

Vapor–liquid phase equilibria of triacontane isomers: Deviations from the principle of corresponding states

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Abstract

Coupled-decoupled configurational-bias Monte Carlo simulations in the Gibbs ensemble were carried out to determine the vapor–liquid coexistence curves for *n*-triacontane and 2,6,10,15,19,23-hexamethyltetracosane (squalane). The transferable potentials for phase equilibria–united atom (TraPPE–UA) force field was used for these simulations. The simulated systems consisted of 200 molecules and the production periods extended to 100,000 Monte Carlo cycles, a system size about twice as large and a simulation length about one order of magnitude longer than used in previous simulations. The simulation results are in satisfactory agreement with the available experimental data. Examination of the coexistence curves in reduced units for the two triacontane isomers and for *n*-octane and 2,5-dimethylhexane shows that both molecular weight and branching can lead to deviations from the principle of corresponding states. Analysis of the molecular structures in the vapor and liquid phases points to a partial collapse (self-solvation) of the triacontane isomers as the likely origin of the deviations from the principle of corresponding states.

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