A Monte Carlo Study of Structure and Retention in Reversed-Phase Liquid Chromatography Systems

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Various structural models for the stationary phase and driving forces for analyte retention in reversed-phase liquid chromatography (RPLC) have been suggested from thermodynamic and spectroscopic measurements and theoretical considerations. To provide a molecular picture of a typical RPLC system and the retention process, configurational-bias Monte Carlo simulations in the Gibbs ensemble are performed for dimethyl octadecyl silane bonded to a model siliceous substrate (at a coverage of 2.9 micro mole per square meter) and in contact with mobile phases containing various water/methanol concentrations. Analytes investigated include normal alkanes (from methane to butane) and primary alcohols (from methanol to propanol). It is shown that the alkyl chain conformation depends only weakly on the solvent composition. Residual surface silanol groups provide hydrogen bonding sites that lead to the formation of substrate bound water and methanol clusters, including bridging clusters that penetrate the bonded phase region all the way from the substrate to the interface with the mobile phase. In contrast, the analyte partitioning is strongly influenced by changes in the mobile phase composition.