Design, Synthesis, and Characterization of New Ionic Liquids

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20031119 031
Design, Synthesis and Characterization of New Ionic Liquids

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Ionic Liquids

Those involved in this work

Ms. Kerri Tollison
Synthesis and Characterization

Greg Kaplan
Synthesis and Characterization

Jerry Boatz
Theoretical Calculations

Jeff Mills
Theoretical Calculations

Leslie Hall
Synthesis & x-ray work

Ashwani Vij
X-ray crystallography

Tommy Hawkins
6.2 Propellant Development

Greg Drake
6.1 Research Synthesis
Ionic Liquids

Table salt Na\(^+\)Cl\(^-\) m.p. = 804 °C Very high
Cryolite Na\(_3\)AlF\(_6\) m.p. nearly 1000 °C (Hall Process for Al production)
Eutectic of Li\(^+\)Cl\(^-\) and K\(^+\)Cl\(^-\) m.p. 355 °C

Molten salts are very hot!
Not commercially viable
Corrosion and energy issues
Giant lattice of miniature magnets stuck together
Ionic Liquids

What are Ionic Liquids?
A class of salts consisting of cation/anion pair that has a very low melting point.

Definition of an ionic liquid is open to some debate amongst researchers in the area, but most in the area use one of two.


(2) An ionic compound that has a melting point at or below ambient temperatures. These are often called RTILs (Room Temperature Ionic Liquids) T. Welton, R. Rogers.

But many of the salts fit both definitions and (2) is really a more specific class of (1).
1. Asymmetry of cation as well as anion
2. Packing efficiency
3. Charge delocalization in cationic/anionic species
4. "Sheer size" differentials
Ionic Liquids

**Hydroxylammonium nitrate (HAN)**
\[ \text{NH}_3\text{OH}^+][\text{NO}_3^-] \text{ m.p. } 39-40 \degree \text{C} 

**Ethylammonium nitrate**
\[ \text{CH}_3\text{CH}_2\text{NH}_3^+][\text{NO}_3^-] \text{ m.p. } 12 \degree \text{C} 

Serious issues...
- can be treacherous
- acidic
- very hygroscopic
Ionic Liquids

1,2-bis(oxyamine)ethane

1,2-bis(oxyamine)ethane mono salts
$X^- = NO_3^-, ClO_4^-, C(NO_2)_3^-, N(NO_2)_2^-$

1,3-bis(oxyamine)propane very stable, watery liquid
b.p. = 65-70 °C @ 0.3 torr; f.p. = glasses at -40 °C

1,3-bis(oxyamine)propane mono salts
$X^- = NO_3^-, ClO_4^-, C(NO_2)_3^-, N(NO_2)_2^-$

Bisoxynamines are stable as neutrals but protonated versions are not (extremely friction and impact sensitive!) Direct contrast with simple mono oxyamines.
Ionic Liquids

Single crystal x-ray structure of ethylene bisoxyamine monoperchlorate. Material has unusual amount of hydrogen bonding present (ρ = 1.83 g/cm³!!!), but that doesn’t explain its extreme sensitivity to impact and friction.
Ionic Liquids

Extended lattice of ethylene bisoxyamine monoperchlorate.
Ionic Liquids

Since its western discovery in the late 1980's, by Jeff Bottaro, the dinitramide anion, \( N(\text{NO}_2)_2^- \) has received tremendous attention as a potential new oxidizing anion for energetic materials. A closely related anion, the nitrocyanamide anion, \( N(\text{NO}_2)(\text{CN})^- \), was discovered in the early 1950's by McKay, and shortly thereafter, Harris investigated many heavy metal salts, as possible replacement initiators. However, it has been virtually ignored since that time.

\[
\begin{align*}
\text{N(\text{NO}_2)_2^- (dinitramide)} & & \text{N(\text{NO}_2)(\text{CN})^- (nitrocyanamide)}
\end{align*}
\]

Ionic Liquids

Calculations using B3LYP/cc-pvdz and CCSD(T)/cc-pvdz levels of theory reveal a planar anion ($C_s$ symmetry) with expected bond distances and angles.

\[
\begin{align*}
\alpha(O1-N1-O2) &= 122.6(122.7) \\
\alpha(O1-N1-N2) &= 115.9(115.7) \\
\alpha(O2-N1-N2) &= 121.5(121.6) \\
\alpha(N1-N2-C1) &= 113.7(111.3) \\
\alpha(N2-C1-N3) &= 171.0(171.2)
\end{align*}
\]
Ionic Liquids

