

## Synthesis and Characterization of Dual Acidic Ionic Liquids

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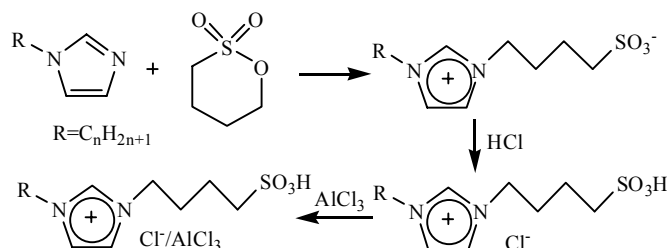
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**Abstract:** Novel ionic liquids with dual acidity, of which the cation contains Brønsted acidity and anions contain Lewis acidity were synthesized. These ionic liquids obtained were identified by NMR, FT-IR, SDT and FAB-MS. Their acidities were determined by pyridine probe on IR spectrography.

**Keywords:** Ionic liquids, functional, dual acidity, synthesis, characterization.

In recent years, acidic ionic liquids (ILs) are receiving extensive interest for their catalysis character<sup>1</sup>. Acidic ILs play as solvent and catalyst in acid-catalysis alkylation reactions<sup>2</sup>. The alkylation of isobutane and butane has been studied in Lewis ILs<sup>3</sup>. The mechanism is considered as that the Brønsted acid initiates the reaction and the Lewis acid catalyzes the reaction further<sup>4</sup>. However, development of acidic ILs is currently in preliminary stage and the number of published acidic ILs is very limited so far<sup>5,6</sup>. There is no report on ILs containing Brønsted acidity and Lewis acidity simultaneously. In this contribution, we report a new type of dual acidic ILs, of which the cation contains Brønsted acidity and the anion contains Lewis acidity.

**Scheme 1** Synthetic approach of dual acidic ionic liquids

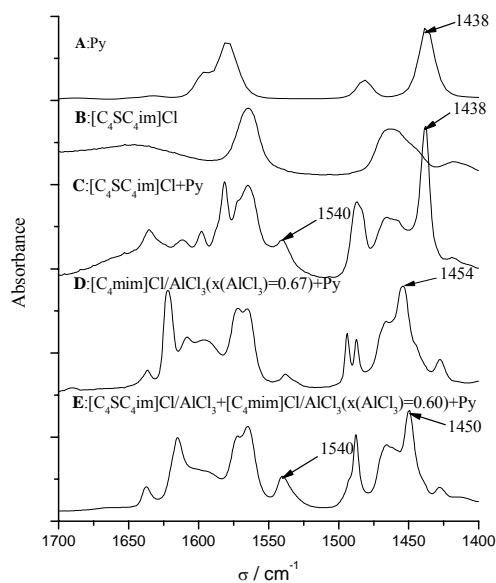


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The synthesis approach is made up of three-step atom economic reactions. (**Scheme 1**) The zwitterionic-type precursors of these ILs were obtained as described in the literature<sup>2</sup> through a one-step direct sulfonation reaction of 1-alkylimidazole and 1,4-butane sultone. The zwitterion acidification is accomplished by mixing of zwitterion with HCl (1:1 mol) to convert the pendant sulfonate group into an alkane sulfonic acid, 3-alkyl-1-(butyl-4-sulfonyl)imidazolium chloride ( $[\text{C}_4\text{SC}_n\text{im}]\text{Cl}$ ). The result is the transformation of the zwitterion into an IL cation bearing an appended sulfonic acid group, with the chlorine anion becoming the ILs' anion. The  $[\text{C}_4\text{SC}_2\text{im}]\text{Cl}$  and  $[\text{C}_4\text{SC}_4\text{im}]\text{Cl}$  are transparent liquids at room temperature, *i.e.* new room temperature ILs have not been reported. Then in the IL such as  $[\text{C}_4\text{mim}]\text{Cl}/\text{AlCl}_3$ , the acidification products  $[\text{C}_4\text{SC}_n\text{im}]\text{Cl}$  can act with  $\text{AlCl}_3$  to obtain dual acidic ILs,  $[\text{C}_4\text{SC}_n\text{im}]\text{Cl}/\text{AlCl}_3$ . Here the  $[\text{C}_4\text{mim}]\text{Cl}/\text{AlCl}_3$  IL is an initiator or promoter for that  $[\text{C}_4\text{SC}_n\text{im}]\text{Cl}$  itself is difficult to act with  $\text{AlCl}_3$  rapidly and homogeneously.

