

Electronic Supporting Information

Mixtures of Alcohols and Water confined in Mesoporous Silica- An Advanced Solid-State NMR Study

Bharti Kumari,^a Martin Brodrecht,^a Hergen Breitzke,^a Mayke Werner,^a Bob Grünberg,^b H.-H. Limbach,^b Sandra Forg,^c Elvira P. Sanjon,^c Barbara Drossel,^{c*} Torsten Gutmann,^{a*} Gerd Buntkowsky^{a*}

^a *Eduard-Zintl Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Alarich-Weiss-Str. 8, D-64287 Darmstadt, Germany*

^b *Institut für Chemie und Biochemie, Freie Universität Berlin, Takustrasse 3, 14195 Berlin, Germany.*

^c *Institut für Festkörperphysik, Technische Universität Darmstadt, Hochschulstraße 6, 64289 Darmstadt, Germany*

Corresponding authors: drossel@fkp.tu-darmstadt.de
gutmann@chemie.tu-darmstadt.de
gerd.buntkowsky@chemie.tu-darmstadt.de

Characterization of SBA-15 material

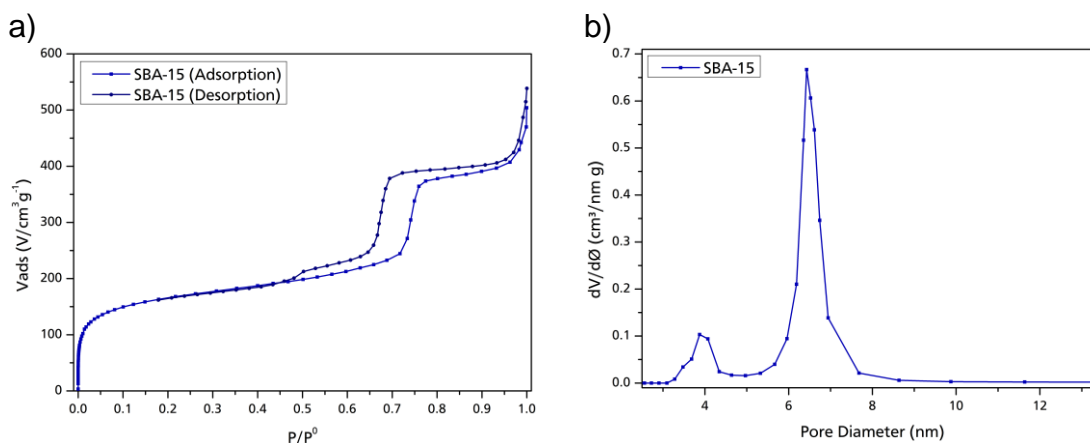


Figure S1: (a) Nitrogen adsorption-desorption isotherms of the synthesized SBA-15 material. (b) BJH plot of the synthesized SBA-15 material. *Note:* The obtained isotherm in (a) shows a hysteresis at $p/p_0 = 0.7$. The BJH plot (b) further shows a small artificial peak at around 4 nm which results from the not fully closed desorption and adsorption in the isotherm.

