Theoretical Studies of ionic liquids + nanoclusters as hybrid fuels

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Viewgraph/Briefing Charts

N/A
Outline

1. Introduction

2. Boron nanoparticles/ionic liquid systems
   a) theoretical model
   b) conventional solvents vs. ionic liquids
   c) improved dispersion via B-H functionalized surface

3. Aluminum nanoparticles
   a) production via ball milling
   b) surface chemistry of milling agents

4. Summary and Conclusions

5. Acknowledgements
Aerospace Systems Directorate

RQ-West (EAFB, CA)
- Rocket Engines & Motors
- Satellite Propulsion
- Combustion Devices
- Fuels and Propellants
- System Analysis
- R&D Rocket Testing

RQ-East (WPAFB, OH)
- Air Vehicle Structures
- Controls
- Turbine Engines
- Ramjet Engines
- Hypersonic Engines
- Aircraft Power
- Thermal Management
- Fuels and Propellants
- System Analysis

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What We Are Doing

Identify and develop advanced chemical propellants for rocket propulsion applications

- Isp (specific impulse) is a major metric of propellant performance
- Density can also be a significant contributor
Why We Are Doing It

% Payload Increase

10% density increase
10% Isp increase
10% increase in both

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AF-M315 Monopropellant Class

AF-M315 monopropellants produced from ionic liquids

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Hydrazine</th>
<th>“IL-1”</th>
<th>“IL-2”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point (°C)</td>
<td>&lt; 1.0</td>
<td>-50 (glass)</td>
<td>≈15</td>
</tr>
<tr>
<td>Vapor Pressure (torr)</td>
<td>14.3</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>1.00</td>
<td>1.42</td>
<td>1.68</td>
</tr>
</tbody>
</table>

**Toxicology**

<table>
<thead>
<tr>
<th>Ames (mutagenic)</th>
<th>5/5 positive</th>
<th>2/5 positive</th>
<th>0/5 positive</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD50, rat (mg/kg)</td>
<td>60</td>
<td>367</td>
<td>325</td>
</tr>
<tr>
<td>Skin Irritation</td>
<td>Corrosive</td>
<td>Slight</td>
<td>Moderate</td>
</tr>
</tbody>
</table>

- Time consuming
- Expensive

- Low hazard
- Low cost

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IL/metal hybrid fuels

• Bulk aluminum powder is a commonly used ingredient in solid propellants.
  • large heat of combustion, enhanced burn rate, ...

• Can Group 3A metals (B, Al) be utilized in liquid fuels?
  • Particles must be small enough (nanoscale) to form stable colloidal suspensions
  • Resistant to formation of inert oxide surface layer to preserve energy density and ignition efficiency
IL/metal hybrid fuels

Boron nanoparticles (BNPs) phase separate from some solvents

B1s Region

B\(^{\text{0}}\) = 188 eV

B\(^{\text{3+}}\) = 192 eV

Indicates surface oxidation of BNP

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BNPs form stable suspensions in 1-methyl-4-amino-1,2,4-triazolium dicyanamide (MAT-dca)

B1s Region XPS of Boron milled with IL in EtOH

B0 = 188 eV

B-N = 191 eV

Indicates chemisorption of IL to BNP?

Boron powder milled in EtOH w/ MAT DCA

IL/metal hybrid fuels
IL/metal hybrid fuels

• Why do BNPs form stable suspensions in some solvents/ILs but not others?

• What types of chemical interactions occur between solvent/IL and BNPs?

• Can we predict which solvents/ILs will inhibit oxide layer formation in BNPs?
**IL/metal hybrid fuels**

**Computational model**

- $B_{80}$ cluster used to represent BNP
- Single solvent molecule or IL ion pair
- Calculate structure and interaction energies
  - Correlation between interaction energy and formation of stable colloid?
IL/metal hybrid fuels

Computational model – why $B_{80}$??

