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Synthesis and Characterization of Task-Specific Ionic Liquids Possessing Two Brönsted Acid Sites

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Abstract: Task-specific ionic liquids possessing two Brönsted acid sites with –COOH, HSO_4^-, or $H_2PO_4^-$ groups have been designed, synthesized, and characterized. Under mild conditions and without any additional organic solvent, the esterification of isopropanol by chloroacetic acid could be carried out in these new task-specific ionic liquids. In comparison with most of acidic ionic liquids in current use, these ionic liquids are halogen free and more environmentally benign as media and catalysts.

Keywords: Brönsted acid, characterization, synthesis, task-specific ionic liquids

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INTRODUCTION

Ionic liquids (ILs) have recently gained recognition as environmentally benign alternative solvents for separations, chemical synthesis, electrochemistry, and catalysis. Generally, they are nonvolatile, nonexplosive, recyclable, easy to handle, and thermally robust. Therefore, ILs are regarded as "green solvents." They have also been refered to as "designer solvents" because their chemical and physical properties could be adjusted by a careful choice of cation/anion. Therefore, the covalent tethering of a functional group to one or both of the ions of an ordinary ionic liquid can imbue the resulting salt with a capacity to interact with dissolved substrates in specific ways. These low-melting salts are called task-specific ionic liquids (TSIL). Until recently, this area of TSIL research has been the most active, and TSILs are finding an increasing number of applications in synthesis, separations, catalysis, and electrochemistry.[1]

In recent years, nonchloroaluminiate acidic ionic liquids, which are air and moisture stable, have been synthesized and used successfully in etherification,[2] esterification,[3] Friedel–Crafts alkylation,[4] Beckmann rearrangement,[5] and so on. However, most of them described currently in the literature for catalytic and other solvent applications contain halogen atoms such as Cl or F.[6] With regard to the environmental impact of technical processes using these ionic liquids, their presence may cause—under certain conditions—serious concerns.[7] Therefore, further investigation is necessary to look for new, even greener acidic ionic liquids.

In our previous work, our group had synthesized several acidic ionic liquids and applied them to some reactions, such as oxidation, esterification, Beckmann rearrangement, and alkylation.[8] Here we describe the synthesis and characterization of two Brönsted acid site functionalized ionic liquids with imidazolium. Under mild conditions and without any additional organic solvent, the esterification of isopropanol by chloroacetic acid could be carried out in these new task-specific ionic liquids. In comparison with most of acidic ionic liquids in current use, these TSILs are halogen free and more environmentally benign. To the best of our knowledge, they are reported here for the first time. All TSILs are characterized with Fourier transform infrared spectroscopy (FTIR), ^{1}H NMR, ^{13}C NMR, thermal gravimetric analysis (TGA), and elemental analysis.

In summary, several task-specific ionic liquids possessing two Brönsted acid sites were synthesized. Under mild conditions and without any additional organic solvent, the esterification of isopropanol by chloroacetic acid could be carried out in these new TSILs. Good yields were obtained, and the ester formed a separate phase that was decanted. The ionic liquid could be reused after removal of water under vacuum. Being acidic ionic liquids, they have other great potential applications as catalysts and/or media in many reactions, such as etherification, Friedel–Crafts reaction, oxidation reaction, and so on. Some investigations about applications of these TSILs and their acidity–catalytic activity—structure relationships are in progress at our laboratory.

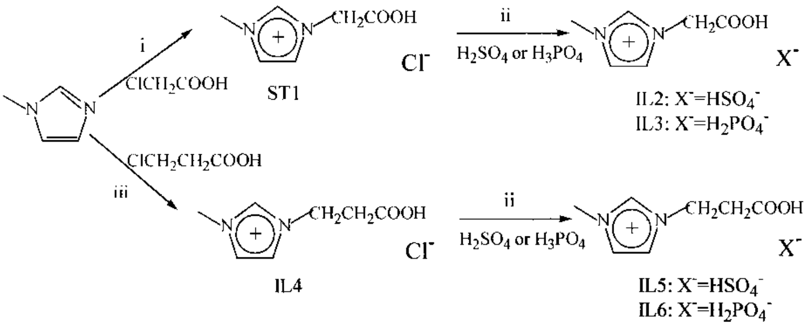
EXPERIMENTAL

All solvents and chemicals in the experiment were commercially available and used without further purification unless otherwise stated. *N*-Methylimidazole was purchased from Aldrich, and the others were all from Shanghai Chemical Reagent Corporation Ltd. The C, N, and H elemental analyses were performed on an Elementar Vario EL element analyzer. IR spectra (FTIR) were recorded on a PE Spectrum^{TM} GX FTIR spectrometer using liquid film or KBr tablet. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were obtained on Varian Mercury-Plus 300BB instruments as solutions in deuterium-substituted reagent. Chemical shifts were reported in parts per million (ppm, d). The thermal decomposition point of ionic liquids was determined by TGA (Perkin-Elmer TGA Pyris1 instrument, 10 K min^{-1} heating rate under nitrogen). Densities were measured using a U-shape vibrating-tube densimeter (model DA-500) operating in a static mode. The rheometer used (Brookfield, RVDV-III$^+$) allows measurements from 293 to 393 K at atmospheric pressure and in a wide viscosity range (from 100 to 3M cP).

