

Binary phase behavior and aggregation of dilute methanol in supercritical carbon dioxide: A Monte Carlo simulation study

John M. Stubbs and J. Ilja Siepmann*

Departments of Chemistry and of Chemical Engineering and Material Science,
University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455-0431, USA

Abstract

Configurational-bias Monte Carlo simulations in the Gibbs and isobaric-isothermal ensembles using the TraPPE force field were carried out to investigate the thermophysical properties of mixtures containing supercritical carbon dioxide and methanol. The binary vapor-liquid coexistence curves were calculated at 333.15 and 353.15 K and are in excellent agreement with experimental measurements. The self-association of methanol in supercritical carbon dioxide was investigated over a range of temperatures and pressures near the mixture critical point. The temperature dependence of the equilibrium constants for the formation of hydrogen-bonded aggregates (from dimer to heptamer) allowed for the determination of the enthalpy of hydrogen bonding, ΔH_{HB} , in supercritical carbon dioxide with values for ΔH_{HB} of about 15 kJ mol⁻¹ falling within the range of previously proposed values. No strong pressure dependence was observed for the formation of aggregates. Apparently the decrease of the entropic penalty and of the enthalpic benefit upon increasing pressure or solvent density mostly cancel each other's effect on aggregate formation.

* Corresponding author: siepmann@chem.umn.edu