- Calculations predict most stable forms of $B_n$ for $n < 20$ are quasi-planar
- Most stable form of $B_{20}$ is a ring

Table I. The MP2/6-311G* optimized $B_{20}$ geometries and computed relative energies (in eV) of the eight $B_{20}$ isomers at different theoretical levels.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>$C_5v$</th>
<th>$C_{2v}$</th>
<th>$C_2$</th>
<th>$C_1$</th>
<th>$C_1$</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$S_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD(T)</td>
<td>0</td>
<td>0.72</td>
<td>1.46</td>
<td>1.87</td>
<td>1.97</td>
<td>2.31</td>
<td>2.80</td>
<td>3.45</td>
</tr>
<tr>
<td>MP2</td>
<td>0</td>
<td>1.13</td>
<td>1.07</td>
<td>0.94</td>
<td>1.89</td>
<td>1.47</td>
<td>1.16</td>
<td>3.32</td>
</tr>
<tr>
<td>PBE</td>
<td>0</td>
<td>0.67</td>
<td>1.51</td>
<td>1.69</td>
<td>2.26</td>
<td>2.52</td>
<td>2.60</td>
<td>3.80</td>
</tr>
<tr>
<td>TPSS</td>
<td>0</td>
<td>0.68</td>
<td>1.66</td>
<td>1.96</td>
<td>2.17</td>
<td>2.46</td>
<td>3.00</td>
<td>3.35</td>
</tr>
<tr>
<td>TPSSh</td>
<td>0</td>
<td>0.79</td>
<td>1.65</td>
<td>1.93</td>
<td>2.12</td>
<td>2.44</td>
<td>3.09</td>
<td>3.23</td>
</tr>
<tr>
<td>PBE0</td>
<td>0</td>
<td>0.96</td>
<td>1.50</td>
<td>1.68</td>
<td>2.13</td>
<td>2.47</td>
<td>2.90</td>
<td>3.53</td>
</tr>
<tr>
<td>mPW1PW91</td>
<td>0</td>
<td>0.99</td>
<td>1.75</td>
<td>2.15</td>
<td>2.37</td>
<td>2.74</td>
<td>3.74</td>
<td>3.75</td>
</tr>
<tr>
<td>M06-2X</td>
<td>0</td>
<td>1.11</td>
<td>1.03</td>
<td>0.93</td>
<td>1.61</td>
<td>1.98</td>
<td>1.13</td>
<td>2.71</td>
</tr>
<tr>
<td>B3LYP</td>
<td>0</td>
<td>0.99</td>
<td>3.25</td>
<td>4.24</td>
<td>3.82</td>
<td>4.39</td>
<td>4.80</td>
<td>5.34</td>
</tr>
<tr>
<td>BLYP</td>
<td>0</td>
<td>0.75</td>
<td>3.38</td>
<td>4.39</td>
<td>4.04</td>
<td>4.58</td>
<td>4.78</td>
<td>5.63</td>
</tr>
</tbody>
</table>

IL/metal hybrid fuels

Computational model – why B$_{80}$??

- IL interactions with small 3D clusters (e.g., B$_{12}$) inconsistent with larger clusters

\[ \text{B}_{12} + [\text{MAT}][\text{DCA}] \]
\[ \text{E}_{\text{int}} = 104.5 \text{ kcal/mol} \]

\[ \text{B}_{80} + [\text{MAT}][\text{DCA}] \]
\[ \text{E}_{\text{int}} = 51.5 \text{ kcal/mol} \]

Distinct differences in
- interaction energies (2x)
- binding of cation
- binding of anion
How do nonionic solvents interact with BNPs?

B<sub>80</sub> + ethanol
E<sub>int</sub> = 14.9 kcal/mol

B<sub>80</sub> + ethanolamine
E<sub>int</sub> = 4.2 kcal/mol
**IL/metal hybrid fuels**

How do ionic solvents interact with BNPs?

B$_{80}$ + MAT-dca

$E_{\text{int}} = 39.2$ kcal/mol  
$E_{\text{int}} = 30.1$ kcal/mol  
$E_{\text{int}} = 50.3$ kcal/mol
**EIL interactions with $B_{80}$**

**Role of IL cation vs anion**

<table>
<thead>
<tr>
<th>Combination</th>
<th>$E_{int}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation + anion</td>
<td>$-45.5$</td>
</tr>
<tr>
<td>Cation only</td>
<td>$-27.5$</td>
</tr>
<tr>
<td>Anion only</td>
<td>$-58.7$</td>
</tr>
</tbody>
</table>

Electron-rich anion interacts more strongly with BNPs (e- deficient)
EIL interactions with $B_{80}$

IL cation: BNP interactions – a deeper look

- $E_{\text{int}} = -27.5$ kcal/mol
  - Covalent bond to $B_{80}$ surface not present

- $E_{\text{int}} = -61.8$ kcal/mol
  - H-atom transfer from cation to $B_{80}$, C-B bond formed

- $E_{\text{int}} = -35.2$ kcal/mol
  - C-B bond to $B_{80}$ surface is formed

Cation can form covalent bond to BNP, but likely has to overcome energy barrier (calculation of barrier in progress)
**IL/metal hybrid fuels**

