Ionic Liquids as Novel Lubricants and Additives

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Needs for Improved Lubricants

- In transportation sector, 10~15% of the energy generated in automobile engines is lost to friction. In addition, production engine oils
  - are one of the barriers for higher combustion temperatures to increase engine efficiency, limited by their low thermal stability above 250° C, and
  - contribute hydrocarbon exhaust emissions due to oil blow-by and burn-out.

A new class of more effective, environmentally-friendly lubricants could lead to huge energy savings.

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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 chemical synthesis, electrochemistry, catalysis, etc.

- Properties
  - Inherent polarity
  - High thermal stability
  - Negligible volatility
  - Non-flammability
  - High flexibility of IL molecular design
  - Economical and environmentally friendly synthesis

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

Common cations:
- 1-alkyl-3-methylimidazolium
- N-alkylpyridinium
- Tetraalkylammonium
- Tetraalkylphosphonium (R₁,₂,₃,₄ = alkyl)

Common anions:
- water-insoluble: [PF₆]⁻, [(CF₃SO₂)₂N]⁻ (or Tf₂N⁻), [(C₂F₅SO₂)₂N]⁻ (or BETI⁻), [BR₁R₂R₃R₄]⁻

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

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**Viscosity Strongly Correlates to Molecular Structure**

- **Examples**
  - With same cation, Cl\(^-\), Br\(^-\), or PF\(_6\)^- generate higher viscosities than Tf\(_2\)N or BETI.
  - With same anion, higher # of carbon in alkyl of cation leads to higher viscosity and lower density.
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>ρ (g/cc) @ 23 °C</th>
<th>η (cP) @ 23 °C</th>
<th>η (cP) @ 40 °C</th>
<th>η (cP) @ 100 °C</th>
<th>Viscosity Index</th>
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</thead>
<tbody>
<tr>
<td><strong>Hydrocarbon oils</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mineral Oil</td>
<td>0.86</td>
<td>159</td>
<td>56</td>
<td>6.3</td>
<td>78</td>
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<tr>
<td>15W40 Oil</td>
<td>0.86</td>
<td>229</td>
<td>91</td>
<td>11.3</td>
<td>128</td>
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<tr>
<td><strong>Imidazolium ionic liquids</strong></td>
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<td></td>
<td></td>
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<tr>
<td>C\textsubscript{4}mim.PF\textsubscript{6}</td>
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<td>108</td>
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<td>110</td>
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<td>C\textsubscript{6}mim.Br</td>
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<td>630</td>
<td>n/m*</td>
<td>n/m*</td>
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<td>122</td>
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<tr>
<td>C\textsubscript{8}mim.BETI</td>
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<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>
<td></td>
</tr>
<tr>
<td>[C\textsubscript{6}H\textsubscript{13}]\textsubscript{3}NH.Tf\textsubscript{2}N</td>
<td>1.12</td>
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<td>72</td>
<td>9.7</td>
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<tr>
<td>[C\textsubscript{8}H\textsubscript{17}]\textsubscript{3}NH.Tf\textsubscript{2}N</td>
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<td>89</td>
<td>11.7</td>
<td>124</td>
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<tr>
<td>[C\textsubscript{8}H\textsubscript{17}]NH\textsubscript{3}.Tf\textsubscript{2}N</td>
<td>1.37</td>
<td>331</td>
<td>125</td>
<td>14.2</td>
<td>100</td>
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<td>[C\textsubscript{2}H\textsubscript{5}]\textsubscript{3}NH.BETI</td>
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<td>67</td>
<td>9.3</td>
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<td>[C\textsubscript{8}H\textsubscript{17}]NH\textsubscript{3}.BETI</td>
<td>1.45</td>
<td>763</td>
<td>265</td>
<td>n/m*</td>
<td>n/m*</td>
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</tbody>
</table>

* n/m - not measured

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### ILs Have High Thermal Stability

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>$T_{onset}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15W40 oil</td>
<td>236</td>
</tr>
<tr>
<td>$C_{10}$mim.$\text{Tf}_2\text{N}$</td>
<td>$&gt;400$</td>
</tr>
<tr>
<td>$[\text{C}<em>8\text{H}</em>{17}]_3\text{NH}.\text{Tf}_2\text{N}$</td>
<td>357</td>
</tr>
</tbody>
</table>

![TGA Graph](image.png)

