Accurate Computation of Hydrofluorocarbon Solubility in Ionic Liquids with Molecular Simulation

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Hydrofluorocarbons (HFCs) are a class of molecules that are widely used as refrigerants. Though HFCs do not have the detrimental impact to the ozone layer of their chlorofluorocarbon predecessors, some HFCs have high global warming potential (GWP). Therefore, certain HFC molecules are due to be phased out under the 2016 Kigali amendment to the Montreal Protocol. Unfortunately, many refrigerants currently in use are azeotropic mixtures of low and high GWP HFCs. Ideally, these mixtures would be separated and the high GWP components would be disposed while the low GWP components would be recycled. Our goal is to design custom ionic liquids (ILs) for novel separation schemes to separate HFC refrigerant mixtures. Since there are millions of potential ILs, computational design methods can help screen for promising ILs.

Here, we report calculations of HFC solubility in ILs with molecular simulations. Borrowing well-established techniques from the field of protein-ligand binding, we use Hamiltonian replica exchange molecular dynamics and multistate Bennet's acceptance ratio to compute the chemical potential of HFCs in ILs with an accuracy greater than 0.2 kJ/mol. The gas phase chemical potential as a function of pressure can be determined from an equation of state or Widom insertion methods. By computing the chemical potential as a function of HFC concentration in the IL, we determine the solubility as a function of pressure. We evaluate the accuracy of our results for several HFCs/IL combinations. For difluoromethane in 1-butyl-3-methylimidazolium hexafluorophosphate molecular simulations agree with experiment to within 3 mol% from 0.1 bar to 10 bar. A single solubility curve can be computed in less than 1 week, making the method competitive with experiments and feasible for screening large numbers of ILs. We close by discussing additional approximations to reduce the computational cost and move the workflow towards a high-throughput screening paradigm.