



Carbon Capture Using Ionic Liquids

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Molecular Modeling Application Area: Carbon Capture Using Ionic Liquids (ILS)

Carbon capture is very challenging and developing suitable materials for CO₂ capture at certain conditions (such as post-combustion carbon capture and pre-combustion carbon capture) is the key to efficiently capture CO₂. Ionic liquids (ILs) are being investigated for carbon capture due to their unique properties, such as high solvating capacity for polar and nonpolar compounds, tunability, low vapor pressure, wide liquid temperature range, high thermal stability, non-flammability, and etc. We rely heavily on NETL super-computers to investigate ILs for CO₂ capture by using the simulation tools including atomistic molecular dynamics, atomistic Monte Carlo simulation, quantum *ab initio* gas phase and quantum *ab initio* condensed phase calculations. By performing these theoretical studies along with the experimental investigations, the time and efforts (money) to develop new materials will be minimized.

From the simulation we have identified an ionic liquid ([emim][CH₃COO]) to exhibit very high separation performance for CO₂/H₂ separation in the pre-combustion carbon capture [1]. This is due to two reasons, that is the strong type I CO₂ interaction with the [CH₃COO]⁻ anion (Figure 1), which leads to high CO₂ solubility in [emim][CH₃COO] and high CO₂ permeability in the supported IL membrane; and the small molar volume for [emim][CH₃COO], which leads to low H₂ solubility and low permeability in this IL. The theoretical prediction has also been experimentally confirmed at NETL [1].

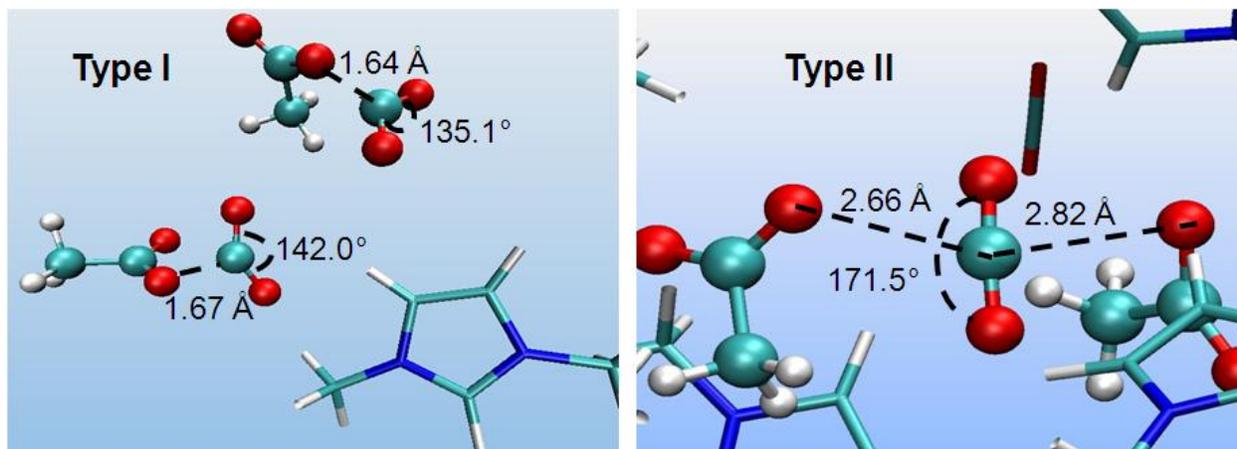


Figure 1. The strong Type I and weak Type II CO₂ interactions with the [CH₃COO]⁻ anion in the condensed phase of [emim][CH₃COO] ionic liquid obtained from quantum *ab initio* molecular dynamics simulations.

Thermodynamically, although ionic liquids could exhibit very high CO₂ absorption capacity, they are typically very viscous and lead to very slow gas mass transport in ILs, which in turn leads to unfavorable large equipment size and large capital cost for CO₂ capture. Increasing gas mass transport in the viscous ILs is very important for ILs to be used in carbon

capture and other applications. From our theoretical modeling, we have found for the first time that gas diffusivity in ILs could be increased by one magnitude when confining ILs inside nanoporous materials, such as carbon nanotube and silica slit pores [2,3]. This is partly due to gas absorption at the interface region between the wall of the solid and the ILs (Figure 2). Gas molecules adsorbed in this region are expected to experience less frequent collisions with other atoms compared with gas absorption inside the bulk IL molecules. Additionally, CO₂ solubilities in the confined ILs are also increased due to the increase molar volume for the confined IL compared with neat IL. The theoretical predictions of increased gas solubility, diffusivity and permeability in confined IL compared with neat IL have also been experimentally observed in other research groups. This work shows that confined IL inside nanoporous materials may improve CO₂ capture.

