Isolating the Effective Intermolecular Potential for Water-Alkane Interactions from Water Solubility: Implications for Theory and Simulation

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Intermolecular potential models for water and alkanes describe pure component properties fairly well, but fail to reproduce solubility of water in alkanes. Understanding interactions between water and non-polar molecules like alkanes has important implications for flow assurance in gas processing and oil production as well as in biological processes. Although non-polar solutes in water have been widely studied, much less work has focused on water in non-polar solvents. We use molecular simulation and the SAFT model to calculate the solubility of water in different alkanes (methane to dodecane) at ambient conditions where the water content in alkanes is very low so that the non-polar water-alkane interactions determine solubility. Only the alkane-rich phase is simulated since the fugacity of water in the water rich phase is calculated from an accurate equation of state. Using the SPC/E model for water and TraPPE model for alkanes along with Lorentz-Berthelot mixing rules for the cross parameters produces a water solubility that is an order of magnitude lower than the experimental value. It is found that an effective water Lennard-Jones energy $\varepsilon W/k=220$ K is required to match the experimental water solubility in TraPPE alkanes. This number is much higher than used in most simulation water models (SPC/E: $\varepsilon W/k=78.2$ K). It is surprising that the interaction energy obtained here is also higher than the water-alkane interaction energy predicted by studies on solubility of alkanes in water. The reason for this high water-alkane interaction energy is not completely understood. Some factors that might contribute to the large interaction energy, such as polarizability of alkanes, octupole moment of methane, and clustering of water at low concentrations in alkanes, are examined. It is found that, though important, these factors do not completely explain the anomalously strong attraction between alkanes and water observed experimentally.