Determining Thermodynamic Solubility Parameters for Nanoscale Building Blocks

Patrick S. Redmill[1], Clare McCabe[1], Peter T. Cummings[1,2]

1. Department of Chemical Engineering, Vanderbilt University, Nashville, TN 37235-1604

2. Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831-64943

Motivation

- Nanoscale building blocks (NBBs), such as buckyballs and Polyhedral Oligomeric Silsesquioxanes (POSS) are increasingly being incorporated into new realms, including biological applications.
- Obtaining thermodynamic properties of NBBs in an experimental setting can be difficult, as these are novel products and can be prohibitively expensive.
- The calculation of these parameters via MD simulation may prove to be reliable and cost efficient.

Background

- MD simulations will be used in conjunction with a method called *thermodynamic integration*.
- Thermodynamic integration (TI) is a process of growing a single solute molecule into a bulk solvent phase.
  1. This is accomplished by incorporating an additional parameter (λ) into the standard solvent-solute interactions.
  2. Using the produced trajectory files from a battery of simulations ranging from $0 < \lambda \leq 1.0$, $\langle dU/d\lambda \rangle$ can be plotted against λ to give the TI curve.
- The calculation of ΔG^{solv} will be used to derive biologically relevant thermodynamic data, such as Henry's Law constants and $\log K_{ow}$ va

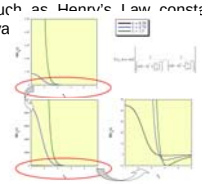


Figure 1a: An illustration of softened van der Waals potentials used for thermodynamic integration

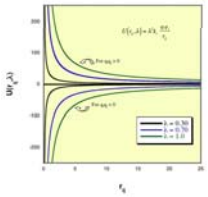


Figure 1b: An illustration of softened electrostatic potentials used for thermodynamic integration

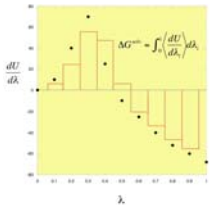
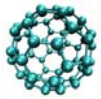


Figure 2: Prototype of thermodynamic integration curve

Objectives

- To calculate the Henry's Law coefficients and $\log K_{ow}$ parameters for C_{60} and several variations of the POSS molecule.



A C_{60} buckminsterfullerene

- To observe the response in solubility with change in fullerene aspect ratio.
- To elucidate the relationship between the solubility of the POSS monomer and varying functional group types, such as -H, $-(CH_3)_n$, -OH, and -F.

An -H functionalized POSS monomer

Simulation Detail

- NPT ensemble with Nosé-Hoover thermostat/barostat
  1. T = 298.15 K
  2. P = 1.01325
  3. N ~ 1,000 - 10,000
- Molecular Styles
  1. TRAPPE force field for alcohols
  2. Rigid SPC/E for water
  3. Curro PDMS force field for POSS

Sample Curves and Results

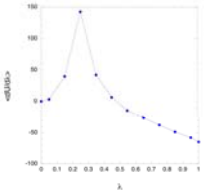


Figure 3a: TI curve for van der Waals contribution in H-POSS/water system

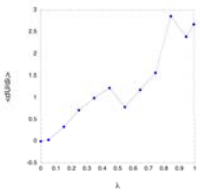


Figure 3b: TI curve for electrostatic contribution in H-POSS/water system

- H-POSS/Octanol

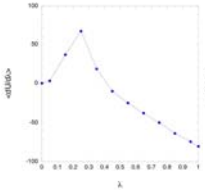


Figure 4a: TI curve for van der Waals contribution in H-POSS/octanol system

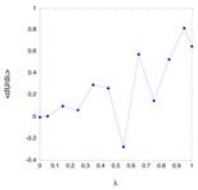


Figure 4b: TI curve for electrostatic contribution in H-POSS/octanol system

Particle	Solvent	ΔG^{solv} (kcal/mol)	$H_{U,V}$ (kbar)
H-POSS	Water	8.21	1.44×10^{6}
	Octanol	-13.39	2.40×10^{-11}
Methyl-POSS	Water	8.95	4.94×10^{6}
	Octanol	-23.48	9.61×10^{-16}
C_{60}	Water	4.90	5.83×10^{3}
	Octanol	-26.16	1.04×10^{-20}

Conclusions

Particle Solubility

- Hydrophobic qualities mirror experimental findings
- All particles energetically favor the octanol phase, and will likely strongly partition into the organic phase
- Highly non-ideal mixtures of the particles in octanol disallows K_{ow} formulations using ΔG^{solv}. Alternative methodologies, such as UNIFAC, will be required.

Acknowledgements

- The P.T. Cummings Group
- The POSS Group (UVA and UM)
- NSF grant DMR-0103399