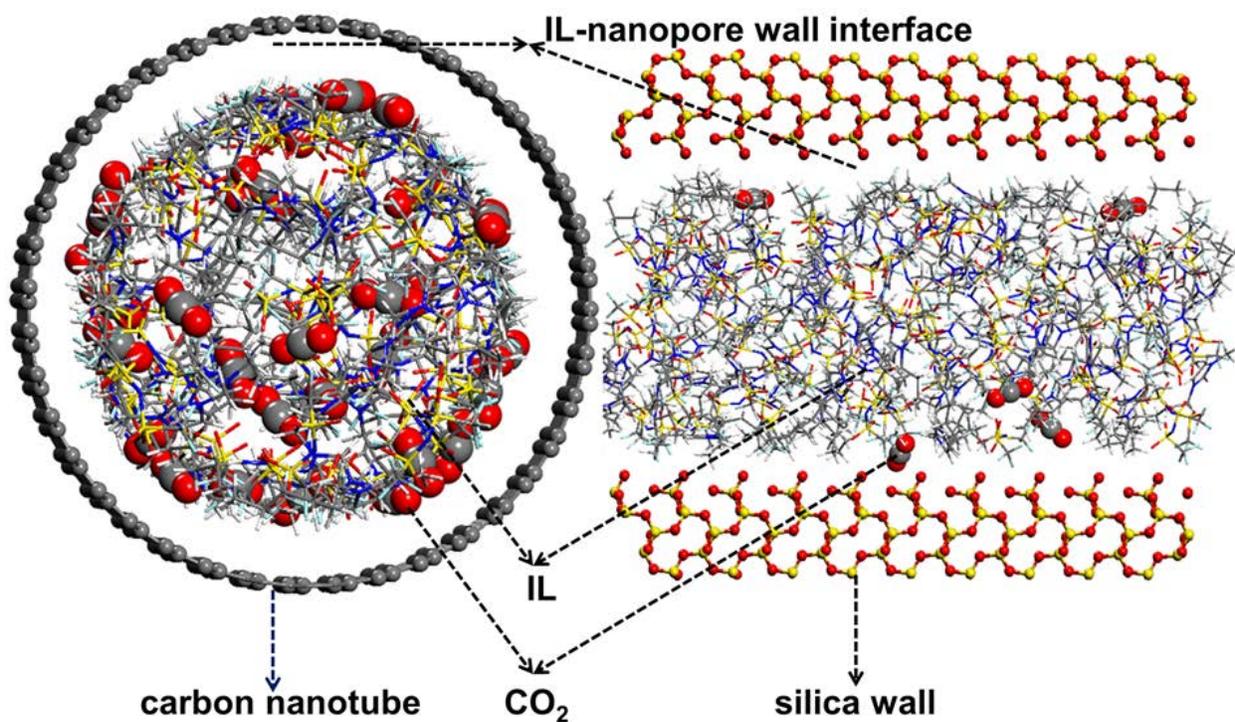


Figure 2. CO₂ Absorption into ionic liquid confined inside carbon nanotubes (left) and silica slit pores (right) obtained from classical molecular dynamics and Monte Carlo simulations.

Due to strong water-anion interactions, water is very soluble in ILs. The IL hygroscopicity has profound effects on IL properties. For example, IL diffusivity could exhibit a complicated non-linear behavior [4] due to different water-IL interactions at different water concentrations (Figure 3). Due to the formation of water-[CH₃COO]⁻ hydrogen bonding network at $x_{\text{H}_2\text{O}}=0.5$, both simulations and experiments show that IL molecules exhibit the smallest diffusivity at this water concentration. This work shows that by adding water in ILs at different water concentrations may enhance or impede CO₂ mass transport in ILs and affect CO₂

capture performance. Additionally, large water solubility in ILs will lead to large energy penalty for CO₂ capture during the solvent regeneration step because water will absorb heat and evaporate from the IL phase to the gas phase in the CO₂ desorption process.

