

Electronic Supplementary Material for PCCP  
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# Supplementary Material: Solvent Structures of Mixed Water/Acetonitrile Mixtures at Chromatographic Interfaces from Computer Simulations

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## Supplementary Material

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Figure S1: Average solvent density profiles (over 100 ps from 1900 ps to 2000 ps of simulation time) for low coverage ( $0.88 \mu\text{mol}/\text{m}^2$ ) chromatographic systems with functionalized alkyl chains and 50/50 W/ACN solvent composition. (A: unfunctionalized  $\text{C}_{18}$ , B:  $\text{C}_{17}$ -CN, C:  $\text{C}_{18}$ - $\text{NH}_2$ , D:  $\text{C}_{18}$ - $\text{NO}_2$ , E:  $\text{C}_{17}$ -phenyl and F:  $\text{C}_6$ -phenyl). Blue traces correspond to water density, red traces to ACN density. The vertical dashed lines give the average extension of the alkyl chains measured from the top of the quartz layer which is defined by the plane through the oxygen atoms of the SiOH group. The  $y$ -axis gives the density of the solvent as defined in Equation (1) [main text].

Figure S2: Average solvent density profiles (over 100 ps from 1900 ps to 2000 ps of simulation time) for high coverage ( $2.65 \mu\text{mol}/\text{m}^2$ ) chromatographic systems with functionalized alkyl chains and 50/50 W/ACN solvent composition (A: unfunctionalized  $\text{C}_{18}$ , B:  $\text{C}_{17}$ -CN, C:  $\text{C}_{18}$ - $\text{NH}_2$ , D:  $\text{C}_{18}$ - $\text{NO}_2$ , E:  $\text{C}_{17}$ -phenyl and F:  $\text{C}_6$ -phenyl). Blue traces correspond to water density, red traces to ACN density. The vertical dashed lines give the average extension of the alkyl chains measured from the top of the quartz layer which is defined by the plane through the oxygen atoms of the SiOH group. The  $y$ -axis gives the density of the solvent as defined in Equation (1) [main text].

Figure S3: Temporal development of the phase size for unfunctionalized  $\text{C}_{18}$ ,  $\text{C}_{17}$ -CN,  $\text{C}_{18}$ - $\text{NH}_2$ ,  $\text{C}_{18}$ - $\text{NO}_2$ ,  $\text{C}_{17}$ -phenyl and  $\text{C}_6$ -phenyl (from top to bottom) for high surface coverage ( $2.65 \mu\text{mol}/\text{m}^2$ ). Color codes for the different traces are pure water (black); 80/20 volumic fraction W/ACN (red); 50/50 volumic fraction of W/ACN (blue).

Figure S4: Normalized distribution for the position of the functionalization above the quartz layer which is defined by the plane through the oxygen atoms of the SiOH group from 40000 snapshots. Left for low surface coverage, right for high surface coverage. Blue traces for 100/0 W/ACN, red traces for 80/20 W/ACN and black traces for 50/50 W/ACN. From Top to bottom: unfunctionalized  $\text{C}_{18}$  chains,  $\text{C}_{17}$ -phenyl,  $\text{C}_6$ -phenyl.

