

# Chain Conformation and Solvent Partitioning in Reversed-Phase Liquid Chromatography: Monte Carlo Simulations for Various Water/Methanol Concentrations

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## Abstract

Many structural models for the stationary phase in reversed-phase liquid chromatography (RPLC) systems have been suggested from thermodynamic and spectroscopic measurements and theoretical considerations. To provide a molecular picture of chain conformation and solvent partitioning in a typical RPLC system, a particle-based Monte Carlo simulation study is undertaken for a dimethyl octadecyl ( $C_{18}$ ) bonded stationary phase on a model siliceous substrate in contact with mobile phases having different methanol/water concentrations. Following upon previous simulations for gas–liquid chromatography and liquid–liquid phase equilibria, the simulations are conducted using the configurational-bias Monte Carlo method in the Gibbs ensemble and the transferable potentials for phase equilibria force field. The simulations are performed for a chain surface density of  $2.9 \mu\text{mol}/\text{m}^2$ , which is a typical bonded-phase coverage for mono-functional alkyl silanes. The solvent concentrations used here are pure water, approximately 33% and 67% mole fraction of methanol, and pure methanol. The simulations show that the chain conformation depends only weakly on the solvent composition. Most chains are conformationally disordered and tilt away from the substrate normal. The interfacial width increases with increasing methanol content and, for mixtures, the solvent shows an enhancement of the methanol concentration in a 10 Å region outside the Gibbs dividing surface. Residual surface silanol groups are found to provide hydrogen bonding sites that lead to the formation of substrate bound water and methanol clusters, including bridging clusters that penetrate from the solvent/chain interfacial region all the way to the silica surface.

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