

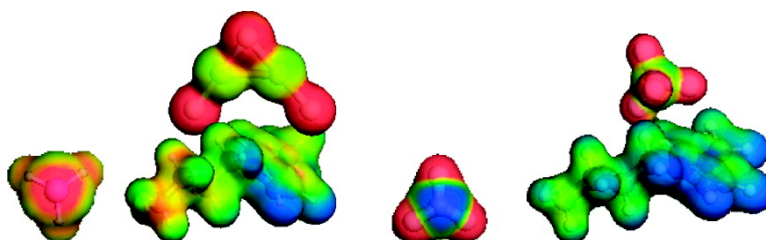
Communication

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## High Gas Storage Capacities for Ionic Liquids through Chemical Complexation

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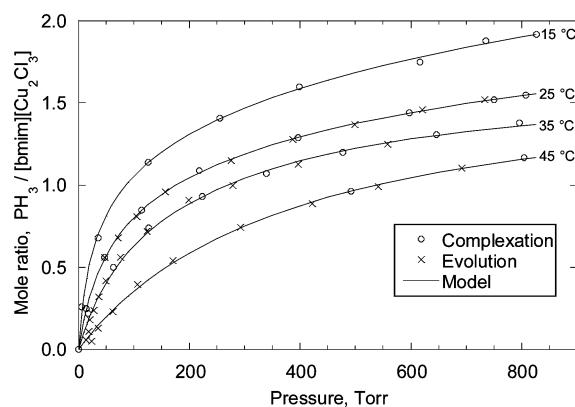
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Storing, transporting, and delivering toxic, flammable, or reactive gases present significant technological challenges. An unintended or uncontrollable release of a hazardous gas from a pressurized container could result in significant harm to life and the environment. Alternatives to conventional gas processing methods that rely on high pressures are needed for many important industrial applications.<sup>1</sup> The unique properties of ionic liquids (ILs)<sup>2</sup> offer an opportunity to develop systems capable of reversibly storing a variety of molecular species in the liquid phase without imparting solvent impurities. Here we report a combined experimental and theoretical study of IL complexes for storing two toxic gases, PH<sub>3</sub> and BF<sub>3</sub>. These gases are used as precursors for selectively doping silicon semiconductors with phosphorus or boron atoms through ion implantation.<sup>1b,c,3</sup> We show that carefully selected ILs can reversibly bind the gas molecules via chemical complexation with unusually high capacities and moderate heats of reaction.

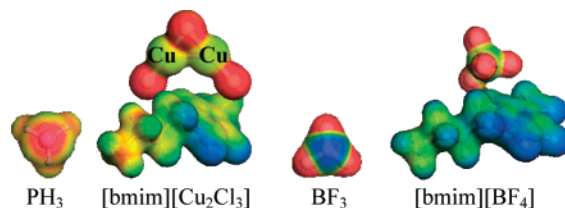
Most ionic liquids have no measurable vapor pressure, are easy to process, and can be recycled and reused. In addition, anions and cations can be selected to provide a wide range of physicochemical properties. Most studies for gas processes using ionic liquids are based on dissolution<sup>4</sup> with notable exceptions for CO<sub>2</sub> and SO<sub>2</sub> capture utilizing amine-functionalized ionic liquids.<sup>5</sup> Our approach was to design IL complexes by making use of IL chemical reactivity toward specific molecular species to drastically increase storage capacity at low pressures. For storing PH<sub>3</sub>, we considered Lewis acidic ionic liquids such as Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> and Cu<sub>2</sub>Cl<sub>3</sub><sup>-</sup>, which form complexes with the gas molecule via charge transfer from the electron lone pair of PH<sub>3</sub> to the empty s-orbital of the metal atoms. In contrast, for BF<sub>3</sub>, we used Lewis basic ILs to bind the Lewis acidic gas molecule.

Experiments were carried out isothermally on a 2 g scale by cascading known pressures and volumes of gas into a continuously stirred reactor containing a known quantity of ionic liquid for gas complexation, and the procedure was reversed to collect data for gas evolution. The equilibrium gas capacities were determined as mole ratios<sup>6</sup> (moles of complexed gas per mole of IL) by using the ideal gas law. Reaction isotherms were obtained by plotting the capacity of the IL for the gas as a function of pressure. In parallel, quantum chemical calculations using gradient-corrected density functional theory were performed to understand the interactions between the IL complexes and gas molecules. The computational study utilized the Perdew–Wang’s exchange–correlation functional (PW91) and a double numerical atomic basis set augmented with polarization functions as implemented in DMol3 package.<sup>7</sup> All molecular structures were fully optimized. Reaction energies were evaluated with zero-point energy corrections.<sup>8</sup>

