

# Synthesis, characterization and thermal properties of thiosalicylate ionic liquids

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MS received 23 June 2013; revised 15 August 2013; accepted 21 August 2013

**Abstract.** In an attempt to produce new functionalized ionic liquids, a series of thiosalicylate ionic liquids based on imidazolium, ammonium, phosphonium, choline and pyrrolidinium cations were synthesized. The compounds were characterized by Infra Red (IR), Nuclear Magnetic Resonance (NMR) and mass spectra (ESI-MS). Their glass-transition temperatures, melting points and decomposition temperatures have been measured. Physicochemical properties of ionic liquids are influenced by alkyl chain length and nature of the cation of ionic liquids.

**Keywords.** Thiosalicylate; imidazolium; ammonium; phosphonium; choline; pyrrolidinium.

## 1. Introduction

Ionic liquids (ILs) are organic salts that become liquids usually below about 200°C. They are salts where the ions are poorly coordinated. At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice, resulting in it being liquid below 200°C. Properties such as melting point, viscosity and solubility of starting materials and other solvents are determined by substituents on the organic component and the counter ion. Ionic liquids are non-volatile, have high thermal stability and have recently gained interest in new solvent applications such as electrochemistry,<sup>1,2</sup> separation,<sup>3–5</sup> synthesis<sup>6,7</sup> and catalysis.<sup>8–12</sup> Many ILs have been developed for specific synthetic problems. The collection of ILs based on the combinations of cations and anions has dramatically increased, and constantly new salts<sup>13</sup> and solvent mixtures<sup>14</sup> are prepared.

Our interest was kindled from the possibility of preparing a new interesting class of ILs from sulphur-containing anions. There is interest in the coordination chemistry of deprotonated thiosalicylic acid and thiosalicylate, since the combination of hard carboxylate and soft thiolate donors makes it potentially able to form complexes with a wide range of metal centres. The examples in literature are limited to a few ionic liquids and there is a need to synthesis different types of ionic liquids attached to various cations.

Formation of ionic liquids were carried out by quaternization of imidazole with haloalkane. Removal of excess haloalkanes and reaction solvents is generally not a problem, especially for the relatively volatile shorter chain haloalkanes. This is followed by the metathesis process which provides the desired anions of ionic liquids. ILs were also be prepared by acid/base neutralization reaction hydroxide ILs with thiosalicylate acids. A greener method *via* methyl carbonate precursors was applied and precursors then reacted with acids to yield ionic liquids of interest. Seven thiosalicylate ionic liquids were prepared and their molecular structures were confirmed using <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and mass spectroscopy. Their thermal properties, i.e, decomposition temperatures, melting points and glass-transitions temperatures were recorded.