## Figures

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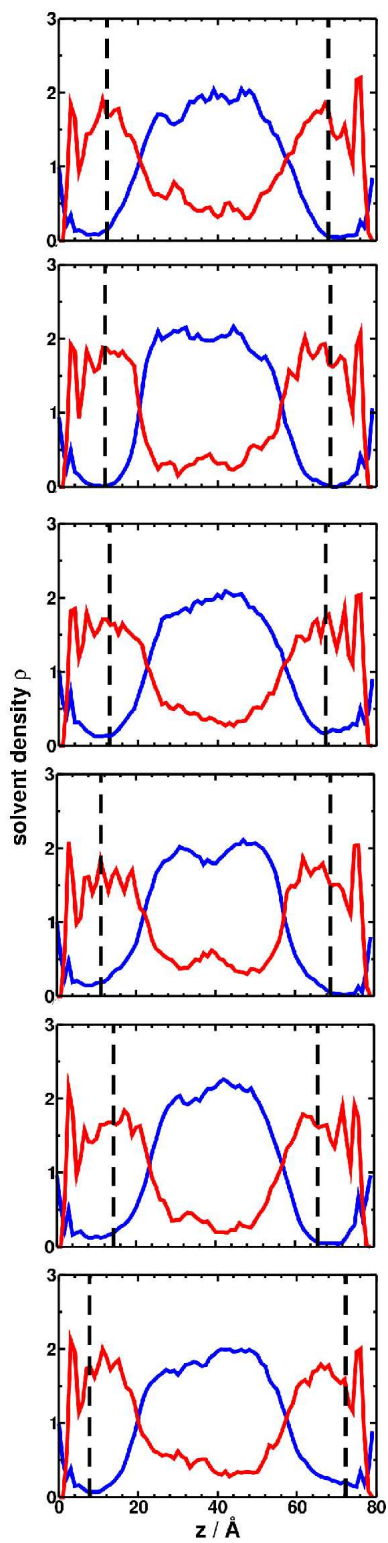


FIG. 1: S1: Braun et al.

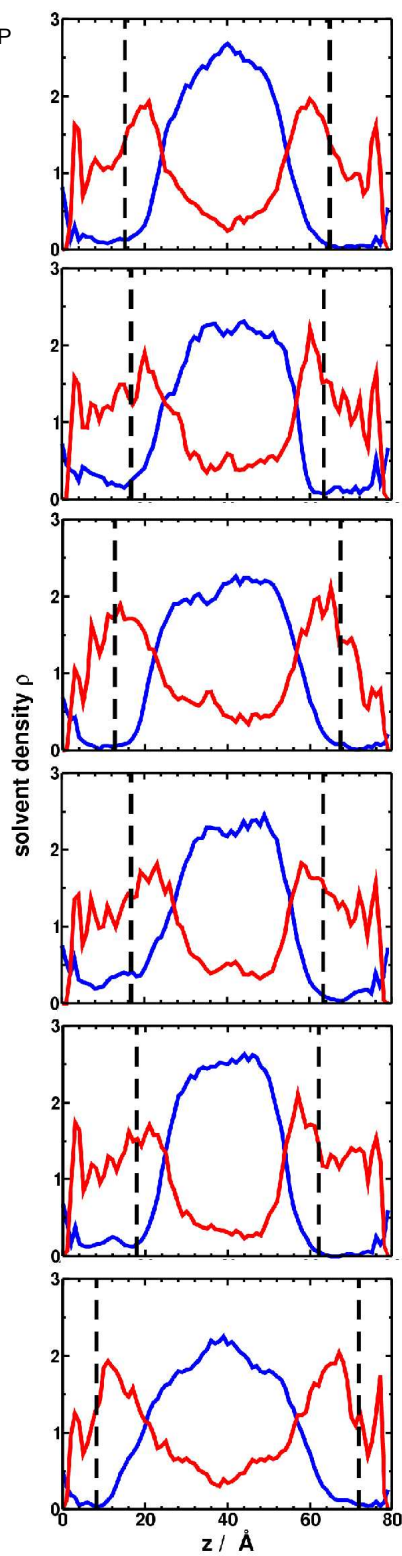


FIG. 2: S2: Braun et al.

