Ionic Liquids as Novel Lubricants and Additives*

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OAK RIDGE NATIONAL LABORATORY  
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Introduction to Ionic Liquids

- Ionic liquids (ILs) are composed of cations and anions, instead of neutral molecules.
  - Currently being used as green solvents in synthesis, electrochemistry, catalysis, etc.
  - Recent studies have demonstrated promising lubricating properties of ionic liquids.

- Properties
  - Inherent polarity (Anti-wear boundary film)
  - High thermal stability
  - Negligible volatility
  - Non-flammability
  - High flexibility of IL molecular design
  - Economical and environmentally friendly synthesis

Ionic liquid  Oil

Coulombic forces  Van der Waals forces
Typical Molecular Structures of Ionic Liquids

Common cations:

1-alkyl-3-methylimidazolium

N-alkylpyridinium

Tetraalkylammonium

Tetraalkylphosphonium (R_{1,2,3,4} = alkyl)

Common anions:

water-insoluble

[PF_6]^-

[(CF_3SO_2)_2N]^-

[(C_2F_5SO_2)_2N]^- (or BETI-)

[BR_1R_2R_3R_4]^-

water-soluble

[BF_4]^-

[CF_3SO_3]^-

[(C_2F_5SO_2)_2N]^-

[CH_3CO_2]^-

[CF_3CO_2]^-, [NO_3]^-

Br, Cl, I


ORNL has been active in various areas of ionic liquids research since early 1990s, with a well equipped organic synthesis laboratory.
**ILs have a Wide Range of Viscosities**

- Densities of ILs are in a narrow band, 1.03-1.46 g/cc @ 23 °C;
- **Viscosities of ILs vary in a wide range**, 50-1500 cP @ 23 °C.

<table>
<thead>
<tr>
<th>Lubricants</th>
<th>$\rho$ (g/cc) @ 23 °C</th>
<th>$\eta$ (cP) @ 23 °C</th>
<th>$\eta$ (cP) @ 40 °C</th>
<th>$\eta$ (cP) @ 100 °C</th>
<th>Viscosity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrocarbon oils</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>0.86</td>
<td>159</td>
<td>56</td>
<td>6.3</td>
<td>78</td>
</tr>
<tr>
<td>15W40 Oil</td>
<td>0.86</td>
<td>229</td>
<td>91</td>
<td>11.3</td>
<td>128</td>
</tr>
<tr>
<td><strong>Imidazolium ionic liquids</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_4$mim.PF$_6$</td>
<td>1.37</td>
<td>281</td>
<td>108</td>
<td>13.3</td>
<td>110</td>
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<tr>
<td>C$_6$mim.Br</td>
<td>1.16</td>
<td>&gt;1500</td>
<td>630</td>
<td><em>n/m</em></td>
<td><em>n/m</em></td>
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<tr>
<td>C$_4$mim.Tf$_2$N</td>
<td>1.42</td>
<td>51</td>
<td>25</td>
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<tr>
<td>C$_{10}$mim.Tf$_2$N</td>
<td>1.23</td>
<td>122</td>
<td>53</td>
<td>8.8</td>
<td>135</td>
</tr>
<tr>
<td>C$_8$mim.BETI</td>
<td>1.34</td>
<td>169</td>
<td>69</td>
<td>9.5</td>
<td>99</td>
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<td><strong>Ammonium ionic liquids</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C$<em>6$H$</em>{13}$]$_3$NH.Tf$_2$N</td>
<td>1.12</td>
<td>170</td>
<td>72</td>
<td>9.7</td>
<td>113</td>
</tr>
<tr>
<td>[C$<em>8$H$</em>{17}$]$_3$NH.Tf$_2$N</td>
<td>1.06</td>
<td>219</td>
<td>89</td>
<td>11.7</td>
<td>124</td>
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<tr>
<td>[C$<em>8$H$</em>{17}$]NH$_3$.Tf$_2$N</td>
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<td>125</td>
<td>14.2</td>
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<td>[C$_2$H$_5$]$_3$NH.BETI</td>
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<td>[C$<em>8$H$</em>{17}$]NH$_3$.BETI</td>
<td>1.45</td>
<td>763</td>
<td>265</td>
<td><em>n/m</em></td>
<td><em>n/m</em></td>
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</tbody>
</table>

* $n/m$ - not measured
ILs Have High Thermal Stability

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Density (g/cc)</th>
<th>Viscosity (cP) @ 40°C</th>
<th>Viscosity (cP) @ 100°C</th>
<th>T_onset (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15W40 engine oil</td>
<td>0.86</td>
<td>91</td>
<td>11.3</td>
<td>236</td>
</tr>
<tr>
<td>[C₈H₁₇]₃NH.Tf₂N</td>
<td>1.06</td>
<td>89</td>
<td>11.7</td>
<td>357</td>
</tr>
</tbody>
</table>

![TGA Graph](image)

**Mineral Oil**

**15W40 Oil**

**[C₈H₁₇]NH₃.NTf₂**

**[C₈H₁₇]₃NH.NTf₂**

**[C₈H₁₇]NH₃.BETI**
ILs Produce Low Friction

Ionic Liquid \([\text{[C}_8\text{H}_{17}]_3\text{NH}.\text{Tf}_2\text{N}]\) vs. 15W40 Engine Oil

- **20-35% friction reduction in all lubrication regimes.**
- Suppress the transition from EHL to boundary lubrication (*Striebeck curve shifted to the left*);

[Graph showing friction coefficient vs. viscosity x sliding speed for 15W40 Oil and \([\text{[C}_8\text{H}_{17}]_3\text{NH}.\text{Tf}_2\text{N}]\).]

Striebeck curves produced by 52100 steel balls sliding against Al 6061-T6 flats at room temperature.
ILs Produce Low Wear

**Ionic Liquid** ([C$_8$H$_{17}$]$_3$NH.Tf$_2$N) vs. **15W40 Engine Oil**
- 45-55% wear reduction for Al alloys
- Virtually no wear on steel balls

Wear data produced by 52100 steel balls sliding against Al flats at room and elevated temperatures.
Adhesion Elimination by Ionic Liquids

Wear scars on the counterface steel balls that rubbed against aluminum

This suggests potential applications, such as die casting.
Benefits of Using ILs as Novel Lubricants or additives

- **Improve system efficiency** by friction reduction and allowing higher combustion temperatures.
- **Extend service life** by wear and adhesion reduction.
- **Expand the usage of lubricants to higher temperatures** with higher thermal stability.
- **Reduce emissions** due to ultra-low vapor pressure and less engine deposits.
- **Require fewer expensive lubricant additives** with better intrinsic properties, e.g. boundary film formability and solvent nature.
- **Safer transportation and storage** because of non-flammability.
- Hydrophobic and hydrophilic ILs available for use as **ashless additives for oil- and water-based lubricants**, respectively.