- Is proton transfer from MAT$^+$ to the BNP possible? (YES)

- If so, what are the reaction barriers? (TBD)
IL/metal hybrid fuels

- Calculations predict strong interactions between DCA\(^-\) and BNP.
  - MAT\(^+\) essentially a “spectator”
  - Contrary to some experimental results (zeta potentials, XPS spectra)

![Zeta Potential Measurements on B milled with Various ILs](image)

![Graph showing zeta potential measurements on B milled with various ILs](image)
IL/BNP hybrid fuels: Summary

- ILs interact more strongly with BNPs than nonionic solvents such as ethanol, ethanolamine
  - Consistent with observed passivation of BNP milled with MAT-DCA and formation of stable colloidal suspensions of BNPs in ILs.

- Proton transfer from MAT$^+$ to BNP is thermodynamically favorable
  - Comparable to interaction energies of DCA$^-$ with BNP.
  - Reaction barriers still to be determined.

- Multiple types of interactions between ILs and BNPs are possible
  - Covalent bond formation between DCA$^-$ and BNP occurs with little or no barrier
  - Formation of covalent bond between MAT$^+$ and BNP is favorable, but likely encounters a barrier (TBD).
Improved dispersion of NPs in ILs

- Ball milling of BNPs in presence of H₂ leads to formation of B-H surface passivated layer
  - Calculations predict barrier of 10 kcal/mol, and exothermicity of 35 kcal/mol for chemisorbed H₂ to dissociate to form two H-Bsurf.
- Observed H₂ uptake in boron ball milling of 5 wt % (36 mol %) consistent with formation of saturated H-terminated BNP surface
  - Calculations show that formation of H₅₈B₈₀ is exothermic by 710 kcal/mol.
- B-H functionalized BNPs react with alkenes and N-rich ILs
  - facilitates dispersion of capped BNPs in polar and non-polar liquids

Perez et al., ACS Appl. Mater. Interfaces, 2015, 7, 9991-10003.
Formation of H-terminated BNPs

1,1 addition of H₂ to B₈₀, followed by H migration

Energy (kcal/mol)

-50 -40 -30 -20 -10 0 10 20

Reaction coordinate (bohr-amu¹/²)

-10 -8 -6 -4 -2 0 2 4 6

-40.2 kcal/mol

4.6 kcal/mol

13.2 kcal/mol

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Aluminum nanoparticles (NPs) are of interest as energetic ingredients in explosives and propellant formulations, due to high energy density, enhanced burn rates due to high surface/volume ratio, etc.

Efficient, gram-level production of Al nanoparticles via ball milling is obtained using NH$_3$, CH$_3$NH$_2$, CH$_3$CN, B$_2$H$_6$, etc., as milling agents.

Milling agents decompose on Al NP surface to produce gaseous products and surface-bound species.

Milling/capping agents can also inhibit formation of inert oxide layer on NP surface.

Surface-coated NPs can be functionalized to enhance/control NP dispersion in hydrocarbons, ILs, etc.
# Ball milling gaseous byproducts

Aluminum nanoparticle production, in presence of milling agent

<table>
<thead>
<tr>
<th>Milling agent → Gaseous byproducts</th>
<th>NH$_3$</th>
<th>CH$_3$NH$_2$</th>
<th>CH$_3$CN</th>
<th>B$_2$H$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>CH$_3$NHCH$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$NH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td></td>
<td></td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CH$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Can theory explain, for example in the case of B$_2$H$_6$ as the milling agent, the predominant formation of H$_2$ as the only observed gaseous byproduct?
$B_2H_6$ physisorbed/chemisorbed on $Al_{80}$

-3.6 (-3.1)

-4.1 (-3.8)

-5.8 (-5.3)

-3.6 (-4.5)

-1.9 (-2.8)

-7.4 (-8.4)

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$B_2H_5 + H$ chemisorbed on $Al_{80}$

+7.1 (+5.5)

+3.4 (+2.1)

-2.9 (-5.9)

-6.7 (-9.5)

-7.7 (-10.4)

Distribution A: Approved for Public Release; Distribution Unlimited. PA# 16409
$B_2H_6:Al_{80} \rightarrow B_2H_5-Al_{80}-H$

$Al_{80} + B_2H_6$

0.0 (0.0)

29.5(26.2)

