

Pressure dependence of the vapor–liquid–liquid phase behavior in ternary mixtures consisting of *n*-alkanes, *n*-perfluoroalkanes and carbon dioxide

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Abstract

Expansion of an organic solvent by an inert gas can be used to tune the solvent’s liquid density, solubility strength, and transport properties. In particular, gas expansion can be used to induce miscibility at low temperatures for solvent combinations that are biphasic at standard pressure. Configurational-bias Monte Carlo simulations in the Gibbs ensemble were carried out to investigate the vapor–liquid–liquid equilibria and the microscopic structures for two ternary systems: *n*-decane/*n*-perfluorohexane/CO₂ and *n*-hexane/*n*-perfluorodecane/CO₂. These simulations employed the united-atom version of the transferable potential for phase equilibria (TraPPE–UA) force field. Initial simulations for binary mixtures of *n*-alkanes and *n*-perfluoroalkanes showed that special mixing parameters are required for the unlike interactions of CH_{*x*} and CF_{*y*} pseudo-atoms to yield satisfactory results. The calculated upper critical solution pressures for the ternary mixtures at a temperature of 298 K are in excellent agreement with the available experimental data and predictions using the SAFT-VR (statistical associating fluid theory of variable range) equation of state. The simulations yield asymmetric compositions for the coexisting liquid phases and different degrees of microheterogeneity as measured by local mole fraction enhancements.

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