We selected 1-butyl-3-methylimidazolium trichlorodocuprate, [bmim][Cu<sub>2</sub>Cl<sub>3</sub>], for detailed experiments using PH<sub>3</sub>.<sup>9</sup> Trichlorodocuprate ILs are readily synthesized through addition of 2 equiv of copper(I) chloride to 1 equiv of a chloride salt precursor.<sup>10</sup> The



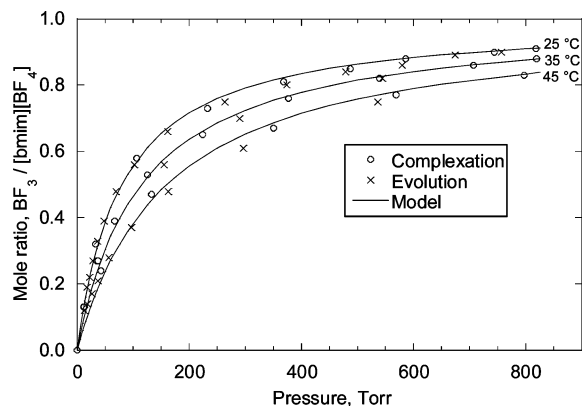
**Figure 1.** Reaction isotherms at 15, 25, 35, and 45 °C for [bmim][Cu<sub>2</sub>Cl<sub>3</sub>] and PH<sub>3</sub>.



**Figure 2.** The calculated electrostatic potentials.

anion formally contains two copper atoms, so 1 mol of IL can accommodate 2 mol of PH<sub>3</sub>.

The forward reaction isotherms for complexation of PH<sub>3</sub> with [bmim][Cu<sub>2</sub>Cl<sub>3</sub>] are co-incident with the reverse isotherms (Figure 1), demonstrating that complexation is completely reversible and that the IL–PH<sub>3</sub> mixture is stable. The reaction isotherms can be described by a two-site thermodynamic model for formation of PH<sub>3</sub> complexes in solution.<sup>11</sup> The heats of reaction for the two sites predicted by the model are –11.9 and –9.69 kcal/mol. The optimized lowest energy structure of [bmim][Cu<sub>2</sub>Cl<sub>3</sub>] exhibits strong Cu–Cu bonding with a bond length of 2.626 Å, which is elongated slightly by 0.082 Å upon binding with PH<sub>3</sub>. The electrostatic potential of [bmim][Cu<sub>2</sub>Cl<sub>3</sub>], projected onto the electron density, indicates that the Cu atoms are positively charged and thus facilitate binding with the electron lone pair of PH<sub>3</sub> (Figure 2). Each [bmim][Cu<sub>2</sub>Cl<sub>3</sub>] molecule binds with two PH<sub>3</sub> molecules. The calculated Cu–P distances are 2.199 and 2.201 Å, indicating that covalent bonds between Cu and P are formed. The calculations yield reaction energies for PH<sub>3</sub> binding at the Cu sites of –12.0 and –7.9 kcal/mol, in good agreement with the fitted experimental values. Chemical complexation between the IL and the gas species gives rise to an unusually high PH<sub>3</sub> storage capacity for this material, while the moderate heats of formation allow the reaction to be readily reversible.



**Figure 3.** Reaction isotherms at 25, 35, and 45 °C for [bmim][BF<sub>4</sub>] and BF<sub>3</sub>.

The observed capacity of 1.92 mol/mol at 826 Torr and 15 °C corresponds to PH<sub>3</sub> complexation with 96% of the available copper coordination sites. In contrast, the chemically unreactive ionic liquid [bmim][PF<sub>6</sub>] had a capacity of only 0.03 mol/mol at atmospheric pressure and temperature. The density difference between the neat IL and the PH<sub>3</sub> complex leads to an increase in volume of ~20% upon complexation at 25 °C and atmospheric pressure. The room temperature <sup>1</sup>H-decoupled <sup>31</sup>P NMR spectrum of the [bmim][Cu<sub>2</sub>Cl<sub>3</sub>]/PH<sub>3</sub> mixture exhibits a singlet at -171.9 ppm versus 85% H<sub>3</sub>PO<sub>4</sub>, while pure PH<sub>3</sub> in the gas phase exhibits a singlet at -252.6 ppm.

