Simulated molecular-scale interaction of supercritical fluid mobile and stationary phases

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ABSTRACT

In supercritical fluid chromatography, molecules from the mobile phase adsorb on the stationary phase. Stationary-phase alkylsilane-terminated silica surfaces might adsorb molecules at the silica, among the silanes, on a silane layer, or in pore space between surfaces. Mobile phases of carbon dioxide, pure and modified with methanol, and stationary phases were simulated at the molecular scale. Classical atomistic force fields were used in Gibbs-ensemble hybrid Monte Carlo calculations. Excess adsorption of pure carbon dioxide mobile phase peaked at fluid densities of 0.002–$0.003 \ \text{Å}^{-3}$. Mobile phase adsorption from 7% methanol in carbon dioxide peaked at lower fluid density. Methanol was preferentially adsorbed from the mixed fluid. Surface silanes prevented direct interaction of fluid-phase molecules with silica. Some adsorbed molecules mixed with tails of bonded silanes; some formed layers above the silanes. Much adsorption occurred by filling the space between surfaces in the stationary-phase model. The distribution in the stationary phase of methanol molecules from a modified fluid phase varied with pressure.

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1. Introduction

Conditions at the inlet in supercritical fluid chromatography (SFC) are customarily above the critical temperature and pressure of carbon dioxide, the most common major component of the mobile phase. A common stationary phase has been silica particles modified with alkylsilanes, especially octadecyldimethylsilane (ODS). Adsorption of CO_2 on the stationary phase was observed by Parcher and Strubinger [1], excess adsorption peaking at a density lower than the critical density of CO_2. Such adsorption has been said to alter retention [2,3]. There is a critical-density adsorption peak [4] when the temperature is near (e.g., within 0.2% of [5]) the critical temperature, but that near-critical phenomenon is not an issue in practical SFC. Of concern in this work is the adsorption of mobile phase that occurs under common SFC conditions, adsorption that has been described as an adsorbed layer [6]. The present work simulates the adsorption at the molecular scale to determine where the adsorption occurs and how it is affected by surface modification, temperature, and the addition of methanol to the mobile phase.

2. Material and methods

2.1. Hybrid Gibbs-ensemble Monte Carlo modeling of SFC mobile and stationary phases

Monte Carlo modeling in the Gibbs ensemble uses two boxes of molecules. In this work, the fluid box contained the mobile phase, which was carbon dioxide, either pure or modified by addition of 7% methanol: that is, 7% by mole. The fluid box was cubic, its volume free to fluctuate. Periodic boundary conditions were applied in all three directions. The main box was rectangular and of fixed size. At its two ends were silica slabs cut from an idealized structure of cristobalite [7,8]. The main box was patterned after the box used by Zhang et al. [9], to simulate reversed-phase liquid chromatography.

Simulations were hybrid in that molecular dynamics was used to propose new Monte Carlo configurations of ODS molecules attached to the silica surfaces. Others have used molecular-dynamics moves to enhance Monte Carlo sampling of long flexible molecules [10–12].

Oxygen atoms on the silica surfaces were bonded to either trimethylsilane (TMS) or ODS. In other studies of stationary-mobile phase interaction in reversed-phase liquid chromatography [7,13] and SFC [14] about half of the oxygen sites were converted to silanols. Half or fewer were converted to alkylsilanes. In this work, all bridging silica oxygen atoms were bonded to either TMS or ODS. Fig. 1 is a snapshot of the main box in a simulation. Car-

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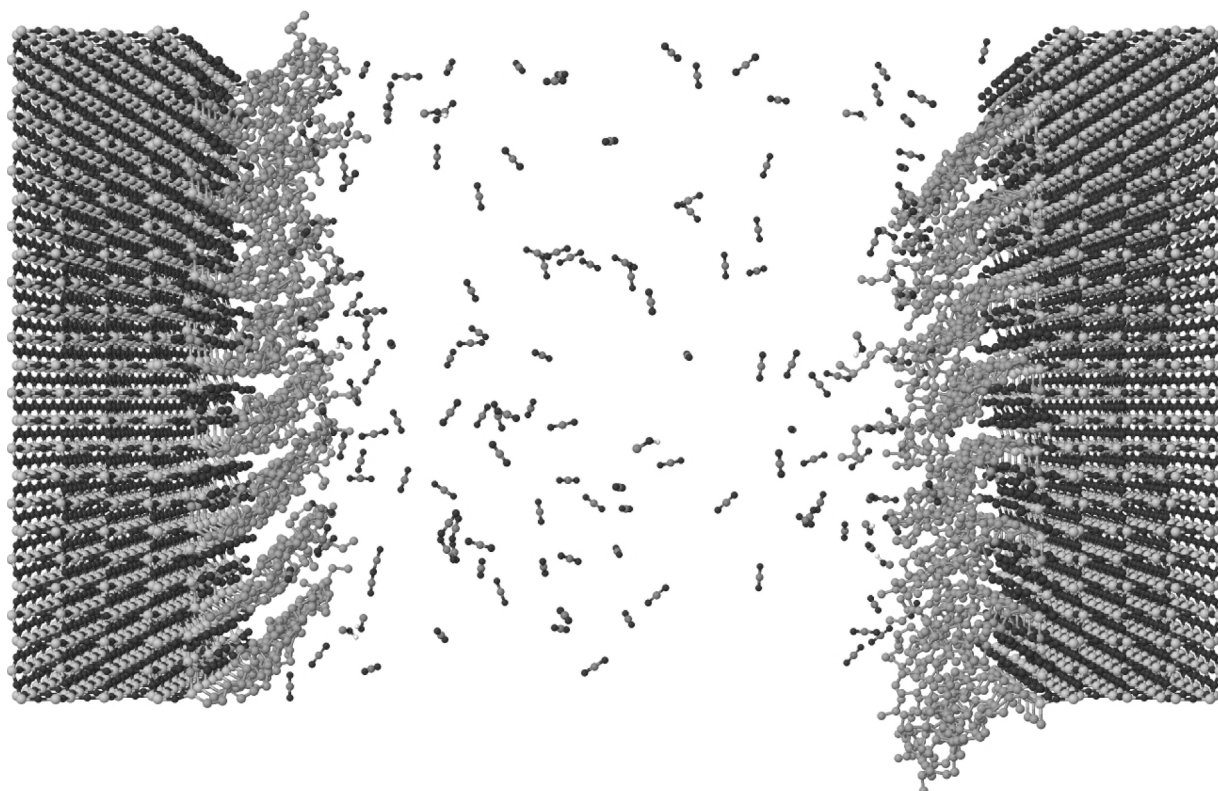2 *P.D. Siders / J. Chromatogr. A xxx (2017) xxx–xxx*