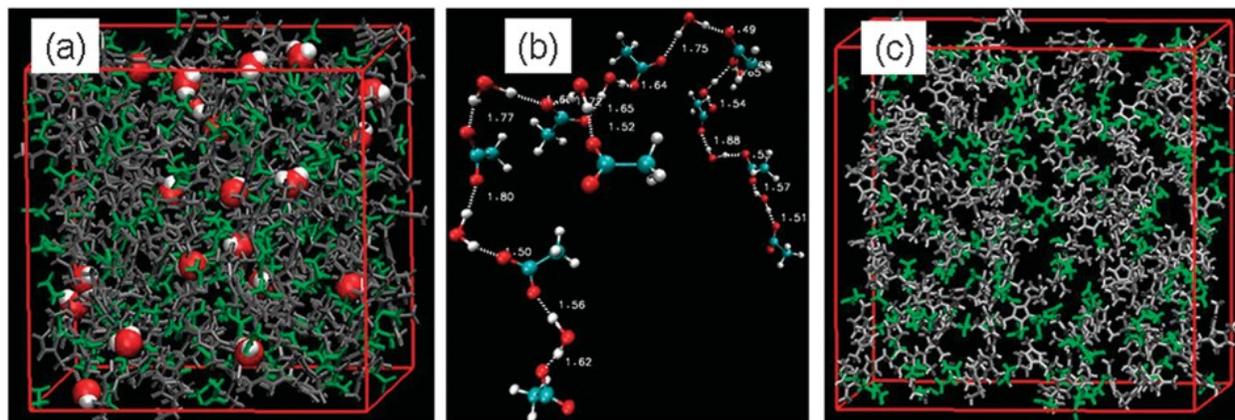


Figure 3. Three representative snap shots obtained from classical molecular dynamics simulation to show water absorption in [emim][CH₃COO] at 313 K and $x_{\text{H}_2\text{O}} =$ (a) 0.11, (b) 0.5, and (c) 0.95. In (a), water molecules are indicated using the vdW graphical representation and the ionic liquid molecules are shown as bonds. In (b), a hydrogen bond network consisting of 10 water molecules and 10 [CH₃COO]⁻ anions are shown. For clarity, all other [emim]⁺ cations, [CH₃COO]⁻ anions, and water molecules are not shown. In (c), only the [emim]⁺ cations and the [CH₃COO]⁻ anions are shown. Water molecules fill in the void space formed between the ionic liquid molecules.

Since ILs are viscous and hygroscopic, which are unfavorable properties for CO₂ capture using ILs, new methods have to be discovered to overcome these two intrinsic problems related with ILs. Recently, we have for the first time to investigate the structures and dynamics of ionic liquid reverse micelle (ILRM) [5], and their potential use for CO₂ capture (Figure 4). Both simulations and experiments show that ILs confined inside the ILRM diffuse 1-2 orders of magnitudes faster compared with neat IL molecules. This is partly due to the fast diffusion of the ILRM particle as a whole in the less viscous benzene solvent. Additionally, simulations show that CO₂ molecules exhibit very different solubility, diffusivity, and permeability in different regions of the ILRM system. Due to the nano size and the large specific surface area for the ILRM nanodroplet, and the hydrophobic feature of the solvent, ILRM is potentially useful to alleviate both the high viscous and hygroscopic problems for ILs.

