**Hypergolic Ionic Liquids to Mill, Suspend and Ignite Boron Nanoparticles (Post Print)**

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**Abstract:**
Boron nanoparticles prepared by milling in the presence of a hypergolic energetic ionic liquid (EIL) are suspendable in the EIL, and the EIL retains hypergolicity, leading to the ignition of the boron. This approach allows for incorporation of a variety of nanoscale additives to improve EIL properties, such as energetic density and heat of combustion, while providing stability and safe handling of the nanomaterials.
Hypergolic ionic liquids to mill, suspend, and ignite boron nanoparticles†‡

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Boron nanoparticles prepared by milling in the presence of a hypergolic energetic ionic liquid (EIL) are suspendable in the EIL and the EIL retains hypergolicity leading to the ignition of the boron. This approach allows for incorporation of a variety of nanoscale additives to improve EIL properties, such as energetic density and heat of combustion, while providing stability and safe handling of the nanomaterials.

Energetic ionic liquids (EILs), salts which melt below 100 °C with potential as energetic materials, have been reported as hypergolic, indicating they spontaneously ignite on contact with a variety of oxidizers, but many challenges still remain to their practical use such as low density and relatively low heats of combustion when compared to the current state of the art hypergols, such as hydrazine.

One approach that can be taken to improve EIL performance is to introduce an additive which does not interfere with the desired IL traits such as low or negligible vapor pressure. Ionic liquids are already known as solvent media to synthesize and stabilize nanoscale additives, such as Pt, Ir, and Pd; however, we are interested in the ability of an IL to passivate the surface of nanomaterials while providing a stable suspension which could lead to higher energy density EILs.

Boron (B) is widely studied for its use as an energetic additive in both micron and nanosizes as a result of its high heat of combustion; however, because it is normally coated by a passivating oxide layer, it requires temperatures over 1500 °C to ignite. Anderson et al. have demonstrated that air-stable and hydrocarbon-dispersible, nanoparticulate B can be prepared by milling micron-sized B with a ligand to create ligand-protected B nanoparticles. For example, oleic acid was utilized as a ligand to create unoxidized B nanoparticles (60 nm in diameter) that are easily dispersible in petroleum based jet fuels. Here, we report the use of the IL 1-methyl-4-amino-1,2,4-triazolium dicyanamide ([MAT][DCA]) as milling agent for B. [MAT][DCA] was chosen based both on the hypergolic nature of this IL and the likely amine-B surface interactions, which we hypothesized would form.

Following the protocols developed by Anderson et al., B with an average diameter of 2 μm was ball-milled using a tungsten carbide milling jar and 1/8” diameter spherical balls to create B nanoparticles (<20 nm in diameter). Boron (2 g) was added to the ball milling apparatus and dry milled, followed by additional milling with either no ligand, a combination of oleic acid and oleyl amine (1.5 mL, 1:1 v/v), or [MAT][DCA] (1.5 mL). Acetonitrile was then added for the final milling as a co-solvent to help reduce the viscosity and easily transfer the nanoparticles.

The resulting acetonitrile suspensions were stable to air and these samples were manipulated on the benchtop. The solvent was removed by rotoevaporation followed by heating and stirring under high vacuum. The samples were then reassembled for the nanoparticle characterization, and availability. [BMIM][DCA] was freeze thawed to remove any dissolved gases or water by placing the vial in a N2 bath while under high vacuum and subsequently allowed to warm, forcing out any trapped gases.

Compositions of 0.2% to 0.7% w/w B from each of the three milled samples were prepared by diluting the weighed B samples with neat [BMIM][DCA] to prepare 1–2 mL samples. Initially a clear IL phase with aggregated B particles resting on the bottom was observed in each case. The vials were then removed from the drybox and vortex mixed and stirred, but without dispersion.

Each of the samples was ultimately dispersed by using a Branson 5510 bath sonicator. The vials were sonicated for 2-3 min cycles until no particles were visible, typically at least eight cycles. In each case black colloids formed with very
weak yellow-orange hues around the edges. These suspensions did
settle out over time (see below), however, each sample (all milling
conditions and loadings) was easily resuspended upon vortex
mixing and sonication (fewer cycles required). All colloids exhibited
the same stability whether freshly prepared or redispersed.

Interesting differences in the stabilities of the particles milled
under different conditions were noted. Boron milled with no
surfactant gave the least stable colloids with aggregation in less
than 24 h. Boron particles milled with the surfactant mixture were
slightly more stable, lasting 24 h, however, the compositions with B
milled in [MAT][DCA] had the greatest stability with colloids
lasting 48 h. In all cases, higher B loadings (0.5–0.7%) were more
prone to aggregation, but little difference in stability was noted for
either the 0.2% or the 0.33% loadings. Boron nanoparticles from
the three milling conditions were next loaded to 0.33 wt% in
[MAT][DCA] utilizing the methods described above (Fig. 1).

Thermal gravimetric analyses were performed on the colloidal
nanofluids in [BMIM][DCA] and [MAT][DCA]. The addition of B
nanoparticles from any preparation did not have an effect on the
decomposition temperature or the characteristic decomposition
profile of either IL (see ESI†). When these tests were conducted
with an air purge, mass gain was noted corresponding to the
oxidation of the B above 400 °C.

Combustion microcalorimetry was used to determine the heats
of combustion of neat [BMIM][DCA] and the colloids using a
Parr (series 425) semimicro oxygen bomb calorimeter (see ESI†).
The samples with B exhibited lower heats of combustion
compared to the neat IL and to the values expected when calculated
using the B contributions indicating that the energies
and temperatures were insufficient to combust B.

