

# Molecular Simulation of Concurrent Gas–Liquid Interfacial Adsorption and Partitioning in Gas–Liquid Chromatography

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## Abstract

The importance of adsorption at the gas–liquid interface on retention in gas–liquid chromatography has been controversial since the pioneering work of Martin in the 1960s. In particular, experimental studies using chromatographic and static techniques to quantify partitioning and adsorption of polar analytes on nonpolar liquid phases yielded conflicting results. In this work, Monte Carlo simulations were carried out for a free-standing liquid slab of squalane surrounded by a helium vapor to investigate interfacial adsorption effects for *n*-pentane, *n*-hexane, *n*-heptane, 1-butanol, and benzene solutes at infinite dilution. The simulations indicate preferential adsorption for the flexible alkane and alcohol solutes in a narrow region just inside the Gibbs dividing surface, but no such effect was observed for the rigid benzene solute. Nevertheless, the extent of the interfacial enrichment is small, as measured by the partition coefficient between the bulk liquid and the interfacial region ( $K_{\text{bulk-interface}} \approx 1.5$ ). In addition, a region that is slightly depleted for all solute molecules is found to separate the interfacial and bulk regions of the squalane slab. Thus, adsorption at the gas–liquid interface should *not* contribute significantly to the retentive behavior observed in gas–liquid chromatography on nonpolar capillary columns, but might play a role in packed-bed columns with low bonded-phase loadings. The origin for the small enrichments and more favorable free energies for solutes at the interface is that the enthalpies of solvation decrease to a smaller relative extent than the entropies of solvation compared to the bulk liquid.

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