Understanding Retention in Reversed-phase Liquid Chromatography and Size Exclusion Chromatography: Insights from Molecular Simulations

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Chromatographic separations involve a delicate interplay of enthalpic and entropic factors arising from interactions of the analyte molecules with the stationary and mobile phases, where the former can be altered by the presence of solvent (mobile-phase) molecules. Particle-based simulations allow one to probe chromatographic systems on the molecular level and to provide detailed information on structural characteristics and retention mechanisms. This talk will highlight recent applications of configurational-bias Monte Carlo simulations in the Gibbs ensemble to understand the retention mechanisms of small flexible analytes and of shape-constrained polycyclic aromatic hydrocarbons in reversed-phase liquid chromatography (RPLC) and of homo- and co-polymers in size exclusion chromatography (SEC). Accurate molecular mechanics force fields are used for the RPLC systems and enable direct comparison to experimental retention data, and the simulations elucidate the influence of mobile-phase composition, embedded polar groups, and grafting density for alkyl-silane based stationary phases. In contrast, simplified coarse-grain models are used for the SEC simulations and comparisons are made to theoretical predictions.