Ionic Liquids for CO$_2$ Capture

- HIGH selectivity
- LOW Capacity

More research is needed to increase IL capacity for CO$_2$! (among other problems associated with IL-CO$_2$ capture)
The first measurement of high physical CO$_2$ solubility in an IL was reported in 1999. Subsequently, there have been numerous studies of the solubility of CO$_2$ in a wide variety of ILs.

The general observations are that the nature of the anion plays a very important role in determining the solubility.

Increasing the length of alkyl chains on the cation can increase CO$_2$ solubility.
“Tweaking” ILs

One solution to the capacity problem is to include functional groups in the IL that can react with CO₂.

This should maintain or increase selectivity while dramatically increasing capacity.¹
Computational Chemistry

- Allows for the simulation of systems that would otherwise be more difficult, more expensive, or less efficient to carry out experimentally.

- Also can be used in conjunction with experiments to help gain a better understanding of experimental results.
  
i.e. can see things on smaller timescales
Molecular Dynamics Simulations of Ionic Liquids

Dr. Steven Corcelli’s group at Notre Dame is researching different properties of various Ionic Liquids using Molecular Dynamics simulations.

My first project is to verify the accuracy of a force field for a specific Ionic Liquid.
What the Diffusion constant can tell us…

- The Diffusion constant has been measured experimentally for many Ionic Liquids.

- Comparison of the calculated diffusion constant from a Molecular Dynamics simulation to the experimental value can help in determining whether a model is accurate for the simulation of a particular IL.
Calculating the Diffusion constant

- Center of Mass

\[ R = \frac{1}{M} \sum m_i r_i \]

- Mean Squared Displacement (MSD) = \( <(R - R_0)^2> \)

- So we get one MSD for all molecules at a given time-step.
MSD as a function of time
The slope of MSD vs. time gives the Diffusion constant

\[ D = \frac{1}{6} \frac{d\text{MSD}}{dt} \text{ or } \frac{m}{6} \]
My Project:

[Bmim][BF₄]

1-Butyl-3-methylimidazolium (Bmim)
Equilibration

Want to mimic the “real world”

- Initial minimization of energy – keeps things far enough away from each other
- Then a run which assigns velocities to atoms by slowly ramping up the temperature.
- Then a constant pressure run allows an average density to form.

[Sample thermo log file]

- NVT run assigns a volume while keeping the avg. density.
- Then adds more energy to break apart any “sticky pseudo-molecules”
- NVE-preproduction

Total 8 ns of equilibration
Production Simulation

- Outputs files such as thermodynamic properties and coordinate files. (my simulation is for 10 ns)

  sample_output.txt

- Need to write computer script which extracts the coordinates from output and calculates the MSD over time.

  MSD_Bmim.f
MSD vs. time for [Bmim] and [BF$_4$] over 10 ns

Bmim

BF$_4$
Diffusion constant

- Diffusion Constant for Bmim (at 300K) = 1.5 x 10^{-11} m^2s^{-1}
- Experimental value (at 298 K) of D = 1.4 x 10^{-11} m^2 s^{-1}

- Diffusion Constant for BF_4 (at 300 K) = 1.16 x 10^{-11} m^2s^{-1}
- Experimental value (at 298 K) of D = 1.3 x 10^{-11} m^2 s^{-1}
My Upcoming Projects

- Take averages of 2.0 ns runs within a 20 ns simulation to get a more statistically relevant value for D.

- Looking at rotation about planes within each molecule and use a correlation functions to study the intra-molecular rotations of the molecules in [Bmim][BF$_4$].
  - How quickly they “de-correlate” from initial rotational positions
  - On the scale of femtoseconds
  - This will help us gain new understanding into the motions occurring on very small timescales in different Ionic Liquids.