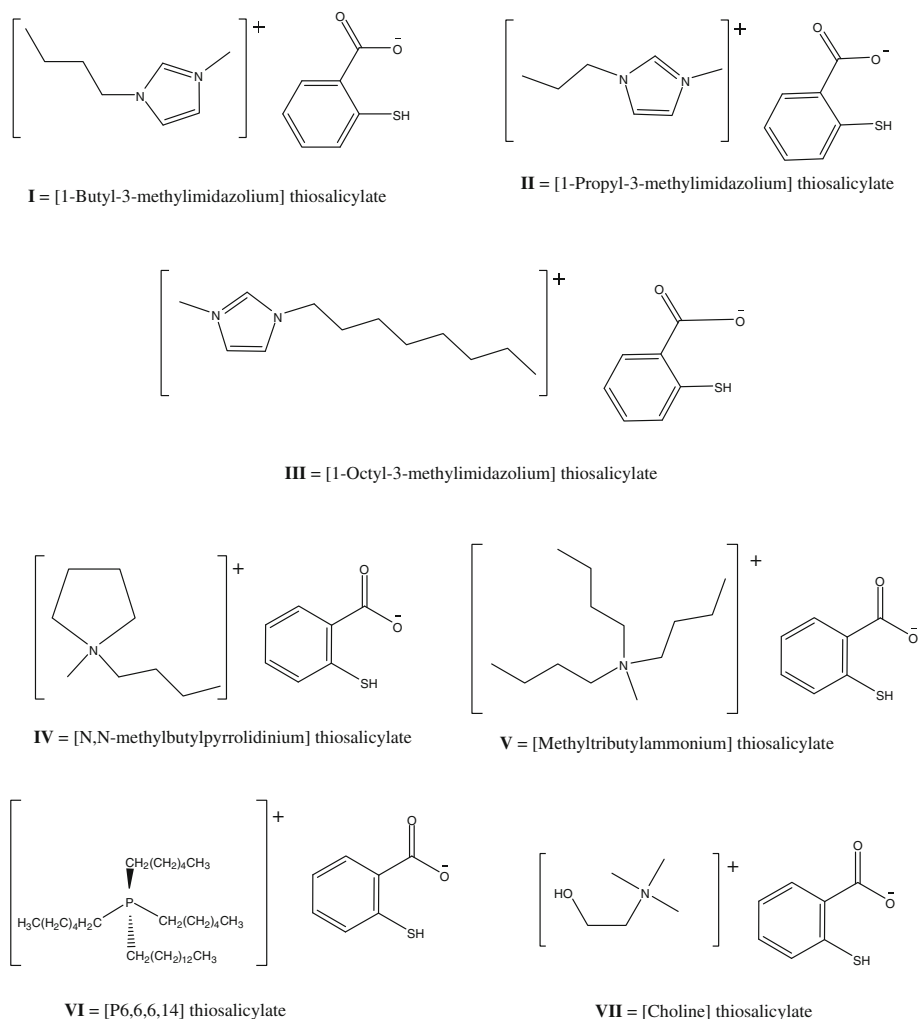
## 2. Experimental

All reagents and solvents were pure analytical grade materials purchased from commercial sources and were used without further purification. Structures of eight thiosalicylate functionalised ionic liquids are shown here in figure 1.

### 2.1 Characterization of ionic liquids

Structures of the ionic liquids were analysed by IR, NMR and ESI-MS. A Bruker Avance 300 Nuclear Magnetic Resonance Spectrophotometers was used to

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**Figure 1.** Structure of ionic liquids.

determine the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of ILs using  $\text{DMSO-}d_6$ . Chemical shifts were reported in parts per million (ppm) from tetramethylsilane, TMS reference ppm units with use of  $\delta$  scale. Multiplicities are abbreviated as s, singlet; d, doublet; t, triplet; and m, multiplet.

The IR spectra were recorded in a Shimadzu FTIR-8400S Fourier Transform Infrared Spectrometer (FTIR) in the mid-region ( $4000\text{--}400\text{ cm}^{-1}$ ) using the Attenuated Total Reflectance (Miracle ATR) measurement mode. ESI-MS spectra were obtained on a Jeol-Agilent system.

Thermal stability of the synthesized ILs was investigated using a thermogravimetric analyzer (TGA, Perkin-Elmer, Pyris V-3.81) at temperatures range of  $50\text{--}500^\circ\text{C}$ , heating rate of  $10^\circ\text{C min}^{-1}$  (with a temperature accuracy better than  $2^\circ\text{C}$ ) and under a nitrogen atmosphere supplied at the rate of  $20\text{ mL min}^{-1}$ . Glass transition temperatures,  $T_g$  and melting points,  $T_m$  were recorded on a Mettler Toledo Differential Scanning Calorimeter (DSC), model and data were evaluated

using Mettler-Toledo STAR software. Measurement was carried out at a scan rate of  $5^\circ\text{C min}^{-1}$ .

## 2.2 Preparation of thiosalicylate functionized ionic liquids

**2.2a [1-Butyl-3-methylimidazolium] thiosalicylate:** 1-Methylimidazole (0.1 mol) and 1-chlorobutane (0.12 mol) was added directly to a 50 ml acetonitrile in a 250 ml round bottomed flask equipped with a reflux condenser and magnetic stirrer. The mixture was left to stir at reflux for 48 h. The top layer was decanted and the bottom phase was extracted thrice with ethyl acetate. The product was evaporated under reduced pressure and dried *in vacuo* at  $70^\circ\text{C}$  for 24 h. Halide salts of 1-butyl-3-methylimidazolium was reacted with equimolar amount of sodium thiosalicylates in a mixture of acetone–water for 12 h. The solvent was removed and methanol added to precipitate sodium halide salt. The salt was filtered out and the filtrate

concentrated and dried in *vacuo*. Yield 76%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  0.89 (3H, t), 1.20 (2H, t), 1.69 (2H, t), 3.69 (3H, s), 4.15 (2H, d), 6.66–6.70 (2H, m), 6.71 (1H, m), 6.91 (1H, m), 7.78 (1H, m), 9.33 (1H, m);  $^{13}\text{C}$  NMR (75 MHz) 10.6, 12.1, 30.25, 35.5, 38.9, 126.2, 126.8, 121.0, 126.8, 126.9, 134.9, 138.1, 157.2, 169.1; IR ( $\nu$ ,  $\text{cm}^{-1}$ ) 3396, 2960, 2360, 1750, 1500, 1160; ES+  $m/z$  139 (100%,  $\text{C}_8\text{H}_{15}\text{N}^+$ ), ES-  $m/z$  153 (100%,  $\text{C}_7\text{H}_5\text{O}_2\text{S}^+$ ).