Simulations

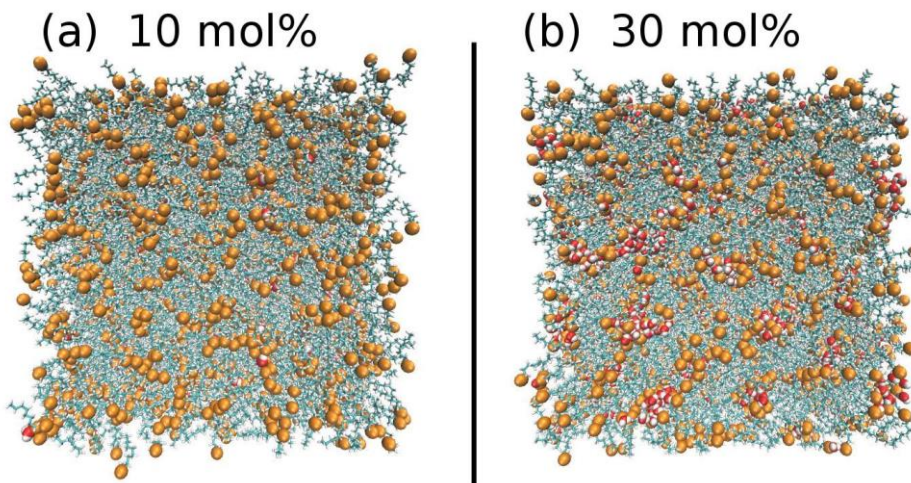


Figure S2: Snapshot of the final configuration of (a) 10 mol% and (b) 30 mol% bulk mixtures at 300 K, showing complete mixing at 10 mol% and partial demixing at 30 mol%, with water molecules accumulating near the oxygens centers of the octanol molecules. This agrees with the demixing ratio of 26% earlier proposed¹⁻⁴ and in simulations.

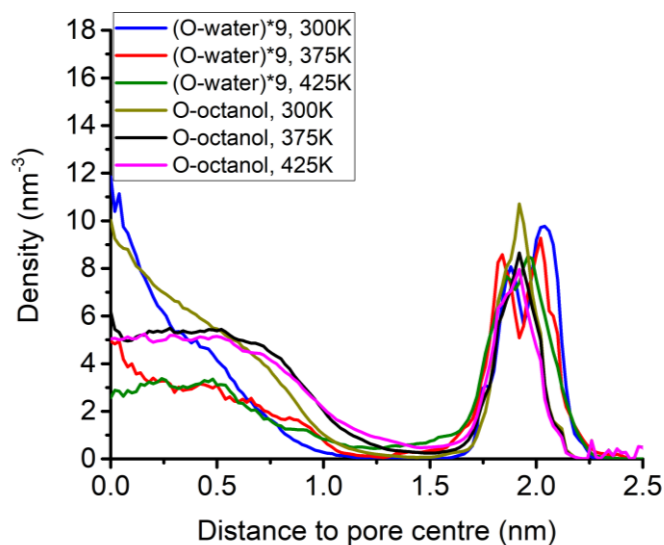


Figure S3: Number density profile of oxygens of water and octanol molecules for the 10 mol% mixture confined at different temperature. The density of water molecules is multiplied by the indicated factor for a better comparison. The distribution near the pore wall is almost identical between the different temperature.