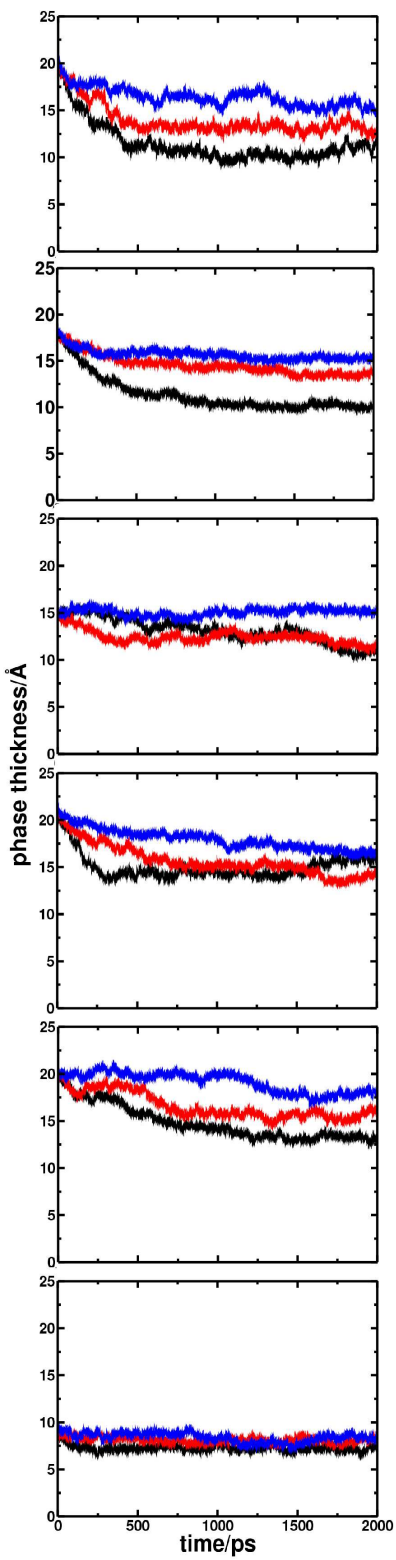


FIG. 3: S3: Braun et al.

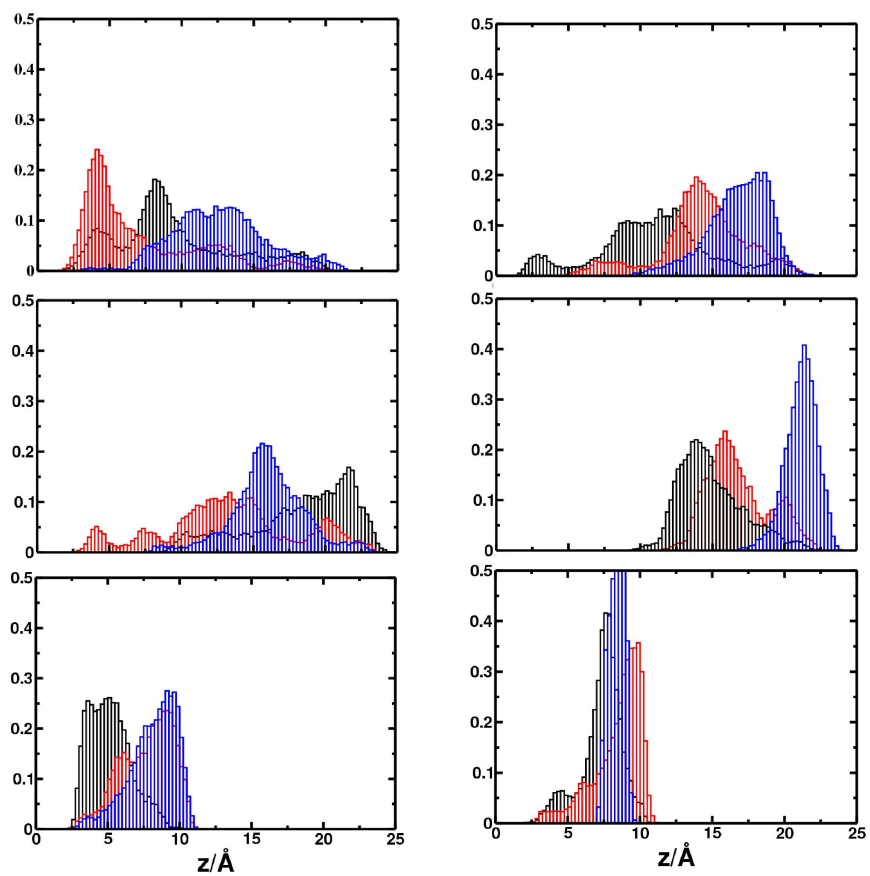


FIG. 4: S4: Braun et al.