Monomethylhydrazinium nitrocyanamide

Diaminoguanidinium nitrocyanamide

Methoxyammonium nitrocyanamide
Ionic Liquids

- The syntheses of several nitrooxyanamide salts were accomplished through the metathesis reactions of the appropriate halide salt with silver nitrooxyanamide as Harris reported in 1958.

\[[\text{Ag}^+][\text{N(NO}_2\text{)(CN)}^–][\text{Cation}^+]\text{[X]} \rightarrow [\text{Ag}^+][\text{X}^-] + [\text{Cation}^+]\text{[N(NO}_2\text{)(CN)}^–]\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta H_f) (est) Kcal/mole</th>
<th>M.P. (^\circ)C</th>
<th>Density g/cm(^3) (meas.)</th>
<th>Impact kg-cm (5 neg.)</th>
<th>Friction (Newton) (5 neg.)</th>
<th>TGA % Loss/Day at 75(^\circ) C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrazinium nitrooxyanamide</td>
<td>+14</td>
<td>109</td>
<td>1.53</td>
<td>10</td>
<td>76</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>Guanidinium nitrooxyanamide</td>
<td>-13</td>
<td>95</td>
<td>1.39</td>
<td>&gt;200</td>
<td>141</td>
<td>0.68</td>
</tr>
<tr>
<td>Methoxyammonium nitrooxyanamide</td>
<td>-5</td>
<td>99</td>
<td>1.51</td>
<td>18</td>
<td>149</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>Monomethylhydrazinium nitrooxyanamide</td>
<td>+4</td>
<td>57</td>
<td>1.44</td>
<td>&gt;200</td>
<td>&gt;371</td>
<td>1.9</td>
</tr>
<tr>
<td>Aminoguanidinium nitrooxyanamide</td>
<td>0</td>
<td>94</td>
<td>1.50</td>
<td>&gt;200</td>
<td>&gt;371</td>
<td>0.9</td>
</tr>
<tr>
<td>Diaminoguanidinium nitrooxyanamide</td>
<td>+10</td>
<td>108</td>
<td>1.52</td>
<td>&gt;200</td>
<td>&gt;371</td>
<td>1.6</td>
</tr>
</tbody>
</table>

\([\text{NH}_3\text{OH}^+]\) and \([\text{HO-CH}_2\text{CH}_2\text{-NH}_3^+]\) salts were made, but were not stable at ambient temperatures!
Ionic Liquids

1-H-1,2,4-triazole

4-amino-1,2,4-triazole

1-H-1,2,3-triazole

\[ +H-X \]

\[ X^- = \text{NO}_3^-, \text{ClO}_4^-, \text{N(NO}_2)_2^- \]

X-ray single crystal diffraction study of 1,2,4-triazolium perchlorate $\rho = 1.96 \text{ g/cm}^3$
It is felt that this is probably the top of the hill density wise for simple heterocycle salts.

Ionic Liquids

Some major shapes for organic based cations

1-methyl-3-alkyl-imidazolium

1-alkylpyridinium

Tetraalkylammonium

Tetraalkylphosphonium
Ionic Liquids

Significant efforts spent on 1-ethyl-3-methyl-imidazolium based systems and aluminum trichloride systems. More complex than originally thought as \( \text{AlCl}_3 \) and \( \text{Cl}^- \) have an equilibrium based on their respective concentrations.

"Basic"

\[
\begin{align*}
&\text{"Basic"} \\
\text{AlCl}_3 \\
\text{"Neutral"} \\
\text{AlCl}_3 \\
\text{"Strongly acidic"}
\end{align*}
\]

"Neutral"

\[
\begin{align*}
&\text{"Neutral"} \\
\text{AlCl}_3 \\
\text{\"Acidic\"}
\end{align*}
\]

\[
\begin{align*}
&\text{Al}_3\text{Cl}_{10}^- \\
&\text{\"Acidic\"}
\end{align*}
\]

Ionic Liquids

Melting point of MeEtImCl and AlCl₃ mixtures

Ionic Liquids

Cl⁻, mp 87 °C

AlCl₄⁻, mp 7 °C

BF₄⁻, mp 6 °C

CF₃SO₃⁻, mp -9 °C

NO₂⁻, mp 55 °C

NO₃⁻, mp 38 °C

PF₆⁻, mp 58 °C

CF₃CO₂⁻, mp -14 °C

C₄F₉SO₃⁻, mp 28 °C

1-ethyl-3-methylimidazolium cation

(CF₃SO₂)₂N⁻, mp -4 °C


Ionic Liquids

Substituted ammonium salts $R_4N^+X^-$. Variations in melting point based on cation structure.