Isopropanol (0.04 mol), equivalent chloroacetic acid (0.04 mol), and TSILs (0.008 mol) were added in a round-bottom flask with a reflux condenser. The reaction mixture was stirred for 3 h with the oil bath at 60°C. After the reaction, the ester could be simply decanted out from the ionic liquid, and the ionic liquid was reused after removal of water under vacuum (0.01 Torr) at 130°C for 1 h.

General Procedures for the Synthesis of TSILs

The TSILs were prepared by a two-step synthesis (Scheme 1) through 1-methylimidazole combined first with chloroacetic acid or 3-chloropropionic



Scheme 1. Synthesis of TSILs. Reagents and reaction conditions: (i) chloroacetic acid (1 equivalent), anhydrous chloroform, reflux, 50 h; (ii) H_2SO_4 97% or H_3PO_4 85% (1 equivalent), CH_2Cl_2, 0°C then reflux, 48 h; (iii) 3-chloropropionic acid (1 equivalent), 70°C, 50 h.

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acid to form zwitterionic salts, followed by addition of concentrated sulphuric acid (97%) or o-phosphoric acid (85%). The typical synthetic procedure of TSILs is described with IL2 as example.

To a solution of chloroacetic acid (1.0 mmol) in anhydrous chloroform (80 mL) at room temperature, 1-methylimidazole (1.0 mmol) was added. The resulting mixture was stirred for ca. 50 h at reflux. After the reaction, the solid produced was filtrated and washed with anhydrous ethanol to remove any unreacted starting materials. Then it was dried in vacuum, and zwitterionic salt ST1 was obtained.

The IL2 (Scheme 1) were obtained by a dropwise addition of 1 equivalent of concentrated sulphuric acid (97%) to a cooled solution of the corresponding ST1 (1 equivalent) in anhydrous methylene chloride. The mixture was stirred for ca. 48 h at reflux. The HCl, formed in the reaction as a by-product, was distilled out of the condenser under a stream of dry nitrogen and was dissolved in deionized water at 0°C. The acid aqueous solution was monitored by titration with NaOH. When the CH_2Cl_2 was evaporated with a rotary evaporator, the ionic liquid was dried under vacuum (10^{-2} Torr) at 70°C for 6 h.

The spectral data of TSILs are as follows.

Data

ST1: A white solid with yield of 78%. ^{1}H NMR (300 MHz, DMSO-d_6, TMS); 3.89 (s, 3H), 5.21 (s, 2H), 7.78 (s, 2H), 9.33 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, TMS); δ 36.55, 50.39, 123.81, 124.35, 138.33, 168.6. IR (cm^{-1}): 3158, 2580, 2490, 1734, 1572, 1364, 1168, 639, 776, 681. $C_6H_9O_2N_2Cl$ (176.52) calcd.: C, 40.80; H, 5.09; N, 15.86. Found: C, 40.86; H, 5.39; N, 16.00. The thermal decomposition point of IL1 533.2K.

IL2: A yellow viscous liquid with yield of 97.5%; density: 1.377 g/ml (298 K); viscosity: 1000.6 mPa s (353 K). ^{1}H NMR (300 MHz, DMSO-d_6, TMS); 3.87 (s, 3H), 5.11 (s, 2H), 7.70 (s, 2H), 9.10 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, TMS); δ 36.52, 50.26, 123.89, 124.38, 138.35, 168.89. IR (cm^{-1}): 3158, 2509, 1741, 1572, 1364, 1168, 1176, 1050, 852, 639, 588. $C_6H_{10}O_6N_2S$ (237.13) calcd.: C, 34.96; H, 4.85; N, 13.58. Found: C, 34.03; H, 4.90; N, 13.62. The thermal decomposition point of IL2 is 578.5 K.

IL3: A yellow viscous liquid with yield of 96.0%; density: 1.340 g/ml (298 K); viscosity: 9896.9 mPa s(353 K). ^{1}H NMR (300 MHz, D_2O, TMS); 3.22 (s, 3H), 4.44 (s, 2H), 6.81 (t, 2H), 8.10 (s, 1H). ^{13}C NMR (75 MHz, D_2O, TMS); δ 35.74, 49.55, 123.17, 124.11, 136.90, 169.54. IR (cm^{-1}): 3158, 2488, 1734, 1572, 1364, 1212, 1191, 1168, 995, 639, 621. $C_6H_{11}O_6N_2P$ (237.04) calcd.: C, 34.98; H, 5.34; N, 13.59. Found: C, 34.88; H, 5.39; N, 13.60. The thermal decomposition point of IL3 is 572.5 K.