The obtained ILs were identified by NMR (Varian 300 MHz, in  $\text{DMSO-d}_6$ ,  $\delta$  ppm), FT-IR (Bruker Tensor 27) and SIMS (APEXII FT-ICR). NMR spectra of them are almost the same, and basically consistent with that of  $^1\text{H}$  NMR of  $[\text{C}_4\text{SC}_4\text{im}]\text{Cl}$ : 9.46(s, 1H), 7.90(t, 2H,  $J=1.8\text{Hz}$ ), 7.24(s, 1H), 4.23(m, 4H), 2.59(t, 2H,  $J=7.5\text{Hz}$ ), 1.92(m, 2H), 1.79(m, 2H), 1.58(m, 2H), 1.25(m, 2H), 0.89(t, 3H,  $J=7.2\text{Hz}$ ) ppm;  $^{13}\text{C}$  NMR of  $[\text{C}_4\text{SC}_4\text{im}]\text{Cl}$ : 136.30, 122.63, 50.60, 48.66, 48.62, 31.46, 28.68, 21.73, 18.93, 13.43 ppm. IR spectra of the ILs are basically in accordance with that of  $[\text{C}_4\text{SC}_4\text{im}]\text{Cl}$  with peaks of 3139, 3092, 2962, 2876, 1653, 1564, 1463, 1224, 1163, 1036, 753, 599, 525  $\text{cm}^{-1}$ . SIMS of  $[\text{C}_4\text{SC}_4\text{im}]\text{Cl}$  founded

**Figure 1** Determination of acidity of the dual acidic ionic liquids by FT-IR using pyridine (Py) as probe



$m/z$  261.1263(cation) corresponding to the  $C_{11}H_{21}N_2SO_3$  (calcd. 261.1267), demonstrating that the hydrogen of sulfonic acid is bonded to cation. All the mixtures of  $[C_4SC_n\text{im}]\text{Cl} / \text{AlCl}_3$  and  $[C_4\text{mim}]\text{Cl} / \text{AlCl}_3$  are liquids at room temperature. The acidification products  $[C_4SC_n\text{im}]\text{Cl}$  are liquids at room temperature except  $[C_4SC_1\text{im}]\text{Cl}$  is a very viscous slurry. Decomposition temperatures of  $[C_4SC_n\text{im}]\text{Cl}$  determined by TGA ( $10^\circ\text{Cmin}^{-1}$ ,  $\text{N}_2$ ) are around  $320^\circ\text{C}$ . DSC determination (first heating cycle, initially cooling samples to  $-100^\circ\text{C}$ ) show that a glass transition temperature for  $[C_4SC_1\text{im}]\text{Cl}$  is  $-22^\circ\text{C}$ , and that for  $[C_4SC_2\text{im}]\text{Cl}$  and  $[C_4SC_4\text{im}]\text{Cl}$  is  $-19^\circ\text{C}$  and  $-27^\circ\text{C}$ , respectively. No melting points were observed.

The acidity of these dual acidic ILs was determined by IR spectrography using pyridine (Py) as probe. (**Figure 1**) In acidic ILs' IR spectra, the presence of a band near  $1450\text{ cm}^{-1}$  is an indication of pyridine coordinated to Lewis acidic sites, whilst a band near  $1540\text{ cm}^{-1}$  is an indication of the formation of pyridinium ions resulting from the presence of Brønsted acidic sites<sup>7, 8</sup>. Neat pyridine shows a well-resolved band at  $1438\text{ cm}^{-1}$  (**Figure 1A**). When pyridine is added to  $[C_4SC_4\text{im}]\text{Cl}$  (**Figure 1B C**), the position of this band remains no change, indicating that no Lewis acidity is observed for  $[C_4SC_4\text{im}]\text{Cl}$ . It is clear from **Figure 1C** that a band at  $1540\text{ cm}^{-1}$  indicates Brønsted acidity for  $[C_4SC_4\text{im}]\text{Cl}$ . In the mixture of  $[C_4SC_4\text{im}]\text{Cl} / \text{AlCl}_3$  and  $[C_4\text{mim}]\text{Cl} / \text{AlCl}_3$  ( $x(\text{AlCl}_3)=0.60$ ) (**Figure 1E**), both the band at  $1540\text{ cm}^{-1}$  indicating Brønsted acidity and the band at  $1450\text{ cm}^{-1}$  indicating Lewis acidity are present. However comparing the band at  $1454\text{ cm}^{-1}$  observed for  $[C_4\text{mim}]\text{Cl} / \text{AlCl}_3$  ( $x(\text{AlCl}_3)=0.67$ ) (**Figure 1D**), the quantitative addition of  $[C_4SC_4\text{im}]\text{Cl}$  makes the band shifting to  $1450\text{ cm}^{-1}$ , indicating the  $\text{Al}_2\text{Cl}_7^-$  anion in  $[C_4\text{mim}]\text{Cl} / \text{AlCl}_3$  reacts with  $\text{Cl}^-$  to form  $\text{AlCl}_4^-$  anion. This result proves that  $[C_4SC_n\text{im}]\text{Cl} / \text{AlCl}_3$  ILs are dual acidic ILs and may own more strong acidity than those commonly used acidic ILs. The research of their application in alkylation is ongoing in our laboratory.

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