Tris-(n-propyl)-undecylammonium cation
- $Br^- m.p. = 67 ^\circ C$
- $ClO_4^- m.p. = 65 ^\circ C$

Tetra-n-pentylammonium cation
- $Br^- m.p. = 101 ^\circ C$
- $ClO_4^- m.p. = 118 ^\circ C$

N-decyl-n-octyl-dimethylammonium cation
- $Br^- m.p. = RTIL$, $ClO_4^- m.p. = RTIL$

N-tetradecyl-triethylammonium cation
- $Br^- m.p. = 170 ^\circ C$, $ClO_4^- m.p. = 152 ^\circ C$

Ionic Liquids

Substituted ammonium salts $[R_4N^+][X^-]$. Recently work has been done by using more desirable anions.

<table>
<thead>
<tr>
<th>Substituted Ammonium Salt</th>
<th>M.P. ($^\circ$ C)</th>
<th>Density (g/cm$^3$)</th>
<th>Viscosity (cp)</th>
<th>$\Lambda$ ($\Omega^{-1}$ cm$^2$/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[(n-C_6H_{13})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$</td>
<td>-74 (g)</td>
<td>1.33</td>
<td>153</td>
<td>1.4</td>
</tr>
<tr>
<td>$[(n-C_7H_{15})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$</td>
<td>-73 (g)</td>
<td>1.28</td>
<td>153</td>
<td>1.4</td>
</tr>
<tr>
<td>$[(n-C_8H_{17})(CH_3)_3N^+][N(SO_2CF_3)_2^-]$</td>
<td>-73 (g)</td>
<td>1.27</td>
<td>181</td>
<td>1.3</td>
</tr>
<tr>
<td>$[(n-C_6H_{13})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$</td>
<td>20</td>
<td>1.27</td>
<td>167</td>
<td>2.5</td>
</tr>
<tr>
<td>$[(n-C_7H_{15})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$</td>
<td>-79</td>
<td>1.26</td>
<td>75</td>
<td>1.9</td>
</tr>
<tr>
<td>$[(n-C_8H_{17})(CH_3CH_2)_3N^+][N(SO_2CF_3)_2^-]$</td>
<td>-74</td>
<td>1.25</td>
<td>202</td>
<td>1.3</td>
</tr>
<tr>
<td>$[(n-C_6H_{13})(n-C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$</td>
<td>26</td>
<td>1.15</td>
<td>595</td>
<td>0.8</td>
</tr>
<tr>
<td>$[(n-C_7H_{15})(n-C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$</td>
<td>-67</td>
<td>1.17</td>
<td>606</td>
<td>0.8</td>
</tr>
<tr>
<td>$[(n-C_8H_{17})(n-C_4H_9)_3N^+][N(SO_2CF_3)_2^-]$</td>
<td>-63</td>
<td>1.12</td>
<td>574</td>
<td>0.7</td>
</tr>
<tr>
<td>$[(n-C_7H_{15})(Et)_3(ipr)_2N^+][N(SO_2CF_3)_2^-]$</td>
<td>-82</td>
<td>1.27</td>
<td>362</td>
<td>1.2</td>
</tr>
<tr>
<td>$[(n-C_8H_{17})(n-C_4H_9)_3N^+][OSO_2CF_3^-]$</td>
<td>-57</td>
<td>1.02</td>
<td>2030</td>
<td>0.07</td>
</tr>
</tbody>
</table>

- Most have very low glass points
- Densities decrease as expected
- Viscosity increases dramatically with increasing alkyl length
- Conductivity decreases with cation size (mobility issue)

Ionic Liquids

Most ionic liquids are based upon imidazolium rings and "heavy" or "dead" anions. We felt that we could use the shape of the cation and the poor fit idea to make much more energetic salts in a simple manner.