**2.2b [1-Propyl-3-methylimidazolium] thiosalicylate:** Similar procedure as earlier was carried out between 1-methylimidazole and *n*-propyl chloride to give [1-propyl-3-methylimidazolium] chloride. The halide salt was subjected to metathesis reaction to give the desired ionic liquid. Yield 83%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  0.85 (3H, t), 1.81 (2H, m), 3.87 (3H, s), 4.13 (2H, t), 6.69 (1H, m), 6.93 (1H, m), 7.24 (1H, m), 7.75 (2H, m), 7.87 (1H, m), 9.19 (1H, s);  $^{13}\text{C}$  NMR (75 MHz) 16.1, 19.8, 22.0, 25.3, 47.3, 62.9, 64.2, 123.3, 136.1, 149.1, 151.2, 167.5; IR ( $\nu$ ,  $\text{cm}^{-1}$ ) 3138, 2965, 1567, 1459, 1169; ES+  $m/z$  124 (100%,  $\text{C}_7\text{H}_{12}\text{N}_2^+$ ), ES-  $m/z$  153 (100%,  $\text{C}_7\text{H}_5\text{O}_2\text{S}^+$ ).

**2.2c [1-Octyl-3-methylimidazolium] thiosalicylate:** Similar procedure as earlier was carried out between 1-methylimidazole and *n*-octyl chloride to give [1-octyl-3-methylimidazolium] chloride. The halide salts underwent metathesis reaction to give the desired ionic liquid. Yield 79%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  0.88 (3H, t), 1.20 (2H, t), 1.68–1.76 (10H, m), 3.72 (3H, s), 4.18 (2H, d), 6.68–6.72 (2H, m), 6.75 (1H, m), 6.92 (1H, m), 7.80 (1H, m), 9.35 (1H, m);  $^{13}\text{C}$  NMR (75 MHz) 10.1, 14.2, 16.5, 19.8, 22.0, 23.2, 25.4, 27.3, 47.5, 62.6, 65.2, 124.3, 137.2, 150.1, 151.5, 168.2; IR ( $\nu$ ,  $\text{cm}^{-1}$ ) 3140, 2960, 1580, 1450, 1164; ES+  $m/z$  195 (100%,  $\text{C}_{12}\text{H}_{23}\text{N}_2^+$ ), ES-  $m/z$  153 (100%,  $\text{C}_7\text{H}_5\text{O}_2\text{S}^+$ ).

**2.2d [N,N-methylbutylpyrrolidinium] thiosalicylate:** 1-Butylpyrrolidine was reacted with excess dimethyl carbonate in methanol in a microwave quartz reaction tube, sealed and heated with magnetic stirring to 130°C. [N,N-methylbutylpyrrolidinium] methylcarbonate. The precursor was then brought to react with thiosalicylic acid at room temperature for 4 hour. The solvent was removed and the IL dried in *vacuo*. Yield 84%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  0.98 (3H, t), 1.20 (2H, m), 1.46 (2H, m), 1.87 (4H, m), 2.72 (3H, s), 3.04 (2H, m), 3.14 (4H, m), 6.67 (1H, m), 6.89 (1H, m), 7.25 (1H, m), 7.80 (1H, m);  $^{13}\text{C}$  NMR (75 MHz) 12.6, 19.2, 20.9, 25.1, 53.7, 63.7, 120.3, 130.3, 131.0, 135.1,

153.0, 156.0, 172.2; IR ( $\nu$ ,  $\text{cm}^{-1}$ ) 2964, 2876, 1640, 1576, 1541, 1441; ES+  $m/z$  142 (100%,  $\text{C}_9\text{H}_{20}\text{N}^+$ ), ES-  $m/z$  152.99 (100%,  $\text{C}_7\text{H}_5\text{O}_2\text{S}^+$ ).

