Cryo-solvatochromism in Ionic Liquids

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Electronic Support Information

1. Molecular structures

![Scheme S1](image)

Scheme S1 Molecular structures of (left) the ionic liquid, [C2OHmim]BF4, as the donor solvent, and (right) the Cl source compound, [bmim]Cl.

2. General thermo-solvatochromic reaction

\[
\text{[NiCl}_2([C_2\text{OHmim}]\text{BF}_4)_x]\text{Cl}^y + m\text{Cl}^- \quad (S1)
\]

(heating)

\[
\text{NiCl}_2\text{Cl}^y + y[C_2\text{OHmim}]\text{BF}_4
\]

(cooling)

(heptahedral, yellow-green or green)

where \(0 \leq x \leq 4\), \(2 \leq y \leq 6\), \(x + y = 6\), and \(m + y = 4\). These restrictions lead to a maximum of four octahedral complex ions. Charge balancing ions (CBIs: BF4−, [bmin]+ and/or [C2OHmim]+) are not shown in Reaction (S1). The type and number of CBIs in (S1) depend on the value of \(x\), \(y\) and \(m\). In Reaction (1), \(x = y = 3\), \(m = 1\), and the CBI is [bmin]+.

3. Enthalpy changes derived from DSC curves 3 to 5 in Fig. 2C and 2D (Table S1)

<table>
<thead>
<tr>
<th>Solutions (in [C2OHmim]BF4)</th>
<th>(\Delta H) (J g(^{-1})) Heating</th>
<th>(\Delta H) (J g(^{-1})) Cooling</th>
<th>(\Delta H^*) (kJ mol(^{-1})) Heating</th>
<th>(\Delta H^*) (kJ mol(^{-1})) Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14 mol L(^{-1}) [bmin]:NiCl4</td>
<td>2.01</td>
<td>2.02</td>
<td>59.1</td>
<td>59.4</td>
</tr>
<tr>
<td>0.14 mol L(^{-1}) [bmin]:NiCl4 + 0.28 mol L(^{-1}) [bmin]:Cl</td>
<td>3.98</td>
<td>4.06</td>
<td>59.1</td>
<td>59.3</td>
</tr>
<tr>
<td>0.14 mol L(^{-1}) [bmin]:NiCl4 + 0.70 mol L(^{-1}) [bmin]:Cl</td>
<td>3.42</td>
<td>3.81</td>
<td>59.0</td>
<td>59.3</td>
</tr>
</tbody>
</table>

* Estimated using density of [C2OHmim]BF4 (1.37 g mL\(^{-1}\)).

4. Cryochromic film and ionic liquid

![Fig. S1](image)

Fig. S1 Photographs of a composite film (2 cm × 2 cm) of [C2OHmim]BF4-[C2OHmim]Cl-[bmin]NiCl4-PVDF (mass ratio: 5:7:1:10) at (A) 22 °C, (B) –13 °C (in freezer). The insets show the ionic liquid solution at the respective temperatures. Note that the tiny spots in (B) were ice dusts.

5. Colours at different temperatures

![Fig. S2](image)

Fig. S2 Photographs of 0.0207 mol L\(^{-1}\) [bmin]:NiCl4 in [C2OHmim]BF4 in the absence (row A) and presence (rows B to E) of [bmin]:Cl at indicated temperatures and the following concentrations: (A) without [bmin]:Cl; (B) 0.04, (C) 0.10, (D) 0.20, and (E) 0.40 mol L\(^{-1}\) [bmin]:Cl.