1-n-butyl-3-methyl imidazolium cation

1-ethyl-4-amino-1,2,4-triazolium cation

These new ionic liquids have similar shapes and physical properties, BUT higher $\Delta H_p$, higher densities, and better oxygen balances.
Synthesis is from commercial materials
High yield simple isolation has been known in literature for quite some time.

1-n-propyl-4-amino-1,2,4-triazolium bromide (yield >95% very pure)

Ionic Liquids

1-n-butyl-4-amino-1,2,4-triazolium cation

1-(2-ethanol)-4-amino-1,2,4-triazolium cation

1-isopropyl-4-amino-1,2,4-triazolium cation

1-methylcyclopropyl-4-amino-1,2,4-triazolium cation

1-(2-aminoethyl)-4-amino-1,2,4-triazolium dication
Ionic Liquids

1-ethyl-4-amino-1,2,4-triazolium cation

1-n-propyl-4-amino-1,2,4-triazolium cation

1-(2-propenyl)-4-amino-1,2,4-triazolium cation

1-methyl-4-amino-1,2,4-triazolium cation
Ionic Liquids

Physical properties of 1-n-alkyl substituted-4-amino-1,2,4-triazolium bromides.

- increasing melting points with increasing molecular weights,
- decomposition onsets that are relatively low
- densities decrease with increasing alkyl chain length.

<table>
<thead>
<tr>
<th>Substituted 4AT salts</th>
<th>m.p. (°C)</th>
<th>dec. onset (°C)</th>
<th>density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-ethyl</td>
<td>63°</td>
<td>110</td>
<td>1.69</td>
</tr>
<tr>
<td>1-n-propyl</td>
<td>60°</td>
<td>120</td>
<td>1.56</td>
</tr>
<tr>
<td>1-isopropyl</td>
<td>90°</td>
<td>110</td>
<td>1.60</td>
</tr>
<tr>
<td>1-butyl</td>
<td>48°</td>
<td>130</td>
<td>1.46</td>
</tr>
<tr>
<td>1-n-pentyl</td>
<td>54°</td>
<td>130</td>
<td>1.37</td>
</tr>
<tr>
<td>1-n-hexyl</td>
<td>76°</td>
<td>120</td>
<td>1.34</td>
</tr>
<tr>
<td>1-n-heptyl</td>
<td>94°</td>
<td>120</td>
<td>1.30</td>
</tr>
<tr>
<td>1-n-octyl</td>
<td>80°</td>
<td>135</td>
<td>1.27</td>
</tr>
<tr>
<td>1-n-nonyl</td>
<td>81°</td>
<td>140</td>
<td>1.26</td>
</tr>
<tr>
<td>1-n-decyl</td>
<td>90°</td>
<td>135</td>
<td>1.23</td>
</tr>
</tbody>
</table>
Ionic Liquids

proton of 1-n-butyl-4-amino-1,2,4-triazolium bromide solid in d6-DMSO

$^1$H(left) and $^{13}$C nmr spectra of 1-butyl-4-amino-1,2,4-triazolium bromide.
Ionic Liquids

Single x-ray diffraction study of 1-ethyl-4-amino-1,2,4-triazolium bromide.
Ionic Liquids

Single crystal x-ray diffraction study of 1-n-propyl-4-amino-1,2,4-triazolium bromide showing significant hydrogen bond contacts.
Ionic Liquids

Hydrogen bond contacts in solid 1-n-propyl-4-amino-1,2,4-triazolium bromide
Ionic Liquids

Single crystal x-ray diffraction structure of 1-isopropyl-4-amino-1,2,4-triazolium bromide.
Ionic Liquids

Single crystal x-ray diffraction study of 1-hexyl-4-amino-1,2,4-triazolium bromide.
Single crystal x-ray diffraction study of 1-heptyl-4-amino-1,2,4-triazolium bromide.
Ionic Liquids

1-dodecyl-3-methylimidazolium hexafluorophosphate*  1-hexyl-4-amino-1,2,4-triazolium bromide#

Ionic Liquids

But halides are only the start...
Nitrates were best made through silver nitrate metathesis in methanol.

\[ \text{[Molecule]} + \text{AgNO}_3 \rightarrow \text{[Molecule]} - \text{AgBr} \]

This route led to the best materials as the silver bromide was easily removed.
### Ionic Liquids

1-substituted-4-amino-1,2,4-triazolium nitrate salts are more stable.