**2.2e [Methyltributylammonium] thiosalicylate:** Tributylamine was reacted with excess dimethyl carbonate in methanol in a microwave quartz reaction tube, sealed and heated with magnetic stirring to 140°C. The unreacted amine was decanted and the bottom layer washed with excess ethyl acetate. The IL-precursor was then dried and brought to react with thiosalicylic acid at rt for 4 h. The solvent was removed and the IL dried in *vacuo*. Yield 76%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  0.78 (9H, t), 1.18 (6H, m), 1.51 (6H, m), 2.77 (3H, s), 3.03 (6H, m), 6.95–7.64 (4H, m);  $^{13}\text{C}$  NMR (75 MHz) 13.5, 19.7, 23.9, 48.1, 61.9, 124.6, 126.1, 129.9, 130.9, 136.5, 173.3; IR ( $\nu$ ,  $\text{cm}^{-1}$ ) 2956, 2886, 1645, 1597, 1530, 1449; ES+  $m/z$  200.24 (100%,  $\text{C}_{13}\text{H}_{30}\text{N}^+$ ), ES-  $m/z$  152.99 (100%,  $\text{C}_7\text{H}_5\text{O}_2\text{S}^+$ ).

**2.2f [ $\text{P}_{6,6,6,14}$ ] thiosalicylate:** [ $\text{P}_{6,6,6,14}$ ] thiosalicylate chloride was added to equimolar sodium thiosalicylates in a mixture of acetone–water for 12 h. The solvent was removed and methanol added to precipitate the sodium halide salt. The salt was filtered out and the filtrate concentrated and dried in *vacuo*. Yield 72%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  0.92 (12H, t), 1.62 (48H, m), 2.03 (9H, t), 6.60–7.80 (4H, m);  $^{13}\text{C}$  NMR (75 MHz) 15.4, 18.6, 18.7, 22.4, 22.6, 36.8, 37.2, 53.4, 119.2, 120.1, 130.6, 138.4, 139.2, 158.4, 169.1; IR ( $\nu$ ,  $\text{cm}^{-1}$ ) 3394, 2900, 2360, 1650 ES+  $m/z$  483 (100%,  $\text{C}_{32}\text{H}_{68}\text{P}^+$ ), ES-  $m/z$  153 (100%,  $\text{C}_7\text{H}_5\text{O}_2\text{S}^+$ ).

**2.2g [Choline] thiosalicylate:** Equimolar concentration of choline hydroxide was reacted with thiosalicylic acid in acetone at room temperature for 2 h. The solvent was removed and the ionic liquid dried in *vacuo*. Yield 83%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  3.16 (9H, s), 3.42 (2H, m), 3.88 (2H, m), 6.80 (1H, m), 7.07 (1H, m), 7.42 (1H, m), 8.02 (1H, m);  $^{13}\text{C}$  NMR (75 MHz) 54.0, 55.3, 67.1, 120.3, 128.3, 130.7, 132.1, 136.1, 156.8, 170.7; IR ( $\nu$ ,  $\text{cm}^{-1}$ ) 2924, 2842, 1560, 1472, 1365; ES+  $m/z$  104.11 (100%,  $\text{C}_5\text{H}_{14}\text{NO}^+$ ), ES-  $m/z$  153.00 (100%,  $\text{C}_7\text{H}_5\text{O}_2\text{S}^+$ ).

### 3. Results and discussion

#### 3.1 Synthesis

Ionic liquids **I**, **II** and **III** were prepared *via* metathesis of the halide salt of the precursors. The route is straightforward, however the task of removing sodium halides

**Table 1.** Thermal properties of thiosalicylate ionic liquids.

	Ionic liquids	$T_{\text{dec}}/^{\circ}\text{C}$ (5%)	$T_{\text{g}}/^{\circ}\text{C}$
<b>I</b>	[1-Butyl-3-methylimidazolium] thiosalicylate	203.0	−61.95
<b>II</b>	[1-Propyl-3-methylimidazolium] thiosalicylate	224.0	−55.52, 91.22*
<b>III</b>	[1-Octyl-3-methylimidazolium] thiosalicylate	195.0	−64.45
<b>IV</b>	[ <i>N,N</i> -methylbutylpyrrolidinium] thiosalicylate	216.7	−54.8
<b>V</b>	[Methyltributylammonium] thiosalicylate	188.0	−35.8
<b>VI</b>	[P <sub>6,6,6,14</sub> ] thiosalicylate	225.0	−66.2
<b>VII</b>	[Choline] thiosalicylate	187.5	−49.5