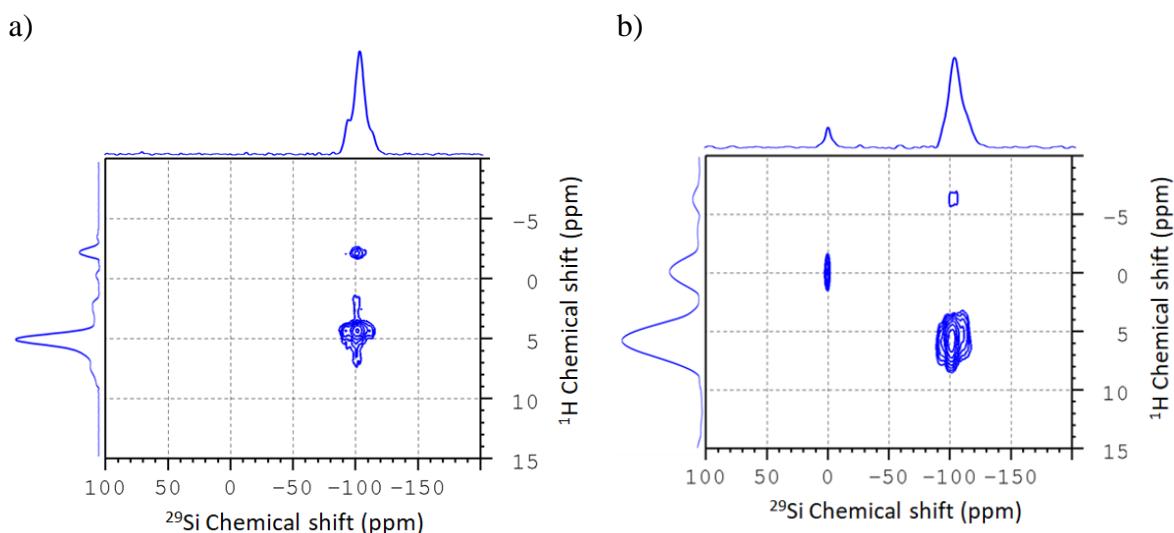


Figure S4: a) Room temperature ^1H - ^{29}Si CP-MAS FSLG-HETCOR experiment measured at 9.7 T and 5 kHz spinning of moist SBA-15 measured with a contact time of 5 ms, NS=128, 128 slices. b) Room temperature ^1H - ^{29}Si CP-MAS FSLG HETCOR experiment measured at 9.7 T and 8 kHz spinning of SBA-15 mixed with TSP and water (SBA-15: 32mg; TSP: 6mg; water: 5ul) measured with a contact time of 7 ms, NS=512, 32 slices. Note that in spectrum b) the signal at -6 ppm in the ^1H dimension refers to locked magnetization.

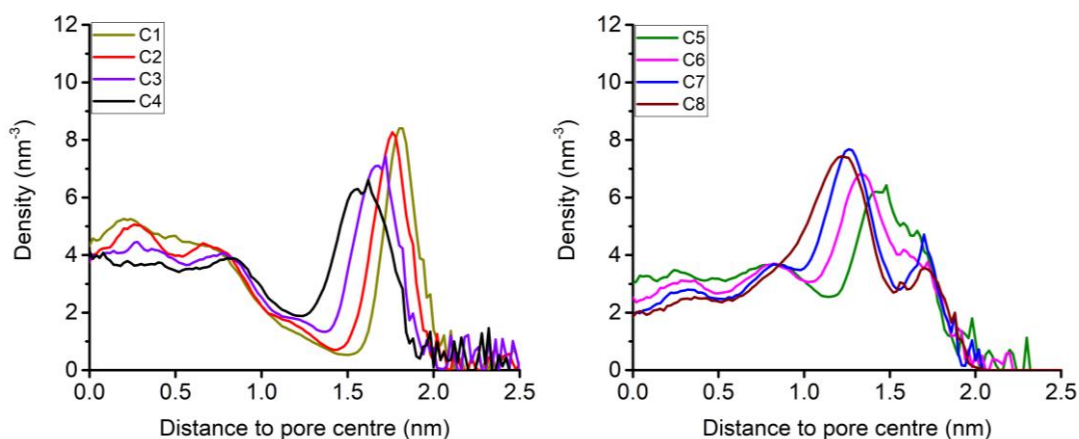


Figure S5: Number density profile of carbons of 1-octanol for 10 mol% at $T=425$ K. (a) C1-C4 are more localized in the pore center or the pore surface region, while (b) C5-C8 aggregates preferentially in the intermediate pore region.

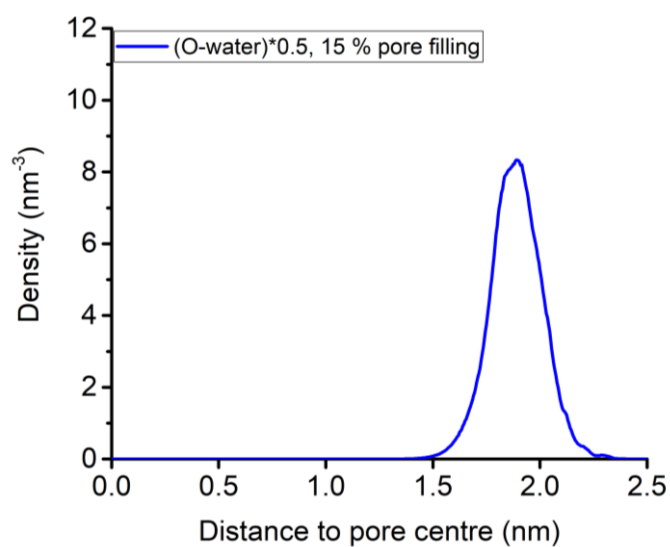


Figure S6: Number density profile of oxygens of water simulated at 300K for the special case of a pore that is partially filled (15% of volume) only with water. The density of water molecules is multiplied by the indicated factor for a better comparison.

