

Confinement effects on distribution and transport of neutral solutes in a small hydrophobic nanopore

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Molecular dynamics simulations are used to study confinement effects in small cylindrical silica pores with extended hydrophobic surface functionalization as realized, for example, in reversed-phase liquid chromatography (RPLC), today the most important separation and purification technique in academic and industrial settings. In particular, we use a 6 nm cylindrical and a 10 nm slit pore bearing the same surface modification with C_{18} chains to compare the conditions inside the smaller-than-average pores within an RPLC column to column-averaged properties. Two small, neutral, apolar to moderately polar solutes are used to assess the consequences of spatial confinement for typical RPLC analytes with water (W)-acetonitrile (ACN) mobile phases at W/ACN ratios between 70/30 and 10/90 (v/v).

Figure 1 illustrates the cross-sectional ACN density profiles and shows that a bulk liquid region with the nominal solvent composition of the contacting mobile phase, here represented by the ACN density in the bulk liquid, $\rho_{ACN,bulk}$ (pink line), is missing in the 6 nm cylindrical pore.¹ Instead, the ACN-enriched solvent layer around the C_{18} chain ends (the ACN ditch), a general feature of hydrophobic interfaces equilibrated with aqueous-organic liquids, extends over the entire pore lumen of the small cylindrical pore. This implies that the actual pore curvature exerts an influence on both position and intensity of the ditch, likely supported by a conformational change of the surface-tethered C_{18} chains (light gray in Figure 1) with respect to a planar silica surface.

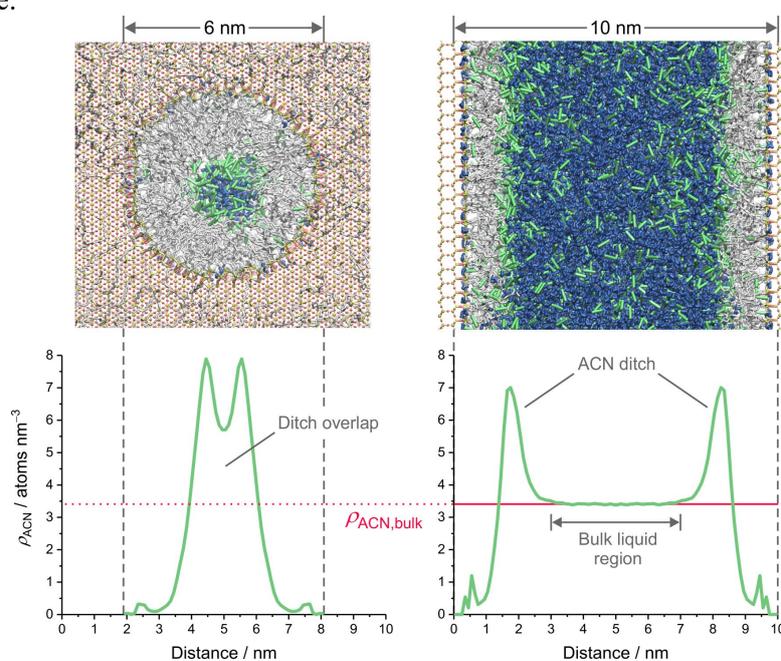


Fig. 1. (Top) Snapshots of the RPLC pore models with cylindrical and slit geometry (left and right, respectively) when equilibrated with a mobile phase of 70/30 (v/v) W/ACN. The bare silica surface is functionalized with C_{18} chains and endcapping groups. (Bottom) ACN number density profiles for the two systems (ρ_{ACN} , green lines) are adjusted to the pore diameter (6 nm) and pore width (10 nm).

The interfacial dynamics inside the small cylindrical RPLC pore are assessed by comparison with a standard RPLC slit pore (Figure 1). The rationale for this is based on earlier work,² where we demonstrated for simple analytes, including ethylbenzene and acetophenone, that the standard RPLC slit pore model reproduced experimental retention data acquired on an RPLC column over the complete range of W/ACN ratios encountered in RPLC practice. The column contains positive and negative surface curvature of different degrees, and the 10 nm slit pore is assumed to represent column-averaged data, whereas the 6 nm cylindrical pore represents a tiny piece of a porous particle inside the column. We determine how the solvent and analyte distributions and mobilities in the narrow cylindrical pore, with its strong curvature and substantial ACN ditch overlap, differ from those in larger pores, where ACN ditch overlap does not occur and bulk liquid properties are attained in the pore center.

The simulated data show that the extension of the ACN-ditch over the entire pore lumen of the small cylindrical pore renders the entire pore a highly hydrophobic environment, where, contrary to column-averaged behavior, neither the local nor the pore-averaged sorption and diffusion of analytes scales directly with the W/ACN ratio of the mobile phase. Additionally, the solute polarity-related discrimination between analytes is enhanced. The consequences of local ACN ditch overlap in RPLC columns are reminiscent of ion transport in porous media with charged surfaces, where electrical double-layer overlap occurring locally in smaller pores leads to discrimination between co- and counterionic species.

References

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