\*Melting point

proved to be tedious. This is because both the ionic liquids containing sulphur and the inorganic salt have similar solubility properties in organic and aqueous solutions. Through screening the compatible solvent for precipitation, we found that sodium halides are less soluble in methanol compared to imidazolium thiosalicylates. Hence, we managed to remove the inorganic salt by adding methanol to the reaction mixture which gave the inorganic salt. The four protons of aromatic hydrogen atoms of these thiosalicylate ionic liquids had chemical shifts at 6.66–7.87 ppm. FTIR spectra of **I**, **II** and **III** showed absorption bands at ~1160, 1466 and 1562 which could be assigned to the stretching and bending vibrations of the aromatic C-H group. For imidazolium, the N-H, C-H and C-N ring stretching vibrations were observed at ~3156, 3116, and 1575 cm<sup>−1</sup>, respectively. The C-H stretching vibration of CH<sub>2</sub> was observed at ~2960 cm<sup>−1</sup>.

All the ESI-MS experiments results showed a single peak at  $m/z = 153.2$ , which could be assigned to the thiosalicylate anion.

Compounds **IV** and **V** were prepared from their methyl carbonate precursor as described in an earlier finding.<sup>15</sup> An excess of dimethyl carbonate solvent with the base was heated in a microwave reactor. Without any work-up, the mixture was then brought to react with thiosalicylic acid at room temperature. The route proved easy and greener as no halide impurities would be present in the ionic liquids, hence separation step is unnecessary.

Compound **VI** was synthesized by exchanging the chloride ion of [P<sub>6,6,6,14</sub>] with thiosalicylate ion. The reaction was carried out in biphasic solution as the ionic liquid produced was immiscible in water. Compound **VII** was easily synthesized by neutralization of choline hydroxide with thiosalicylic acid. This gave a water-soluble ionic liquid.

All the thiosalicylate-based ionic liquids studied previously<sup>16</sup> are immiscible with water. Hydrophilicity of thiosalicylate ionic liquids are very much dependent on the nature of the cation. Findings from this study

gave water-miscible ionic liquids with the exception of [P<sub>6,6,6,14</sub>] cation. It is predicted that hydrophobicity of an ionic liquid increases with the length of the alkyl chain on the cation. The water-miscibility character is important as these ionic liquids could be applied as water pollutant extractants.

### 3.2 Thermal properties

Thermal properties of ionic liquids are shown in table 1.

Thiosalicylates showed glass-transition temperatures, from −66 to −35°C. They are highly viscous liquids, with the exception of **II**, which has a gel-like feature at room temperature, and indicated a clear melting point at 91°C. [P<sub>6,6,6,14</sub>] thiosalicylate exhibited lower glass-transition temperature than those of imidazolium, pyrrolidinium and ammonium. 1-Octyl-3-methylimidazolium thiosalicylate showed lower  $T_{\text{g}}$  than its butyl and propyl chain cations. A longer chain attached to a imidazolium cation is speculated to show better liquidus properties than a shorter one.

The  $T_{\text{dec}}/^{\circ}\text{C}$  (5%) is the onset temperature which was obtained from the intersection of the baseline weight and the tangent of the weight vs temperature curve obtained from TGA analysis as decomposition occurs. From the TGA results, the imidazolium cation is more thermally stable than ammonium cation. Ngo *et al.*<sup>16</sup> and Begg *et al.*<sup>17</sup> reported that the imidazole is resistant to ring fission in thermal exposure. In addition, 1-propyl-3-methylimidazolium thiosalicylate cation showed better thermal stability than its octyl and butyl cations. It is suggested that the thermal stability decreases as the organic content of the molecule increases. [P<sub>6,6,6,14</sub>] thiosalicylate, **VI** showed the highest thermal stability due to its cation structure.

### 4. Conclusion

Seven thiosalicylate ionic liquids have been synthesized. Their glass-transition temperatures, melting

points and decomposition temperatures have been measured. We find a general trend in the influence of alkyl chain length and nature of cation on physicochemical properties of ionic liquids. With similar cations, ionic liquids containing 1-propyl-3-methylimidazolium cations exhibit higher melting points but lower water solubilities than those ionic liquids containing octyl- and butylimidazolium cations. On the other hand, imidazolium cations exhibit greater stability than ionic liquids containing ammonium cations. The most stable ionic liquids among the thiosalicylates were the phosphonium cations.

### Acknowledgement

Authors thank the University Teknologi PETRONAS for providing research and library facilities.

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