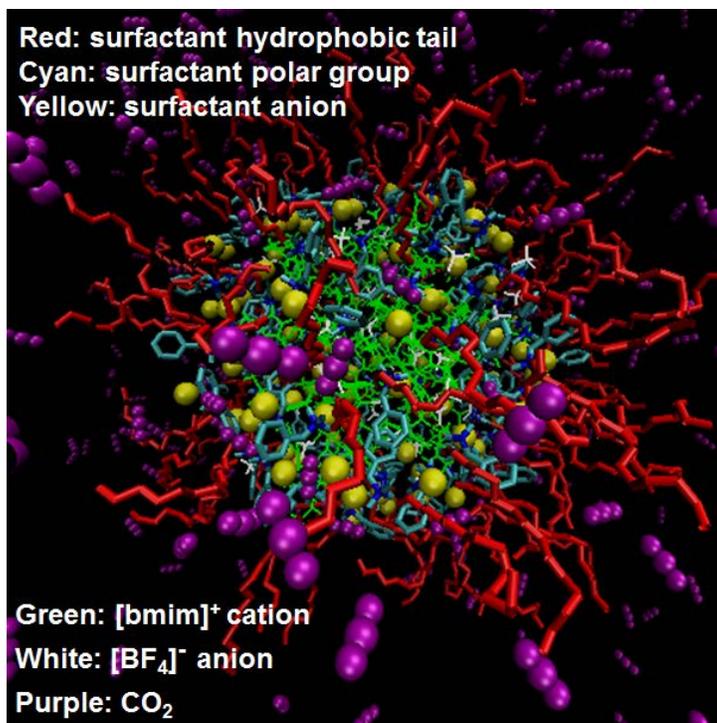


Figure 4. Representative snap shot obtained from classical molecular dynamics simulation to show CO₂ absorption into ionic liquid reverse micelle. For clarity, the benzene solvent molecules are not shown.

Molecular Modeling Tools Development Area

Tools availability is indispensable for simulations. Although many simulation tools are available (free or commercial) and contribute a lot for the researchers to allow them to investigate a lot of properties and phenomena, we still decide to develop in-house codes and in-house tools. There are two reasons for that. Firstly, to develop new advanced simulation algorithms and tools will allow us to perform more challenging calculations and investigations, which cannot be done by using the current commercial softwares. This will significantly enhance our research quality. Secondly, developing these simulation tools in-house will make the integration of the multi-scale modeling at NETL to be much easier.

At NETL, we have developed various classical Monte Carlo simulation tools for many ensembles, such as but not limited to, canonical ensemble, grand canonical ensemble, osmotic ensemble, iso-stress ensemble, Gibbs ensemble, reactive ensemble, and etc. Using these ensembles, we have been able to calculate gas solubility and permeability [6] in solvents, nano porous materials, polymer-like materials, liquid-solid composite materials, and etc . Additionally, we have also developed other tools for important thermodynamic property calculations, such as surface tension and heat capacity. Besides the Monte Carlo simulation, the

classical molecular dynamics simulation is very important to obtain other important properties, especially, the transport properties. In order to do that, we have developed tools to calculate mass transport coefficient, ionic conductivity based on the trajectories generated from free softwares such as NAMD program.

There are two types of tool development. The first type is the ones existing in literature but not developed at NETL, which includes the above mentioned surface tension and heat capacity calculation. Another two tools of such type to compute heat conductivity and viscosity (both are challenging calculations) are still under development. The second type of tool development is related with developing *new* simulation algorithm. Such an example is shown below (Figure 5). Using this new algorithm and the related source code we developed at NETL, we are for the first time to be able to calculate CO₂ Henry's law constant in chemically absorbing solvents, such as [P₄₄₄₄][CH₃COO] IL. The simulated Henry's law constants are comparable to the experiment data. From the simulations and experiments, we have unambiguously shown that it is due to the strong CO₂-[CH₃COO]⁻ interactions that [CH₃COO]⁻ type of anion could contribute to significant CO₂ solubility [7].

