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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Consequences of cylindrical pore geometry for interfacial phenomena in reversed-phase liquid chromatography

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Reversed-phase liquid chromatography (RPLC) is an important chemical separation and purification technique today in academic and industrial settings. RPLC separates analytes of low to moderate polarity according to their distribution between a hydrophobic stationary phase and an aqueous–organic mobile phase. The interfacial phenomena behind analyte separation in an RPLC column take place nearly exclusively inside the silica mesopores. Their cylindrical geometry can be expected to shape the properties of the chromatographic interface with consequences for the analyte density distribution and diffusivity. To investigate this topic through molecular dynamics simulations we introduce a cylindrical pore inside a slit pore configuration (Figure 1), where inner curved and outer planar silica surfaces bear the same chemically bonded phase consisting of dimethyl octadecylsilyl (C_{18}) chains and trimethylsilyl (C_1) endcapping groups. The present model replicates an average-sized (9 nm) mesopore in an endcapped C_{18} column equilibrated with a mobile phase of 70/30 (v/v) water/acetonitrile. Simulations performed for the representative analytes ethylbenzene (apolar) and acetophenone (moderately polar) show that the surface curvature shifts bonded-phase and analyte density towards the pore center, decreases the solvent density in the bonded-phase region, increases the acetonitrile excess in the interfacial region, and considerably enhances the surface diffusivity of both analytes. Overall, the cylindrical pore provides a more hydrophobic environment than the slit pore. The ethylbenzene density is decidedly increased in the cylindrical pore, whereas the acetophenone density is nearly equally distributed between cylindrical and slit pore. The cylindrical pore geometry thus sharpens the discrimination between apolar and moderately polar analytes, while enhancing the mass transport of both [1].

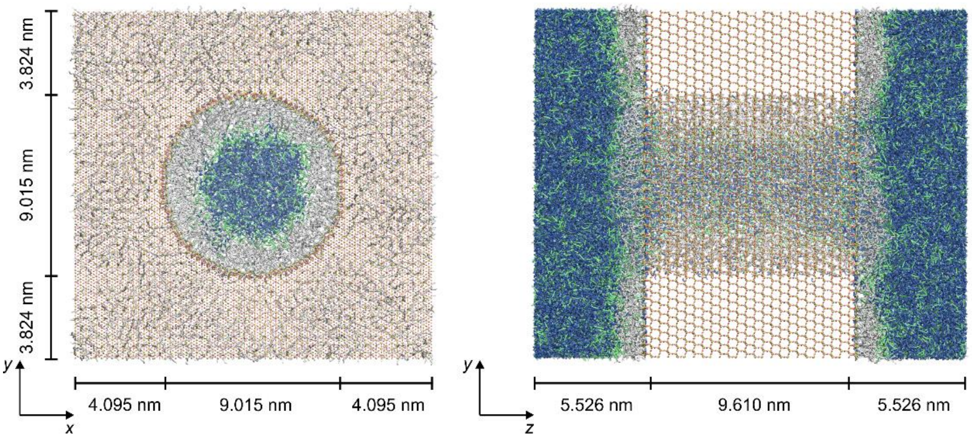

Figure 1: Front (left) and side views (right) of the simulation box. Dimensions of the silica block and the cylindrical pore in *xy*-direction (front view, pore diameter) and in *yz*-direction (side view, pore length) are indicated. In the front view, only solvent molecules inside the cylindrical pore are shown to visualize the modification of the inner curved and outer planar silica surface with the bonded phase. The acetonitrile excess at the inner curved and outer planar surface is clearly visible in the front and side view, respectively. Si and O atoms of the silica block are represented by yellow and red balls, respectively, and Si, O, and H atoms of the silica surface as yellow, red, and white sticks, respectively; united-atoms groups of the bonded phase are shown as grey sticks; water and acetonitrile molecules are shown as dark blue and green sticks, respectively.

References

[1] N. Trebel, A. Höltzel, J. K. Lutz, U. Tallarek: *Consequences of cylindrical pore geometry for interfacial phenomena in reversed-phase liquid chromatography*. J. Phys. Chem. B **125**, 11320–11336 (2021).

diffusion-fundamentals.org, Vol. 35 (2022) 40, URL: https://diffusion-fundamentals.org/journal/35/2022/40.pdf