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Monte Carlo Calculations for Alcohols and Their Mixtures with Alkanes. Transferable Potentials for Phase Equilibria. 5. United-Atom Description of Primary, Secondary and Tertiary Alcohols

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Abstract

The Transferable Potentials for Phase Equilibria–United Atom (TraPPE–UA) force field for hydrocarbons is extended to primary, secondary, and tertiary alcohols by introducing the following (pseudo-)atoms: common hydroxyl O and H for all alcohols, α -CH₃, α -CH₂, α -CH, and α -C for methanol, primary, secondary, and tertiary alcohols, respectively. In the TraPPE–UA force field, the nonbonded interactions of these sites are governed by Lennard-Jones 12–6 potentials and Coulombic interactions of fixed partial charges. The values of these partial charges were borrowed from the Optimized Potentials for Liquid Simulations–United Atom (OPLS–UA) force field [Jorgensen, W. L. *J. Phys. Chem.* **1986**, *90*, 1276]. The Lennard-Jones well depth and size parameters for the new interaction sites were determined by fitting to the single-component vapor-liquid phase equilibria of a few selected model compounds. While the well-depth parameters for the α -carbons could be taken directly from the TraPPE–UA parameters for the corresponding pseudoatoms in alkanes, the size parameters required small adjustments to reflect the differences in C–C and C–O bond lengths. Coupled-decoupled configurational-bias Monte Carlo simulations in the Gibbs and grand-canonical ensembles were carried out to calculate the one-component vapor-liquid coexistence curves for methanol, ethanol, propan-1-ol, propan-2-ol, butan-2-ol, 2-methylpropan-2-ol, pentan-1-ol, pentane-1,5-diol, and octan-1-ol, and to determine the binary phase diagrams for the mixtures of *n*-hexane/methanol and *n*-hexane/ethanol. It was found that the phase equilibria of the pure alcohols are accurately described by the TraPPE–UA force field, with mean unsigned deviations of about 1% from the experimental data for the normal boiling points and the saturated liquid densities. The azeotropic compositions for *n*-hexane/methanol and *n*-hexane/ethanol were predicted to be 0.340 at $T = 448.15$ K and 0.454 at 413.15 K and (in mole fraction of *n*-hexane), which are in good agreement with the experimental results of 0.288 and 0.440, respectively. Analysis of the structures of the *n*-hexane/methanol mixtures shows evidence for significant enhancements in the local mole fraction of alcohols in the vicinity of other alcohols. The magnitude of these local enhancements decreases with increasing alcohol concentration, but the change is gradual and no discontinuity was observed at the azeotropic composition.