

Aggregation in Dilute Solutions of 1-Hexanol in n-Hexane: A Monte Carlo Simulation Study

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Abstract

Configurational-bias Monte Carlo simulations in the isobaric-isothermal ensemble using the non-polarizable TraPPE-UA (transferable potentials for phase equilibria–united atom) force field were performed to study the aggregation of 1-hexanol in n-hexane. The spatial distribution of alcohols was sampled efficiently using special Monte Carlo moves. Analysis of the microscopic structures for 1%, 3%, and 5% solutions at a temperature of 298.15 K and a pressure of 101.3 kPa shows strong aggregation with a preference for tetramers and pentamers for all three concentrations. About half of these tetramers and pentamers are found in cyclic aggregates. The enthalpies for the formation of clusters of a specific size were determined from simulations of a 3% solution at temperatures ranging from 298.15 to 328.15 K. The free energies and enthalpies of cluster formation show the large influences of hydrogen-bond cooperativity that favors clusters larger than dimers, but a decreasing enthalpy gain and an increasing entropic penalty prevents the formation of very large clusters. These results have important implications for the thermodynamic modeling of hydrogen-bonding fluids which commonly use a constant value for the free energy of hydrogen-bond formation. Overall agreement with Fourier-transform infrared spectroscopic measurements on the extent of hydrogen bonding for the same mixtures is satisfactory.

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