

Origins of the Solvent Chain-Length Dependence of Gibbs Free Energies of Transfer

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Abstract

Experimentally measured partition coefficients show that the solubilities of small solutes in normal alkanes depend on the solvent chain length (n_C). The causes for this n_C dependence have not yet been unambiguously determined, and there is considerable controversy as to whether different interactions with methyl and methylene groups or entropic Flory-Huggins-like effects might play the major role. We have performed Gibbs-ensemble Monte Carlo simulations to study the vapor-liquid partitioning of methane in normal alkanes (with 6 to 12 carbon atoms) and related model solvents. The simulations show that the increase in solvent density with increasing n_C is the main origin of the n_C dependence for normal alkanes, that is the solute molecule feels a different environment depending on the alkane chain length.