

Electrostatic and Induction Effects in the Solubility of Water in Alkanes

Dilip Asthagiri^{C, S} and Arjun Valiya Parambathu

*Chemical and Biomolecular Engineering, Rice University, Houston, TX, U.S.A.
dna6@rice.edu*

Deepti Ballal

Material Science and Engineering, Ames Laboratory, Ames, IA, U.S.A.

Walter Chapman

Chemical and Biomolecular Engineering, Rice University, Houston, TX, U.S.A.

Intermolecular potential models for water and alkanes describe pure component properties fairly well, but fail to reproduce properties of water-alkane mixtures. Understanding interactions between water and non-polar molecules like alkanes is important not only for the hydrocarbon industry but has implications to biological processes as well. Although non-polar solutes in water have been widely studied, much less work has focused on water in non-polar solvents. Experiments show that at 298 K and 0.101 325 MPa (1 atm) pressure, the transfer free energy of water from its vapor to liquid normal alkanes C_nH_{2n+2} ($n = 5...12$) is negative. Earlier it was found both on the basis of modeling using the statistical associating fluid theory (SAFT) and atomistic simulations with the united-atom TraPPE model for alkanes and the SPC/E model for water, the attractive alkane-water cross interaction required to capture this behavior was much larger than predicted on the basis of the pure component properties and standard mixing rules. In this talk we will present a revised calculation of the transfer free energy using the polarizable AMOEBA and the non-polarizable Charmm General (CGenFF) force fields. We test both the AMOEBA03 and AMOEBA14 water models; the former has been validated with the AMOEBA alkane model while the latter is a revision of AMOEBA03 to better describe liquid water. We calculate the transfer free energy using the test particle method. With CGenFF, the transfer free energy is positive and the error relative to experiments is about 1.5 kT. With AMOEBA, the transfer free energy is negative and deviations relative to experiments are between 0.25 kT (AMOEBA14) and 0.5 kT (AMOEBA03). Quantum chemical calculations in a continuum solvent suggest that zero point effects may account for some of the deviation. Force field limitations notwithstanding, electrostatic and induction effects, commonly ignored in consideration of water-alkane interactions, appear to be decisive in the solubility of water in alkanes.