Molecular Simulation of a Deep Eutectic Solvent Inside Nanoporous Materials

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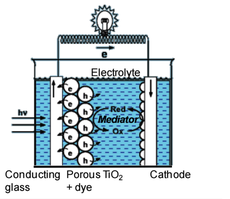
Abstract

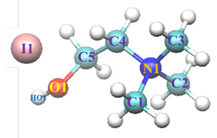
Producers of solar energy utilize dye-synthesized solar cells (DSSCs), used to convert sunlight into energy. Within the cell, ionic liquids (ILs) act as electrolytes to move the charges which create energy. These ILs have properties negative for the environment, such as their toxicity, and are more costly than alternatives which are still in development. One such alternative is the deep eutectic solvent (DES) which is a mixture of two solids (an acceptor and a donor of hydrogen bonds) which, when mixed in a particular ratio, has a lower melting point than either of its components and forms a liquid at room temperature. DESs have been experimentally found to have similar chemical and physical properties as ILs while having a significantly lower cost and almost no toxicity. Here, molecular dynamics (MD) simulations were performed in order to understand fundamental and molecular properties of a choline iodide/glycerol DES in nanopores of different chemical composition, compared against that in bulk. Results of density profiles showed that the DES aggregated near the pore walls in both confined systems. Our results suggest that glycerol tends to form hydrogen bonds with the titania walls, and as a result, the dynamics of the DES in titania are much slower than that in graphite and in the bulk. Overall, results show a notable difference between the properties of the DES in pores of different chemical composition, and in bulk versus non-bulk samples.

Introduction

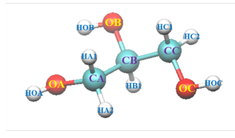
DESs are used as alternative electrolytes in DSSCs.
They share physical, chemical properties of ILs, but are less expensive and (mostly) nontoxic.
The DES studied was a 1:3 mole ratio mixture of choline iodide and glycerol.



Scheme of a Dye-Synthesized Solar Cell



Choline iodide
(2-Hydroxyethyl)trimethylammonium iodide



Glycerol
Propane-1,2,3-triol

Composition of DES studied

Materials and Methods

- **GROMACS and VMD (Visual Molecular Dynamics) software to run simulation:**
  - **DES (1:3 mol ratio Choline Iodide and Glycerol)**
  - **in 2.5 nm pore of titania or graphite**
  - **and in bulk system**
  - **under applied force field, general AMBER force field (GAFF)**
  - **under initial temperature 500K**

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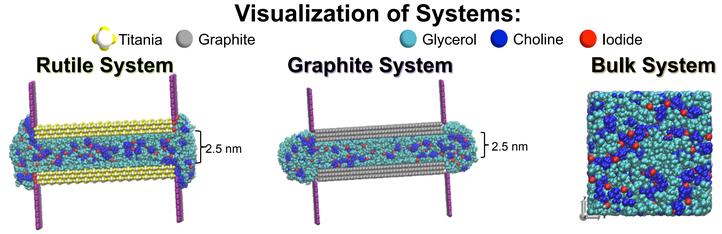
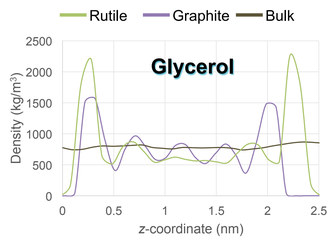
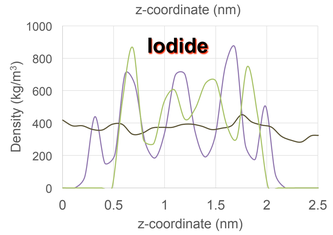
Results

Visualization of Systems:

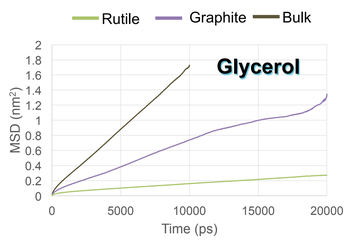


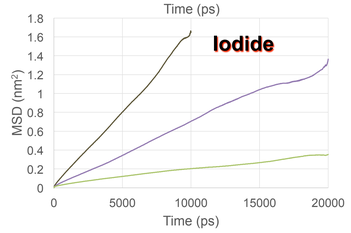
Local Densities of Species:



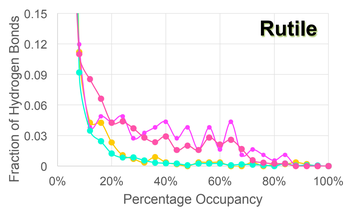


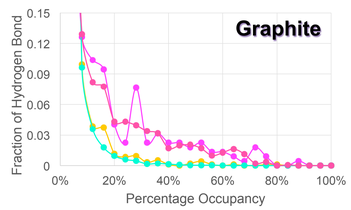
Mean Squared Displacements:

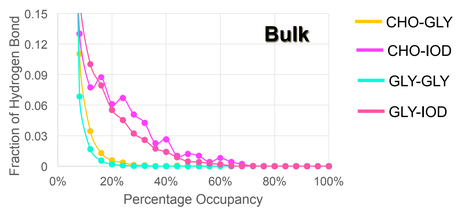




Hydrogen Bonding of Systems







Interpretation

Local densities

- **Partial densities reflect volume of planes 1/10 the height of the entire system, the length of the system's pore wall, and the width of the system's pore wall (2.5 nm) divided by the mass of solvent in that volume.**
- **No peaks (i.e., consistent density profiles) of all species in bulk proves effect of chemical interactivity with pore walls.**
- **High local density of glycerol near pore walls, more prominently in rutile system (titania pore walls)**
  - **Glycerol can hydrogen bond to titania walls; no hydrogen bonds with graphitic walls.**

Mean Square Displacements

- **MSD represents displacement of molecules of each species the 20 ns simulation of each system.**
- **Linear MSD plots reflect diffusive displacement (random).**
- **Exponential MSD plots (such as the final portions of those of the graphite and bulk systems) indicate a directionality of movement.**

Hydrogen Bonding

- **Plots answer the question, "what fraction of this bond type appears this percentage of the 20 ns simulation?"**
  - **This is important to consider because hydrogen bonds affect melting point, the characteristic which takes DES from solid to liquid when mixed; the bonds affect phase of solvent.**
- **All plots reflect high number of fleeting bonds and low number of enduring bonds.**
- **Plots reflect generally similar hydrogen bonding behavior in confined systems vs. bulk; especially the GLY-GLY bond.**
- **GLY-GLY bond behaves similarly regardless of system.**
- **GLY-IOD behaves differently in bulk than in confinement; higher fraction of this bond type exists at low percentage occupancy.**

Conclusions

- **Dynamic properties of all three species change when in confinement; particularly the density of hydrogen bonding properties of glycerol.**
- **Of the confined systems, the graphite system shows behavior more similar to that of the bulk system (e.g., subtler density peaks, non-linear ends to MSD within 20 ns, displacement).**
- **More study can be done to analyze the behavior of species among density layers**
- **All data can be used to further compare behavior of DESs to ILs in confinement and evaluate DESs as a substitute.**

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