 3.88 (s, 8H).

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