<table>
<thead>
<tr>
<th>Salt</th>
<th>melting point ($^\circ$C)</th>
<th>decomp onset ($^\circ$C)</th>
<th>$\rho$(g/cm$^3$, est.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-methyl</td>
<td>54</td>
<td>185</td>
<td>1.57</td>
</tr>
<tr>
<td>1-ethyl</td>
<td>5</td>
<td>185</td>
<td>1.39 (1.38)</td>
</tr>
<tr>
<td>1-n-propyl</td>
<td>34</td>
<td>190</td>
<td>1.35</td>
</tr>
<tr>
<td>1-isopropyl</td>
<td>53</td>
<td>175</td>
<td>1.37 (1.43)</td>
</tr>
<tr>
<td>1-n-butyl</td>
<td>-25 (g)</td>
<td>190</td>
<td>1.31</td>
</tr>
<tr>
<td>1-(2-ethanol)</td>
<td>-50 (g)</td>
<td>180</td>
<td>1.48</td>
</tr>
<tr>
<td>1-methylcyclopropyl</td>
<td>56</td>
<td>190</td>
<td>1.36 (1.44)</td>
</tr>
<tr>
<td>1-(2-propenyl)</td>
<td>10</td>
<td>165</td>
<td>1.23</td>
</tr>
<tr>
<td>1-n-pentyl</td>
<td>26</td>
<td>170</td>
<td>1.29</td>
</tr>
<tr>
<td>1-n-hexyl</td>
<td>-2</td>
<td>160</td>
<td>1.26</td>
</tr>
<tr>
<td>1-n-heptyl</td>
<td>31</td>
<td>160</td>
<td>1.24</td>
</tr>
<tr>
<td>1-n-octyl</td>
<td>29</td>
<td>170</td>
<td>1.22</td>
</tr>
<tr>
<td>1-n-nonyl</td>
<td>53</td>
<td>175</td>
<td>1.20</td>
</tr>
<tr>
<td>1-n-decyl</td>
<td>49</td>
<td>185</td>
<td>1.18</td>
</tr>
</tbody>
</table>
Ionic Liquids

Sample: 1-PROPYL-4-AT NITRATE
Size: 1.9000 mg
Method: greg
Comment: 10C/min/10ml/minhermeticalpans

DSC of 1-n-propyl-4-amino-1,2,4-triazolium nitrate
Ionic Liquids

Single crystal x-ray diffraction study of 1-methycyclopropyl-4-amino-1,2,4-triazolium nitrate.
Ionic Liquids

Single crystal x-ray diffraction structure of 1-isopropyl-4-amino-1,2,4-triazolium nitrate
Ionic Liquids

The new energetic cations are weakly acidic in nature, aqueous solutions have a pH of around 4 which suggests the equilibrium involving a zwitterionic 1-alkyl-4-amido-1,2,4-triazolium species. This equilibrium could be one possible way for the ionic liquids to “come apart”.
Ionic Liquids

Summary and Conclusions

Oxyamines and nitrocyanamide ions make for low melting and energetic salts, however both are plagued by poor thermal behavior and impact/friction sensitivity.

A large new class of low melting salts which should be considered as new members of the well known class of materials referred to as ionic liquids has been synthesized and well characterized.

Using asymmetric cation shapes and poor cation-anion fit, an analogue system to the well known 1,3-dialkylsubstituted imidazolium cation family, based upon 1-substituted-4-amino-1,2,4-triazolium cations paired with the bromide and nitrate ions has been explored.

Facile synthesis routes from commercially available materials coupled with high yield and purity reactions make these new materials very exciting.

Several single crystal x-ray diffraction studies of several structures have been carried out proving the expected structure as well as revealing extensive hydrogen bonding in the solid state.

Physical properties of 1-substituted-4-amino-1,2,4-triazolium salts included much higher viscosities, higher densities, and much more polar behavior than that of imidazolium ionic liquids.
ACKNOWLEDGEMENTS

- MIKE BERMAN (AFOSR)
- WAYNE KALLIOMAA; RONALD CHANNELL(AFRL/PRSP)
- JOHN WILKES (USAFA)
- JEFF SHEEHY(NASA/MARSHALL AND UA/HUNTSVILLE)
- CLAUDA MERRILL
- TOMMY HIGHSMITH
- JEFF BOTTARO, MARK PETRIE (SRI, INT.)
- MIKE HUGGINS (AFRL SUPPORT)