Having shown that a Lewis basic gas can be reversibly complexed with an IL, we extended the concept to a Lewis acidic gas, BF<sub>3</sub>. Our computational study predicted that tetrafluoroborate salts should be well suited for reversibly complexing Lewis acidic BF<sub>3</sub>. The calculated minimum energy structure suggested that [bmim][BF<sub>4</sub>] can form an adduct, [bmim][BF<sub>3</sub>-F-BF<sub>3</sub>], upon exposure to BF<sub>3</sub>, with a heat of reaction of -9.7 kcal/mol. The distance between B in BF<sub>3</sub> and the bridged F is 1.635 Å, indicative of a covalent bond. The bonding is dictated by the charge transfer from the negatively charged F in [bmim][BF<sub>4</sub>] to the electron-deficient B in BF<sub>3</sub> as clearly illustrated by the calculated electrostatic potential shown in Figure 2. Indeed, this IL complex was found to exhibit a high capacity for BF<sub>3</sub>. On the basis of the experimental reaction isotherms (Figure 3), the heat of reaction for binding with BF<sub>3</sub> was determined to be -6.76 kcal/mol. Assuming 1:1 reactivity, 91% of the IL reactive sites are complexed at 25 °C and 819 Torr. The liquid volume increases by ~20% under these conditions. The BF<sub>3</sub> capacity of [bmim][PF<sub>6</sub>] was less than 0.10 mol/mol at 25 °C and 760 Torr.

Both our experimental evidence and theoretical results suggest that BF<sub>3</sub> complexes with the BF<sub>4</sub><sup>-</sup> anion through a bridged fluorine interaction. The room temperature <sup>19</sup>F NMR spectrum of the neat [bmim][BF<sub>4</sub>]/BF<sub>3</sub> adduct exhibits a sharp singlet at -145.2 ppm (referenced to CFCl<sub>3</sub>), which is intermediate between the chemical shifts from BF<sub>3</sub> in the gas phase (-134.3 ppm) and the anion of neat [bmim][BF<sub>4</sub>] (-150.6 ppm). The presence of a single <sup>19</sup>F NMR resonance at room temperature can be attributed to rapid exchange of all the fluorines. Hartman and Stilbs observed the heptafluorodiborate anion, B<sub>2</sub>F<sub>7</sub><sup>-</sup>, as its tetra-*n*-butylammonium salt by <sup>19</sup>F NMR spectroscopy at temperatures below -110 °C.<sup>12</sup> Other reports citing the formation of BF<sub>3</sub> adducts with BF<sub>4</sub><sup>-</sup> salts have been published.<sup>13</sup> We obtained further evidence for BF<sub>3</sub>-F-BF<sub>3</sub><sup>-</sup> bridging by adding 99.9% isotopically enriched <sup>11</sup>BF<sub>3</sub> to [bmim][BF<sub>4</sub>] containing a natural isotopic abundance of boron (80% <sup>11</sup>BF<sub>4</sub><sup>-</sup>, 20% <sup>10</sup>BF<sub>4</sub><sup>-</sup>). Upon reaching equilibrium at ~760 Torr,

the <sup>11</sup>BF<sub>3</sub> concentration in the headspace of the reactor was diluted to ~90% as is expected for complete fluoride exchange between BF<sub>4</sub><sup>-</sup> and BF<sub>3</sub>.

Both PH<sub>3</sub> and BF<sub>3</sub> are readily recoverable when their complexes with [bmim][Cu<sub>2</sub>Cl<sub>3</sub>] and [bmim][BF<sub>4</sub>] are exposed to reduced pressure. The reactions are completely reversible, and the ILs show no measurable loss in capacity after multiple complexation–evolution cycles. Without external energy input, the rate of gas evolution under vacuum is limited by mass transport; however, low flow rates (5–10 sccm per liter of IL) can be sustained to equilibrium pressures below 20 Torr. Thus, the systems are suitable for storing and delivering gases for applications that require low flow rates such as ion implantation.

In summary, we have demonstrated that the inherent properties of ILs are ideally suited for selectively storing a large quantity of pure gas in a small volume at low pressures. Exceptionally high gas storage capacities for the selected gases were achieved by taking advantage of weak chemical complexation between the gas species and the carefully selected ILs. The reverse reaction at room temperature allows for delivery of the gas at modest flow rates without stirring. Liquid phase sub-atmospheric storage and delivery offers an important advantage over conventional compressed sources for highly reactive gases and represents an important new application for ionic liquids.

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**Supporting Information Available:** Coordinates of fully optimized molecular structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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