Fig. 1. The main box containing CO_2 and methanol between silylated silica walls. Conditions: $T = 328$ K, $P = 12$ bar, 1/3 of the silica oxygen sites terminated with ODS, the other 2/3 terminated with TMS. The solvent was 7% methanol in carbon dioxide. The z axis is horizontal. Periodic boundary conditions apply in the x and y directions.

bon dioxide and methanol molecules were free to move between the main and fluid boxes. The box in Fig. 1 has (x,y,z) dimensions (70.15,60.75,110) Å. Most main boxes used for the present work had half of those x and y dimensions. All main boxes had the same z dimension. A few low-pressure simulations, including the 12-bar simulation shown in Fig. 1, used larger main boxes to get enough fluid-phase molecules, especially methanol molecules, for good statistics. Periodic boundary conditions applied in the x and y directions.

The length of the main box (110 Å) was chosen so that ODS molecules on opposite walls were separated by more than the potential-energy cutoff distance even if fully extended, preventing direct interaction. Near-critical long-range correlation in the fluid molecules could effectively connect opposite walls. Long-range near-critical wall effects were not observed, perhaps because the lowest simulation temperature, 313 K, was too far above the critical temperature of carbon dioxide. Nevertheless, the main box length may exert some effect at high pressures. Systematic study of the effect of box length would be good but was not part of the present work.

Some simulations modeled coexistence of two fluid phases. Those simulations used two fluid boxes, no main box, and molecules moved between them. Some two-fluid simulations used the original Gibbs-ensemble method [15,16], also known as Gibbs-VT, in which the total volume was constant and the two boxes exchanged volume fluctuations. Other two-fluid simulations used fixed pressure, the Gibbs-PT method, and allowed the fluid box volumes to fluctuate independently. To simulate the main box at fixed volume and the fluid box at variable volume, the Gibbs-FP ensemble [17] was used. In the case of all main-fluid-box results in Section 4 the pressures stated are the fixed pressures from Gibbs-FP simulations.

The force fields used for silica, silanes and carbon dioxide were described previously [18]. Briefly, non-bonded interactions were described by Lennard-Jones plus Coulomb potentials. Details of the potential-energy functions and parameters for all molecules except methanol are described in Ref. [18], as are the procedures used for truncating and shifting long-range potentials. The force field for methanol was not published previously; its parameters are in Section 2.2.

The Monte Carlo program, including its hybrid molecular dynamics move of ODS, were programmed in gnu C++ and were compiled at optimization level 3. Coding emphasized portability and took advantage of the multiple short serial runs offered by the Open Science Grid.

A run consisted of multiple cycles of moves. Each cycle consisted of configuration changes for ODS and relaxation of TMS bonded to silica, of rotation and translation of carbon dioxide and methanol, plus bending of methanol, of volume changes or exchanges (but not for the main box), and of carbon dioxide and methanol transfers between boxes. Molecule transfers were not biased; simple deletion and insertion were used. The number of each type of move in a cycle varied depending on pressure, temperature and mole fraction. Typical moves in one cycle were five hundred and twelve molecule transfers, thirty-two volume changes, eight conformation moves of each ODS, two moves of each TMS, and four rotations and translations of each carbon dioxide and methanol molecule. For each cycle, moves were attempted in random order until the schedule of moves was exhausted. Acceptance rates for molecule transfers varied greatly depending on density. Acceptance rates for translation, rotation, and conformation change were near 40%. Although the number of cycles in a run varied, ten thousand cycles was typical.

Simulations that equilibrated a fluid box and a main box used 400–450 molecules in the fluid box. The number of carbon dioxide and methanol molecules in the main box varied greatly, being