

Influence of Analyte Overloading on Retention in Gas-Liquid Chromatography: A Molecular Simulation View

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ABSTRACT

In an attempt to elucidate the molecular basis for concentration (isotherm) effects on retention in gas-liquid chromatography, configurational-bias Monte Carlo simulations in the Gibbs Ensemble were carried out to investigate changes in analyte partitioning caused by overloading the chromatographic system with either an alkane or an alcohol. Squalane was used as the stationary phase material, and the analytes included *n*-pentane, *n*-hexane, *n*-heptane, butan-1-ol, and pentan-1-ol. Three systems were studied that differed in the mobile phase composition: (i) a helium vapor, (ii) a *n*-hexane vapor, and (iii) a pentan-1-ol saturated helium vapor. While the amount of helium that partitions into the stationary phase is very small, both *n*-hexane and pentan-1-ol partition strongly into and thereby swell the stationary phase. Although the swelling of the stationary phase leads to a reduction in the partition coefficients for the alkane solutes for both the *n*-hexane and pentan-1-ol swollen stationary phases, the effects on the alcohol solutes differ markedly. Whereas saturation by *n*-hexane causes a decrease of the alcohol partition constants (to a similar extent as for the alkane solutes), the saturation by pentan-1-ol causes a dramatic increase of the alcohol partition coefficients, e.g., a butan-1-ol analyte elutes before *n*-pentane for both helium or *n*-hexane vapor phases, but elutes after *n*-hexane for the pentan-1-ol saturated vapor phase. The formation of hydrogen-bonded alcohol clusters in the liquid phase is the microscopic origin for the dramatic effect of pentan-1-ol saturation on the retention of alcohols.