



A molecular simulation study of the effects of stationary phase and solute chain length in reversed-phase liquid chromatography

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ABSTRACT

The effects of stationary phase and solute chain length are probed by carrying out Monte Carlo simulations of dimethyl triacontyl (C_{30}), dimethyl octadecyl (C_{18}), dimethyl octyl (C_8), and trimethyl (C_1) silane grafted, and bare silica stationary phases in contact with a water/methanol mobile phase and by examining the retention of solutes from 1 to 14 carbons in length. Fairly small differences in structure are observed when comparing the C_{30} , C_{18} , C_8 systems and the retention mechanism of nonpolar alkane solutes shows contribution from both partitioning and adsorption on all three of these stationary phases. Unlike in the other systems, the mobile phase solvent is highly structured at its interface with the C_1 and bare silica phases, the former being enriched in methanol and the latter in water. Alkane solutes are unretained at the bare silica surface while alcohol solutes are only slightly enriched at the silica surface due to hydrogen bonding with surface silanols and surface bound solvent. With regard to solute size, it appears that the retention mechanism is not affected by the chain length of the solute.

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1. Introduction

Reversed-phase liquid chromatography (RPLC) is an extremely versatile and widely used technique for chemical separations, purifications, and analyses. One of the powerful aspects of the RPLC technique is the number of chromatographic parameters that can be adjusted in order to achieve the desired selectivity and/or efficiency for a given separation. However, a molecular-level description of how changes in these parameters lead to changes in retention and selectivity remains lacking for many RPLC systems [1]. A better understanding of these parameters should aid in the optimization of current RPLC systems and in the development of new separation technologies.

Particle-based simulations have been employed by a few research groups to study structural, dynamic, and thermodynamic properties of RPLC systems [2–13]. It has been the ongoing goal of this research group to systematically investigate various chromatographic parameters including retention mechanisms using advanced molecular simulation techniques that allow for a

molecular-level viewpoint. In previous reports we have detailed the effects of solvent composition [14–17], grafting density [18,19], polar-embedded groups [20], pressure [21], and pore shape [21] on the structure of the RPLC stationary phase and on the molecular mechanism of retention. In the current work, we examine what effect the length of the alkyl chains in the stationary phase has on structure and retention in RPLC and also if the solute chain length plays any role in altering the retention mechanism.

The two most popular stationary phase chain lengths used in RPLC are C_8 and C_{18} ; however, numerous studies of chain lengths ranging from C_1 to over C_{30} have appeared in the literature. Generally, it is observed that retention increases, but selectivity is little affected with increasing stationary phase chain length [22–29]. However, it should be noted that the selectivity between geometrically constrained solutes, such as polycyclic aromatic hydrocarbons, can increase with longer chain lengths which has been used to infer that the longer chains are more conformationally ordered [30]. This increased order has been confirmed through spectroscopic measurements [31–34].

With regard to solute chain length, it has been observed from retention measurements with various homologous series (for example normal alkanes or alcohols with varying chain length) that retention increases with increasing solute length, but there is a break in the slope in plots of $\log k'$ versus number of carbons [27,35,36]. This break occurs about where the number of carbons

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in the solute exceeds the number of carbons in the stationary phase chains. From this observation it was suggested that the solutes fully embed themselves (partition) into the stationary phase until their length exceeds the length of the stationary phase and, after this, the remaining portion of the solute is forced to reside outside the stationary phase and adsorb at the surface. However, a regular curvature has been observed in plots of $\log k'$ versus homolog number in some cases [37].

In the present study, Gibbs ensemble simulations using efficient configurational-bias Monte Carlo (CBMC) algorithms and transferable force fields were carried out to probe chain length effects in RPLC. The structural properties and retention behavior were investigated for five stationary phases differing in the length of the alkyl silane ligand (C₃₀, C₁₈, C₈, C₁, and bare silica). The effects of solute chain length (ranging from ethane to tetradecane) on the retention mechanism were studied for the C₈ stationary phase.

2. Simulation details

To examine the effects of chain length in RPLC, coupled-decoupled configurational-bias Monte Carlo simulations (CBMC) [38–41] in the isobaric-isothermal version of the Gibbs ensemble [42] are employed. The simulations make use of three separate simulation boxes that are in thermodynamic contact but do not share an explicit interface. The first simulation box is elongated with $L_x = 20.0$ Å, $L_y = 26.0$ Å, $L_z = 90.0$ Å. The center of this box contains a silica slab consisting of five layers of β -cristobalite with its two (1 1 1) surfaces exposed in the x - y plane. In one set of simulations the silanols on these two surfaces were left unreacted, whereas in the other sets of simulations these surfaces were modified by the grafting of trimethyl (C₁), dimethyl octylsilane (C₈), dimethyl octadecylsilane (C₁₈), or dimethyl triacontylsilane chains (C₃₀) at a density of $2.9 \mu\text{mol}/\text{m}^2$ (9 chains on each surface) resulting in a residual silanol density of $4.8 \mu\text{mol}/\text{m}^2$ (15 silanols on each surface). In each of these four systems, the silane chains were placed in the exact same surface arrangement. In contact with this stationary phase, and connected through the periodic boundaries used in the simulations, is the mobile phase solvent. Thus, the setup in this first box corresponds to a planar slit pore. Snapshots from the simulations of each system showing one of the silica surfaces in contact with the mobile phase solvent are presented in Fig. 1.