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IL4: A yellow viscous liquid with yield of 98.0%; density: 1.115 g/ml (298 K); viscosity: 1175.4 mPa s (353 K). ^{1}H NMR (300 MHz, DMSO-d$_6$, TMS); 2.84 (t, 2H), 3.82 (s, 3H), 4.31 (s, 2H), 7.71 (s, 1H), 7.79 (s, 1H), 9.33 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d$_6$, TMS); δ 34.92, 36.36, 45.53, 123.02, 124.05, 137.60, 172.45. IR (cm^{-1}): 3158, 2586, 1743, 1572, 1364, 1168, 639. $C_7H_{11}O_2N_2Cl$ (190.53) calcd.: C, 44.13; H, 5.77; N, 14.70. Found: C, 44.23; H, 5.59; N, 14.88. The thermal decomposition point of IL4 is 516.4 K.

IL5: A yellow viscous liquid with yield of 96.0%; density: 1.195 g/ml (298 K); viscosity: 9677.1 mPa s (353 K). ^{1}H NMR (300 MHz, D_2O, TMS); 2.28 (t, 2H), 3.16 (s, 3H), 3.74 (t, 2H), 6.70 (s, 1H), 6.79 (s, 1H), 8.01 (s, 1H). ^{13}C NMR (75 MHz, D_2O, TMS); δ 33.84, 35.65, 44.71, 122.21, 123.59, 136.29, 173.87. IR (cm^{-1}): 3158, 3098, 2602, 2486, 1749, 1572, 1364, 1287, 1168, 1069, 1006, 885, 850, 639, 614, 454. $C_7H_{12}O_6N_2S$ (252.14) calcd.: C, 38.19; H, 5.45; N, 12.12. Found: C, 38.23; H, 5.49; N, 12.37. The thermal decomposition point of IL5 is 524.3 K.

IL6: A yellow viscous liquid with yield of 97.0%; density: 1.233 g/ml (298 K); viscosity: 9539.6 mPa s (353 K). ^{1}H NMR (300 MHz, D_2O, TMS); 2.47 (t, 2H), 3.36 (s, 3H), 3.94 (t, 2H), 6.90 (s, 1H), 6.97 (s, 1H), 8.22 (s, 1H). ^{13}C NMR (75 MHz, D_2O, TMS); δ 33.89, 35.64, 44.60, 122.20, 123.52, 136.30, 174.05. IR (cm^{-1}): 3158, 1726, 1572, 1364, 1167, 1109, 997, 639, 621. $C_7H_{13}O_6N_2P$ (252.05) calcd.: C, 38.21; H, 5.91; N, 12.72. Found: C, 38.43; H, 5.79; N, 12.58. The thermal decomposition point of IL6 is 506.1 K.

The Esterification of Isopropanol by Chloroacetic Acid

The esterification reactions of chloroacetic acid with alcohols are very useful in the medicinal industry. Recently, a few examples of synthesis of esters in ILs with or without an additional catalyst have been reported and demonstrated good catalytic performance.[9] However, most cases dealt with aliphatic esters and arylic esters, and little information about chloroacetate synthesis in ILs was found. Our efforts were directed toward investigating the formation of an important commodity ester, isopropyl chloroacetate, from isopropanol and chloroacetic acid using different TSILs as the solvent/catalyst in a batch-type process. The results of experiments are summarized in Table 1. In all cases, good and moderate yields were obtained. Because the TSILs reported here are miscible with water but immiscible with esters, the esterifications proceeded smoothly to completion even without simultaneous removal of the produced water, even though esterification is a reversible reaction. The data in entries 1–4 (Table 1) indicate that the yield of esters in IL2 and IL5 is considerably higher than that in IL3 and IL6.

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Table 1. Results of esterification of isopropanol by chloroacetic acid under different TSILs

Entry	IL	IL/substrate (Mol/Mol)	T (°C)	Time (h)	Yields of esters (%)[a]
1	IL2	1:5	60	3	94.5
2	IL3	1:5	60	3	75.2
3	IL5	1:5	60	3	87.8
4	IL6	1:5	60	3	80.6
5[b]	IL2	1:5	60	3	94.6

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

[b] Five times reused.

It is suggested that the TSIL's anion has a significant impact on its catalytic activity. This phenomenon can be explained in terms of the different Brønsted acidities of the anions. $[HSO_4]^-$ has a higher Brønsted acidity than $[H_2PO_4]^-$, so the esterification has a better conversion in IL2 and IL5 than in the others. Furthermore, the fundamental studies on the acidities of the Brønsted acidic ionic liquids and their acidity–catalytic activity–structure relationships are now under way.

After reaction, the product could be conveniently decanted out from IL2. After treatment under vacuum (0.01 Torr) at 130°C for 1 h, the reactor containing the used IL2 was charged with isopropanol and chloroacetic acid. It is to be noted that IL2 can indeed be reused several times without visible loss of activity (Table 1, entry 5). This indicated that IL2 as catalyst for the esterification was recyclable.

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