

# Partial Molar Volume and Solvation Structure of Naphthalene in Supercritical Carbon Dioxide: A Monte Carlo Simulation Study

John M. Stubbs,<sup>†</sup> Dylan D. Drake-Wilhelm, and J. Ilja Siepmann\*

*Departments of Chemistry and of Chemical Engineering and Materials Science,  
University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455-0431*

## Abstract

Monte Carlo simulations were used to investigate the solvation of naphthalene in supercritical carbon dioxide at a temperature of 308.4 K just above the solvent's critical temperature and at pressures of 74.6, 79.7, 87.8, and 310.2 bar covering a range from just below to far above the solvent's critical pressure. The Monte Carlo simulations were carried out in the isobaric-isothermal ensemble and employed the transferable potentials for phase equilibria (TraPPE) force field. Systems containing 2000 carbon dioxide molecules and from 0 to 4 solute molecules were used for all four state points, and additional simulations with 16000 solvent molecules were carried out at  $p = 79.7$  bar. In agreement with experiment, the simulations yield large negative partial molar volumes of naphthalene near the critical pressure at 79.7 bar, with values of  $-4340 \pm 750$  and  $-3400 \pm 620$  cm<sup>3</sup> mol<sup>-1</sup> for the 2000 and 16000 molecule systems, respectively. Structural analysis through radial distribution functions and the corresponding number integrals yields good agreement with neutron diffraction data and shows evidence for a long-range density enhancement around solutes, but lacking any specific solute-solvent clustering. Solvatochromatic shifts estimated from the local solvent structure correlate well with the experimental data over the entire pressure range.

---

<sup>†</sup>Present address: Department of Chemistry, Grinnell College, Grinnell, Iowa 50112

\*Corresponding author: siepmann@chem.umn.edu