

Temperature dependence of hydrogen bonding: An investigation of the retention of primary and secondary alcohols in gas-liquid chromatography

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ABSTRACT

Configurational-bias Monte Carlo simulations in the Gibbs Ensemble were carried out to investigate the analyte partitioning of *n*-pentane, *n*-hexane, *n*-heptane, 1-propanol, and 2-propanol into a dioctyl ether retentive (stationary) phase used in gas-liquid chromatography. The united-atom version of the TraPPE (transferable potentials for phase equilibria) force field was used to model all analytes and the solvent. The analyte partition coefficients, Gibbs free energies of transfer, and Kovats retention indexes were calculated at four different temperatures ranging from 303.15 K to 348.15 K. Although hydrogen bonding is a major contributor to the retention of the alcohol analytes over the entire temperature range, its importance for the separation factor between the primary and secondary alcohol decreases substantially with increasing temperature. The enthalpies and entropies for hydrogen bond formation were also estimated from the temperature-dependence of the corresponding equilibrium constants. In agreement with experimental measurements, it is observed that the hydrogen bond involving 1-propanol is enthalpically favored, but entropically disfavored compared to 2-propanol.

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