submitted for publication to *The Journal of Physical Chemistry B*

Simulation Studies of Retention in Isotropic or Oriented Liquid n-Octadecane

Collin D. Wick,[1] J. Ilja Siepmann,[*,1] and Mark R. Schure[2]

[1] *Departments of Chemistry and of Chemical Engineering and Materials Science, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455-0431, U.S.A.*

[2] *Theoretical Separations Science Laboratory, Rohm and Haas Company, 727 Norristown Road, Spring House, Pennsylvania 19477, U.S.A.*

Abstract

In gas-liquid chromatography with liquid-crystalline stationary phases and in liquid-liquid chromatography with polymeric bonded phases, the retention selectivity has been linked to the orientation of the retentive phase. In an effort to explore the nature of this effect, molecular simulations utilizing the configurational-bias Monte Carlo technique in the Gibbs ensemble were performed. Through this simulation technique the partition coefficients of benzene, naphthalene, *n*-heptane, and *n*-dodecane were calculated when partitioning takes place between an oriented or an isotropic liquid *n*-octadecane phase of equal density and a helium gas phase. The calculated partition coefficients demonstrate that the *n*-alkane solutes prefer the oriented *n*-octadecane phase over the isotropic one, while the opposite behavior (but to a smaller extent) is observed for benzene and naphthalene solutes. The *n*-alkane solute transfer into the oriented *n*-octadecane phase is favored by a smaller entropic penalty and a minor enthalpic gain compared to the isotropic phase. While the entropic cost for partitioning into the liquid phases increases by about 40% from *n*-heptane to *n*-dodecane, there is only a small increase of about 8% from benzene to naphthalene. Minor preferential alignment was observed for *n*-dodecane and naphthalene in the oriented liquid phase, but no significant differences are observed for the solutes' conformational properties in the two solvent environments.

Keywords: Thermodynamics of solute transfer; *n*-octadecane phase; molecular simulation