**Lubricants:**
- Mineral Oil
- 15W40 Oil
- $[\text{C}_8\text{H}_{17}]\text{NH}_3$.NTf2
- $[\text{C}_8\text{H}_{17}]_3\text{NH}.\text{Tf}_2\text{N}$
- $[\text{C}_8\text{H}_{17}]\text{NH}_3$.BETI

**Tonset (°C):**
- Mineral Oil: 365
- 15W40 Oil: 236
- $\text{C}_{10}$mim.$\text{Tf}_2\text{N}$: $>400$
- $[\text{C}_8\text{H}_{17}]_3\text{NH}.\text{Tf}_2\text{N}$: 357

**Tonset (°C) for ILs:**
- $[\text{C}_8\text{H}_{17}]\text{NH}_3$.NTf2: 236
- $[\text{C}_8\text{H}_{17}]_3\text{NH}.\text{Tf}_2\text{N}$: 357
Tribological Evaluation

- **Materials**
  - Al 1100, Al 6061-T6, Al 319
  - Counterface: AISI 52100 steel

- **Lubricants:**
  - 8 imidazolium ionic liquids
  - 5 ammonium ionic liquids
  - Mineral oil and 15W40 engine oil

- **Testing temperature:** RT and 100 °C

- **Test configurations:**
  - Ball-on-flat reciprocating sliding
  - Pin-on-disk unidirectional sliding
## Friction Screening Tests

<table>
<thead>
<tr>
<th>Lubricants</th>
<th>η @ 40 °C (cP)</th>
<th>COF</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrocarbon oils</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineral oil</td>
<td>56</td>
<td>0.10</td>
</tr>
<tr>
<td>15W40 diesel engine oil</td>
<td>91</td>
<td>0.09</td>
</tr>
<tr>
<td><strong>Imidazolium ionic liquids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆mim.Br</td>
<td>630</td>
<td>0.09</td>
</tr>
<tr>
<td>C₄mim.Cl</td>
<td>136</td>
<td>0.21</td>
</tr>
<tr>
<td>C₄mim.PF₆</td>
<td>108</td>
<td>0.18</td>
</tr>
<tr>
<td>C₆mim.PF₆</td>
<td>153</td>
<td>0.20</td>
</tr>
<tr>
<td>C₈mim.PF₆</td>
<td>245</td>
<td>0.07</td>
</tr>
<tr>
<td>C₁₀mim.Tf₂N</td>
<td>53</td>
<td>0.16</td>
</tr>
<tr>
<td>C₈mim.BETI</td>
<td>69</td>
<td>0.21</td>
</tr>
<tr>
<td><strong>Ammonium ionic liquids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C₆H₁₃]₃NH.Tf₂N</td>
<td>72</td>
<td>0.11</td>
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<tr>
<td>[C₈H₁₇]₃NH.Tf₂N</td>
<td>89</td>
<td>0.06</td>
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<tr>
<td>[C₈H₁₇]₃NH₃.Tf₂N</td>
<td>125</td>
<td>0.07</td>
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<tr>
<td>[C₂H₅]₃NH.BETI</td>
<td>67</td>
<td>0.20</td>
</tr>
<tr>
<td>[C₈H₁₇]₃NH₃.BETI</td>
<td>265</td>
<td>0.08</td>
</tr>
</tbody>
</table>
Friction Reduction by ILs in All Lubrication Regimes

- \(\text{[C}_8\text{H}_{17}\text{]}_3\text{NH.Tf}_2\text{N} \) produced 20-35% lower friction than 15W40 Engine Oil in all lubrication regimes.

- Suppress the transition from EHL to boundary lubrication (Striebeck curve shifted to the left);

AISI 52100 steel against Al 6061-T6.

Unidirectional sliding under 38.3 N load, 0.02-1.0 m/s.
ILs Produce Low Friction

**Ionic Liquid** ([C\textsubscript{8}H\textsubscript{17}]\textsubscript{3}NH.Tf\textsubscript{2}N) vs. **15W40 Engine Oil**

- 20-35% friction reduction for Al alloys
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

![Graph showing wear volume comparison between 15W40 Oil and Ionic Liquid ([C$_8$H$_{17}$]$_3$NH.Tf$_2$N)]
Aluminum Had Less Material Transfer (Adhesive Wear) to the Steel Counterface in Ionic Liquid Lubrication

