Solubility in Supercritical Carbon Dioxide: the Importance of the Poynting Correction and Entrainer Polarity

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Gibbs ensemble Monte Carlo simulations using the TraPPE force field were carried out to investigate the effects of entrainers on the solvent strength of supercritical carbon dioxide. Two low-volatility solute species, hexamethylbenzene and benzoic acid, were chosen as solutes with varying polarity, along with two entrainers, methanol and n-octane. In order to reproduce the experimentally observed pressure dependence of the solubility, we find that the application of the Poynting correction to the saturated vapor pressure of the solute species is crucial. Increased solubility with pressure, then, is driven by the increasing saturated vapor pressure of the solute not an increase in the solvent strength of carbon dioxide. The greatest enhancement (~10) was seen for the polar solute–polar entrainer combination, with small enhancements also exhibited for polar solute–nonpolar entrainer and nonpolar solute–nonpolar entrainer combinations. For the polar solute–polar entrainer system, the enhancement arises primarily due to preferential solvation of the solute by the entrainer driven by the formation of hydrogen bonds, whereas no evidence of specific solvation is present in the other systems.