The second simulation box contains a bulk mobile phase reservoir and the third box a helium vapor phase. These boxes are cubic and their volumes are allowed to fluctuate in response to the external pressure. The simulations probing the effects of changes in the bonded-phase chain length were carried out at a temperature of 323 K and a pressure of 10 atm. For these simulations, the mobile phase consisted of a water/methanol mixture containing 33% mol-fraction ($\approx 50\%$ volume fraction) methanol and the probe solutes utilized were C₁ to C₄ normal alkanes and alcohols. For the studies of solute chain length only the C₈ stationary phase was examined; the mobile phase consisted of 67% mol-fraction ($\approx 80\%$ volume fraction) methanol, the temperature was 298 K, the pressure was 10 atm, and the probe solutes were normal alkanes solutes up to 14 carbons in length. A detailed description of the simulation setup and methodology and a discussion on the merits of a three-box Gibbs ensemble setup can be found in a recent review article [43].

To describe the intra- and intermolecular interactions in the model RPLC systems, the TIP4P model [44] was used for water, the silica substrate was represented by a zeolite potential with Lennard-Jones sites on oxygen atoms [45] and explicit charges on silicon, oxygen, and the dangling hydrogens [46,47], and the interactions of all other species (methanol, alkyl ligands, and alkane and alcohol solutes) were described by the united-atom version of

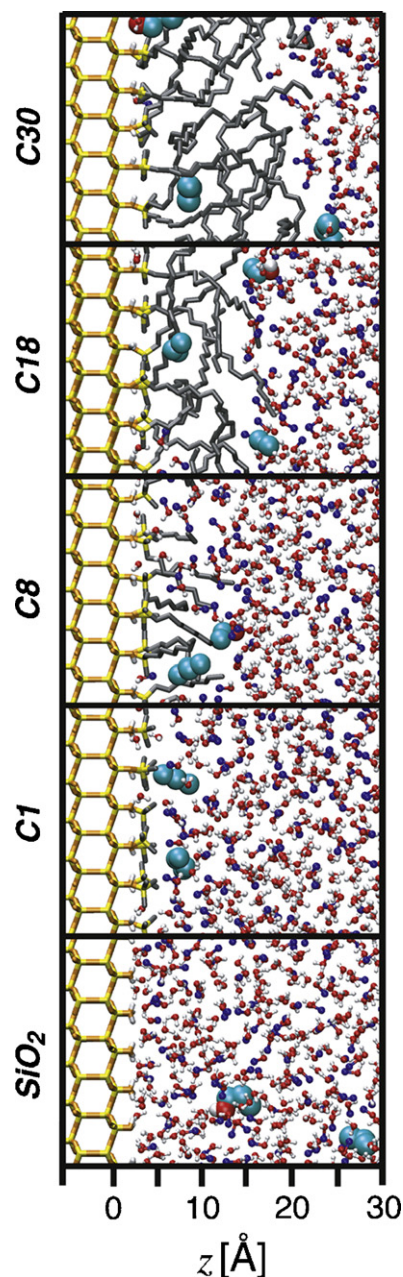


Fig. 1. Simulations snapshots of the five systems. The stationary phase is shown as tubes with silicon in yellow, oxygen in orange, hydrogen in white and carbon in black. The mobile phase is shown in the ball and stick representation with oxygen in red, hydrogen in white, and carbon in blue. The analyte molecules are depicted by large spheres with oxygen in red, hydrogen in white, and carbon in cyan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the transferable potentials for phase equilibria (TraPPE) force field [47,48]. Lennard-Jones interactions were truncated at 10 Å and Coulomb interactions were evaluated with the Ewald summation technique [49] using a direct space cutoff of 10 Å and a convergence parameter of $\kappa = 0.28$. The alkyl ligands, solute molecules, and methanol were treated as semi-rigid species with allowance for bond angle bending and dihedral motion but the bond length being kept rigid, whereas water molecules were kept rigid.

For each model RPLC system, eight independent simulations were carried out. Each independent simulation was equilibrated for at least 2×10^5 Monte Carlo (MC) cycles followed by an additional 5×10^5 MC cycles for production. One MC cycle corresponds

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