

Thermodynamic Functions of Solvation of Hydrocarbons, Noble Gases, and Hard Spheres in Tetrahydrofuran-Water Mixtures

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Abstract

© 2015 American Chemical Society. Thermodynamic solvation properties of mixtures of water with tetrahydrofuran at 298 K are studied. The Gibbs free energies and enthalpies of solvation of n-octane and toluene are determined experimentally. For molecular dynamics simulations of the binary solvent, we have modified a TraPPE-UA model for tetrahydrofuran and combined it with the SPC/E potential for water. The excess thermodynamic functions of neon, xenon, and hard spheres with two different radii are calculated using the particle insertion method. Simulated and real systems share the same characteristic trends for the thermodynamic functions. A maximum is present on dependencies of the enthalpy of solvation from the composition of solvent at 70-90 mol % water, making it higher than in both of the cosolvents. It is caused by a high enthalpy of cavity formation in the mixtures rich with water due to solvent reorganization around the cavity, which is shown by calculation of the enthalpy of solvation of hard spheres. Addition of relatively small amounts of tetrahydrofuran to water effectively suppresses the hydrophobic effect, leading to a quick increase of both the entropy and enthalpy of cavity formation and solvation of low polar molecules.

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