Images of contact areas of the steel counterface

Mineral Oil

Mineral Oil + 10% $[\text{C}_8\text{H}_{17}]_3\text{NH.Tf}_2\text{N}$

$[\text{C}_8\text{H}_{17}]_3\text{NH.Tf}_2\text{N}$
Piston Ring-on-Flat Reciprocating Sliding Test (ASTM G 181-04)

- Materials
  - Slider: Cr-plated piston ring
  - Flat: Grey cast iron with simulated honing marks

- Lubricants
  - 15W40 diesel engine oil
  - IL1 ([C₈H₁₇]₃NH.Tf₂N)

- Temperature: 100 °C
- Normal loads: 240 N
- Sliding speed: 0.2 m/s (ave.)
  - 10 Hz, 10 mm stroke
- Test duration: 6 hours
Latest Results of Piston Ring-on-Flat Reciprocating Sliding Test (ASTM G 181-04)

Compared with 15W40 oil, \([\text{C}_8\text{H}_{17}]_3\text{NH}.\text{Tf}_2\text{N} \text{ (IL1)}\)

- Reduced the initial COF by 25% and the final COF by 55% at the end of the six-hour wear test.
- Reduced the total wear rate (flat+ring) by 15%.

![Bar chart of friction coefficient and wear rate comparison]

- **Friction Coefficient**
  - Ini-COF: 0.12 (15W40) vs 0.09 (IL1)
  - Final-COF: 0.11 (15W40) vs 0.05 (IL1)

- **Wear Rate (mm³/N-m)**
  - GCI Liner: 3.7E-08 (15W40) vs 2.9E-08 (IL1)
  - Cr-Ring: 1.1E-08 (15W40) vs 1.0E-08 (IL1)
Summary

- A group of ammonium ionic liquids have been developed with promising lubricating performance and benchmarked with 15W40 engine oil.
  - 20-35% friction reduction and 45-55% wear reduction in lubricating steel-aluminum contacts.
  - 25-55% friction reduction and 15% wear reduction in lubricating Cr-plated piston rings against cast iron.
  - A surface boundary film was detected and is believed to be responsible for the friction/wear reductions.

- A U.S. Patent was filed on September 19, 2006 (Application# 11533098)

Hint: No single ionic liquid can work for all materials, but with the uncountable species available, one would expect to design appropriate ionic lubricants for specific applications.
Ionic Liquids Offer Significant Potential

- Reduce parasitic energy loss by friction reduction and allowing higher engine combustion temperatures.
- Extend service life and maintenance cycle by wear reduction.
- Expand the usage of lubricants to higher temperatures with higher thermal stability.
- Reduce air emissions due to ultra-low vapor pressure.
- Require fewer expensive lubricant additives with better intrinsic properties, e.g. boundary film formability and solvent nature.
- Serve as ashless additives for oil- and water-based lubricants.
- An effective replacement for catalyst-poisoning ZDDP.
- Safer transportation and storage because of non-flammability.
Corrosion Behavior

Electrochemical measurement

- Potentiodynamic polarization curves – both steel and aluminum showed active-passive corrosion behavior in [CH3(CH2)7]3NH.Tf2N.
Friction Results for 3 Al Alloys

- \([\text{C}_8\text{H}_{17}]_3\text{NH.Tf}_2\text{N}\) produced lower COF by 20-35% than the 15W40 engine oil for different Al alloys.
Wear Results for 3 Al Alloys

- [C\textsubscript{8}H\textsubscript{17}\textsubscript{3}]\textsubscript{NH}.Tf\textsubscript{2}N produced lower wear by 45-55% than that the 15W40 engine oil for different Al alloys.
- C\textsubscript{10}mim.Tf\textsubscript{2}N produced unexpectedly high wear for Al 6061.

Why? React with Mg?
Surface Chemistry - \([\text{C}_8\text{H}_{17}]_3\text{NH.Tf}_2\text{N}\)

- Boundary films are detected on aluminum surfaces.
  - Inherent polarity and tribo-chemical reactions.

XPS analysis of Al 6061 worn surface lubricated by \([\text{C}_8\text{H}_{17}]_3\text{NH.Tf}_2\text{N}\)
Surface Chemistry - \([C_{8}H_{17}]_{3}NH.Tf_{2}N\)

- Possible composition of the surface boundary film: AlF$_{3}$, Al$_{2}$O$_{3}$, Al$_{2}$S$_{3}$, Al metallic phase, and organic compounds.