Hypergolic drop tests were then conducted to determine the
effects, if any, the B nanoparticles might have on ignition delay
and other ignition characteristics. The hypergropic apparatus
and tests described by Schneider et al.2 were employed. A droplet
(10 μL) of the IL was added to a vial, via a Hamiltonian syringe,
containing the oxidizer in large excess (500 μL of 98% white
fuming nitric acid (WFNA)) at 23 °C to ensure complete ignition of
the fuel. The ignition delay and flame duration times were
determined using a Redlake MotionPro HS-4 high speed camera
at 1000 frames per second. Each experiment was repeated for three
ignitions and the values for ignition delay and ignition duration
were averaged. The results are presented in Table 1.

The incorporation of 0.33 wt% B from any of the three
preparations did not have any effect on the observed ignition delay
of either IL tested (Table 1) within the accuracy of determination.
However, as discussed below, differences in the number, intensity,
and duration of the resulting flames were clearly different depending
on which capping agent was utilized in the B milling step.

Neat [BMIM][DCA] exhibited a single medium intensity flame
(See ESI†) as also reported in the literature.2,17 Incorporation of the
B milled with no ligand significantly reduced hypergolic perfor-
mance leading to smaller flames with observable residual mass
deposited on the sides of the vial after ignition. Utilizing B particles
milled in the oleic acid/oleyl amine surfactant mixture led to a
complex flame behavior reproducibly exhibiting two flames
which lengthened the overall time of combustion. The samples
loaded with B milled in [MAT][DCA] gave the most complicated
behavior with three flames (Fig. 2).

It is clear from comparing the runs with neat [BMIM][DCA]
with those loaded with B nanoparticles (e.g., Fig. 2c–g) that
addition of the B nanoparticles did not enhance the reaction.
There is also no evidence that the B ignited in these experiments.
Additionally, such complicated behavior and multiple flames
would provide extremely poor performance.

The hypergolic behavior of [BMIM][DCA] can be contrasted to
that of [MAT][DCA] where significant differences suggest a more
robust hypergolic system. Incorporation of B nanoparticles milled
with no ligand to [MAT][DCA] shortened the duration of the burn
and led to very weak flames. Adding the B milled with the oleic
acid/oleyl amine surfactant mixture also led to a shorter burn, but
flame intensity observed was only slightly reduced.

Adding B milled in [MAT][DCA] led to significant enhance-
ments in performance (Fig. 3). When the 0.33% B loaded
[MAT][DCA] was dropped into WFNA, an extremely powerful
and intense single flame appeared with a very short burn
indicating a very quick and powerful ignition. These drop tests
led to the largest and most intense flames of any of the tested
materials. The extremely bright, white flames qualitatively
indicated B ignition.13,14

Table 1 Hypergolic and stability properties of nanoparticle dispersions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colloidal stability</th>
<th>Ignition delay (ms)</th>
<th>Ignition duration (ms)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][DCA]</td>
<td>N/A</td>
<td>44(2)^a</td>
<td>106(6)</td>
<td>One Flame – Medium</td>
</tr>
<tr>
<td>0.33% B no ligand</td>
<td>&lt; 24</td>
<td>44(3)</td>
<td>108(41)</td>
<td>One Flame – Very weak</td>
</tr>
<tr>
<td>0.33% B surfactant</td>
<td>24</td>
<td>43(3)</td>
<td>110(50)</td>
<td>Two Flames – Medium</td>
</tr>
<tr>
<td>0.33% B [MAT][DCA]</td>
<td>48</td>
<td>44(3)</td>
<td>130(31)</td>
<td>Three Flames – Medium and High</td>
</tr>
</tbody>
</table>

| [MAT][DCA] | N/A | 37(6) | 77(18) | One Flame – Medium |
| 0.33% B no ligand | < 24 | 43(9) | 52(12) | One/Two Flames – Very weak |
| 0.33% B surfactant | 24 | 45(11) | 56(7) | One Flame – Medium |
| 0.33% B [MAT][DCA] | 48 | 45(14) | 43(4) | One Flame – Very Strong |

" As measured from the time the drop hits the oxidizer until the first
sign of a flame. 47 ms has been reported in the literature for this IL.2

Numbers in parenthesis denote calculated standard deviations.

Fig. 1 (a) [MAT][DCA]-milled B, (b) [MAT][DCA], and (c) 0.33% B.
FT-IR data (see ESI) suggests at least one partial explanation for the differences in the hypergolicity after adding B to the two ILs. The data indicate that the hypergolic anion is interacting with the B surface in [BMIM][DCA], but not in [MAT][DCA] with its coordinating cation. Studies to confirm the exact nature of the IL/B surface interactions are currently in progress.

Production of B nanoparticles by milling B in the presence of the hypergolic IL [MAT][DCA] leads to more stable dispersions of these nanoparticles in [BMIM][DCA] and [MAT][DCA]. The presence of these nanoparticles does not change the hypergolic ignition delay for these ILs, however, when added to [BMIM][DCA] there is little enhancement of the hypergolic burn and instead a complicated burn pattern emerges. By contrast, when B nanoparticles are milled in [MAT][DCA] and then dispersed in this IL, a single, shorter, much more intense burn is observed suggesting ignition of the B. These differences could be the result of the differing coordinative abilities of the two ILs to B, where, for example [BMIM][DCA] can coordinate B via the anion, while [MAT][DCA] can coordinate B with the cation, the anion or both.

Taken as a whole, the results reported here suggest EILs can be designed to provide unique stabilizing environments for reactive nanoparticles and that the nanoparticles can provide unique enhancements of the EIL properties such as increased density or hypergolic performance. Future work from our Groups will focus enhancements of the EIL properties such as increased density or nanoparticles and that the nanoparticles can provide unique stabilizing environments for reactive materials. This material is based upon work supported by the Air Force Office of Scientific Research under AFOSR Notes and references