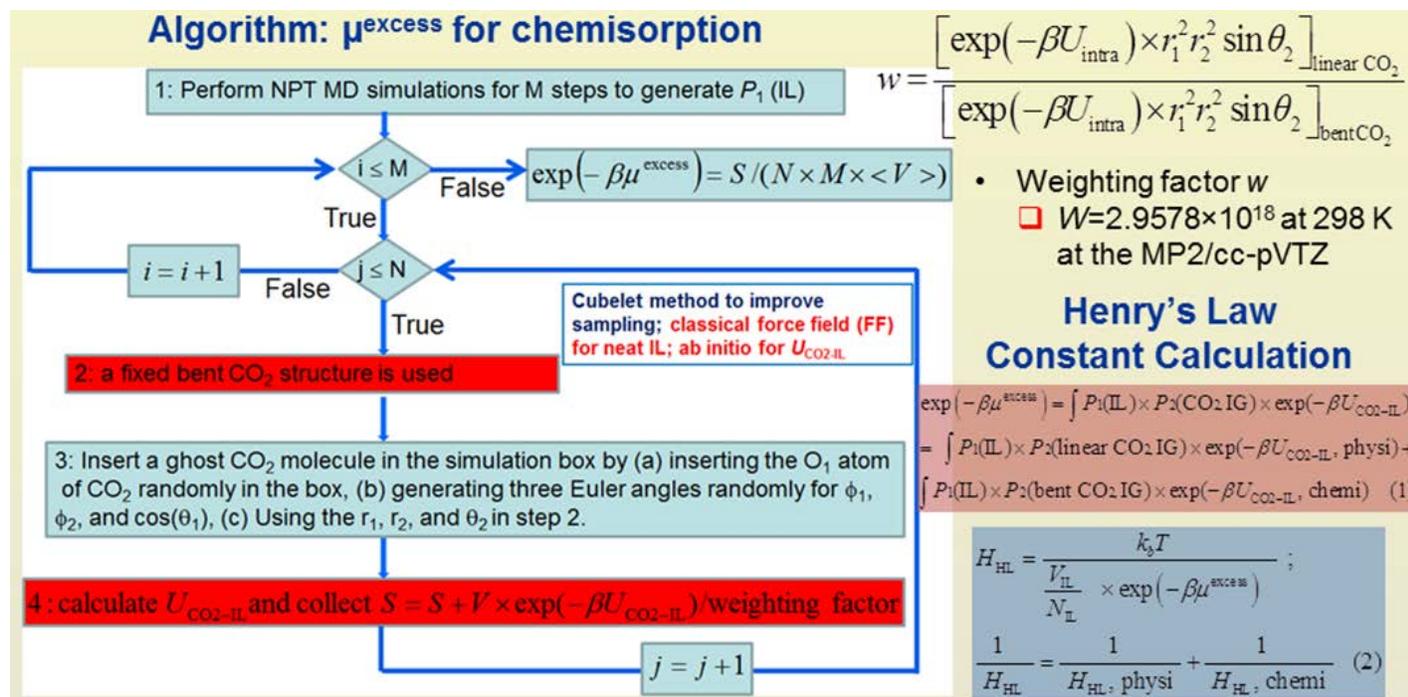


Figure 5. A schematic description of Henry's law constant calculation for gas chemical absorption in solvent. To summarize, tools development is very important for our success of research and development. We are putting a lot effort in developing them, including both new and other important simulation tools.

References:

- [1] Wei Shi, Christina R. Myers, David R. Luebke, Janice A. Steckel, and Dan C. Sorescu, "Theoretical and Experimental Studies of CO₂ and H₂ Separation Using the 1-Ethyl-3-methylimidazolium Acetate ([emim][CH₃COO]) Ionic Liquid", *Journal of Physical Chemistry B*, **2012**, *116*, 283-295.
- [2] Wei Shi, and Dan C. Sorescu, "Molecular Simulations of CO₂ and H₂ Sorption into Ionic Liquid 1-n-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide ([hmim][Tf₂N]) Confined in Carbon Nanotubes", *Journal of Physical Chemistry B*, **2010**, *114*, 15029-15041.
- [3] Wei Shi, and David R. Luebke, "Enhanced Gas Absorption in the Ionic Liquid 1-n-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide ([hmim][Tf₂N]) Confined in Silica Slit Pores: A Molecular Simulation Study", *Langmuir*, **2013**, *29*, 5563-5572.
- [4] Wei Shi, Krishnan Damodaran, Hunaid B. Nulwala, and David R. Luebke, "Theoretical and experimental studies of water interaction in acetate based ionic liquids", *Physical Chemistry Chemical Physics*, **2012**, *14*, 15897-15908.
- [5] Wei Shi, Lei Hong, Krishnan Damodaran, Hunaid B. Nulwala, and David R. Luebke, "Molecular Simulation and Experimental Study of CO₂ Absorption in Ionic Liquid Reverse Micelle", **2014**, submitted
- [6] Wei Shi, Dan C. Sorescu, David R. Luebke, Murphy J. Keller, and Shan Wickramanayake, "Molecular Simulations and Experimental Studies of Solubility and Diffusivity for Pure and Mixed Gases of H₂, CO₂, and Ar Absorbed in the Ionic Liquid 1-n-Hexyl-3-methylimidazolium Bis(Trifluoromethylsulfonyl)amide ([hmim][Tf₂N])", *Journal of Physical Chemistry B*, **2010**, *114*, 6531-6541.
- [7] Wei Shi, Robert L. Thompson, Erik Albenze, Janice A. Steckel, Hunaid B. Nulwala, and David R. Luebke, "Contribution of the Acetate Anion to CO₂ Solubility in Ionic Liquids: Theoretical Method Development and Experimental Study", *Journal of Physical Chemistry B*, **2014**, *118*, 7383-7394.