

## Stationary-phase contributions to surface diffusion at C<sub>8</sub>-modified silica mesopores

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The structure, dynamics, and mobility of binary solvents and solute molecules at adsorbent surfaces play an important role in adsorption, catalysis, and separation. When investigating chemical systems, information gained by experimental data is often limited to the macroscopic view. Molecular dynamics (MD) simulations allow new insights on molecular processes and offer the possibility to study the molecular-level picture at solid-liquid interfaces in detail.

In previous work, we investigated the distribution and mobility of binary water (W) – acetonitrile (ACN) mixtures and four typical aromatic hydrocarbon analytes (benzene, ethylbenzene, acetophenone, and benzyl alcohol) in C<sub>18</sub>-modified silica slit pores, mimicking the conditions in reversed-phase liquid chromatography (RPLC), by MD simulations [1]. The data showed that analytes are retained by a combination of partitioning into and adsorption onto the bonded-phase chains [1]. Furthermore, the local diffusive mobility of the analytes parallel to the surface goes through a maximum in the ACN ditch, an ACN-rich border layer around the terminal parts of the bonded-phase chains, because the solvent composition there is more conducive to analyte mobility than the W-rich mobile phase [1,2]. In this study, MD simulations were carried out for the four analytes in silica slit pores with two different C<sub>8</sub> surface modifications to gain information about the influence of grafting density and chain length on surface diffusion. The first silica surface was modified with 3.11 μmol C<sub>8</sub> chains/m<sup>2</sup> and endcapped with 0.93 trimethylsilyl (TMS) groups/m<sup>2</sup>. For the second surface (high-density C<sub>8</sub> (hd-C<sub>8</sub>)), all endcapping groups were replaced by additional C<sub>8</sub> chains. Due to the increased grafting density, the C<sub>8</sub> chains are more stretched, resulting in a so-called picket-fence structure. For a 70/30 (v/v) W/ACN mobile phase, analyte surface diffusion increases from C<sub>8</sub> over C<sub>18</sub> to hd-C<sub>8</sub> and for 20/80 (v/v) W/ACN, the increase results in the order of C<sub>8</sub>, hd-C<sub>8</sub> and C<sub>18</sub>. For the W-rich mobile phase, the bonded phase contributes positively to surface diffusion. In addition, we show that a shorter chain length of the bonded phase results in a larger overlap between the adsorption and partitioning peak of the analytes

### References

- [1] J. Rybka, A. Höltzel, U. Tallarek: *J. Phys. Chem. C* **121**, 17907-17920 (2017).
- [2] J. Rybka, A. Höltzel, A. Steinhoff, U. Tallarek, *J. Phys. Chem. C* **123**, 3672-3681 (2019).