7.1(5.5)
\[ \text{B}_2\text{H}_6: \text{Al}_{80} \rightarrow \text{B}_2\text{H}_5-\text{Al}_{80}-\text{H} \]

\[ \omega = 690i \text{ cm}^{-1} \]

-3.6 (-4.5)

18.1 (15.5)

+3.4 (+2.1)

Distribution A: Approved for Public Release; Distribution Unlimited. PA# 16409
$BH_3-Al_{80}-BH_3$

-7.5 (-10.8)

-2.1 (-5.2)
$2H:Al_{80} \rightarrow Al_{80} + H_2$
Summary and Conclusions

• Production of Al nanoparticles via ball milling with B$_2$H$_6$
  • B$_2$H$_6$-assisted ball milling of Al powder efficiently produces Al NPs, with H$_2$ as the predominant byproduct.
  • Surface reactions of B$_2$H$_6$ on Al$_{80}$ have been modeled using DFT
    • B$_2$H$_6$ physisorsbs and chemisorbs to Al$_{80}$ with binding energies of 3-8 kcal/mol
    • Fragmentation of bridging B-H bonds is exothermic (6-11 kcal/mol)
    • Fragmentation of terminal B-H bonds is endothermic (2-6 kcal/mol)
    • B-H fragmentation barriers are 20-26 kcal/mol
    • B-B fragmentation to form chemisorbed BH$_3$ is exothermic (5-11 kcal/mol)
    • Formation of H$_2$ via recombination of chemisorbed H atoms is endothermic by 4 kcal/mol and crosses a barrier of 25 kcal/mol
    • B-H fragmentation and subsequent H-H recombination have similar barriers, both of which are energetically accessible under experimental ball milling conditions
Acknowledgements

- **Collaborators**
  - Univ. of Utah: Scott Anderson, ...
  - McGill Univ.: Robin Rogers, ....
  - AFRL: Stefan Schneider, Gammy, Steve Chambreau....

- **GRC organizers**
  - Prof. Mudring

- **Support**
  - AFOSR
  - DoD HPC Modernization Program
Backup Slides
### IL/metal hybrid fuels: summary

<table>
<thead>
<tr>
<th>Solvent/IL + BNP</th>
<th>Forms stable emulsion?</th>
<th>Passivates NP surface?</th>
<th>Calculated interaction energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOH</td>
<td>No</td>
<td>No</td>
<td>14.9</td>
</tr>
<tr>
<td>NH$_2$CH$_2$CH$_2$OH</td>
<td>??</td>
<td>??</td>
<td>4.2</td>
</tr>
<tr>
<td>BMIM-DCA</td>
<td>Yes</td>
<td>No</td>
<td>n/a</td>
</tr>
<tr>
<td>Na-DCA</td>
<td>??</td>
<td>No</td>
<td>47.8</td>
</tr>
<tr>
<td>MAT-DCA/EtOH</td>
<td>Yes</td>
<td>Yes</td>
<td>30.1, 39.2 (MAT DCA only; no EtOH)</td>
</tr>
<tr>
<td>MAT-I/ACN</td>
<td>??</td>
<td>No</td>
<td>54.0 (no ACN)</td>
</tr>
<tr>
<td>MAT-NTf2</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
</tr>
<tr>
<td>MAT-NCA</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
</tr>
<tr>
<td>MAT-acetate</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
</tr>
</tbody>
</table>
IL/metal hybrid fuels

- $B_{80} + \text{Na-dca}$
  - $E_{\text{int}} = 46.6 \text{ kcal/mol}$

- $B_{80} + \text{MAT-I}$
  - $E_{\text{int}} = 23.0 \text{ kcal/mol}$
IL/metal hybrid fuels

Do multiple ion pairs change the nature of the IL/BNP interactions? (YES)
Zeta Potential is a scientific term for electrokinetic potential[1] in colloidal systems. In the colloidal chemistry literature, it is usually denoted using the Greek letter zeta, hence $\zeta$-potential. From a theoretical viewpoint, zeta potential is electric potential in the interfacial double layer (DL) at the location of the slipping plane versus a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle.

A value of 25 mV (positive or negative) can be taken as the arbitrary value that separates low-charged surfaces from highly-charged surfaces.

The significance of zeta potential is that its value can be related to the stability of colloidal dispersions (e.g., a multivitamin syrup). The zeta potential indicates the degree of repulsion between adjacent, similarly charged particles (the vitamins) in a dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation. When the potential is low, attraction exceeds repulsion and the dispersion will break and flocculate. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate as outlined in the table.