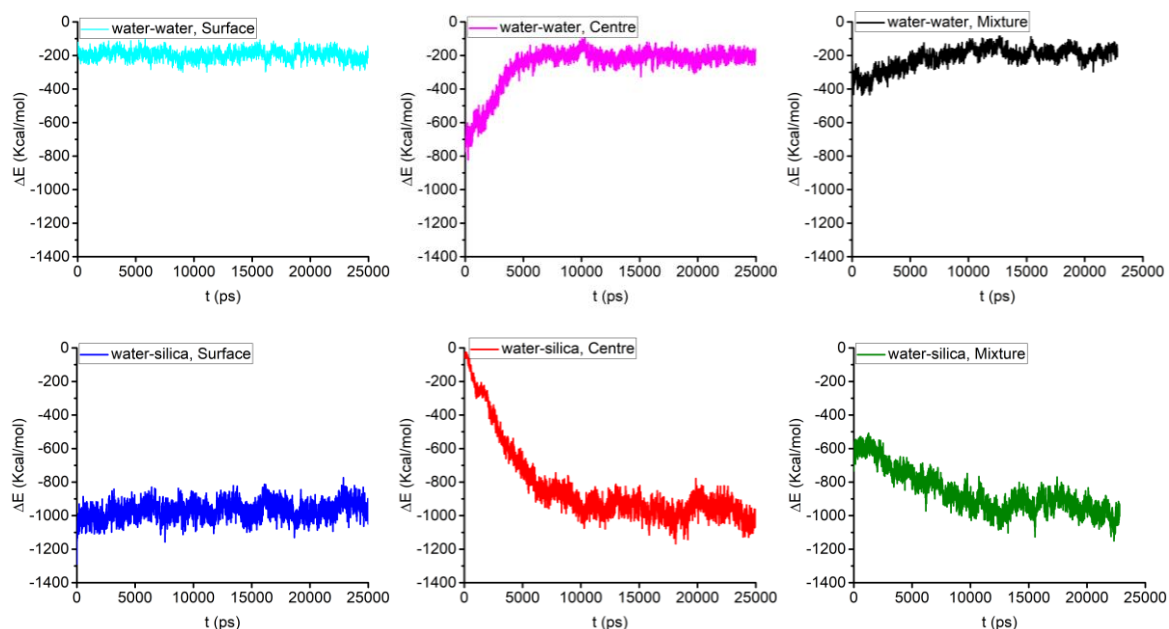


Figure S7a: Electrostatic energy between water-water, and water-silica molecules for “surface”, “center” and “mixture” starting condition for the simulation of 30 mol% water content at 425 K.

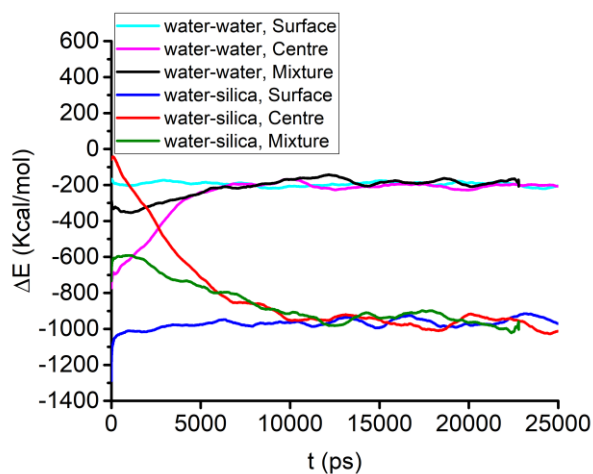


Figure S7b: The comparison of electrostatic energy shown in Figure S7a, between water-water and water-silica molecules for “surface”, “center” and “mixture” starting condition for the simulation of 30 mol% water content at 425 K. The curves have been smoothed using adjacent averaging.

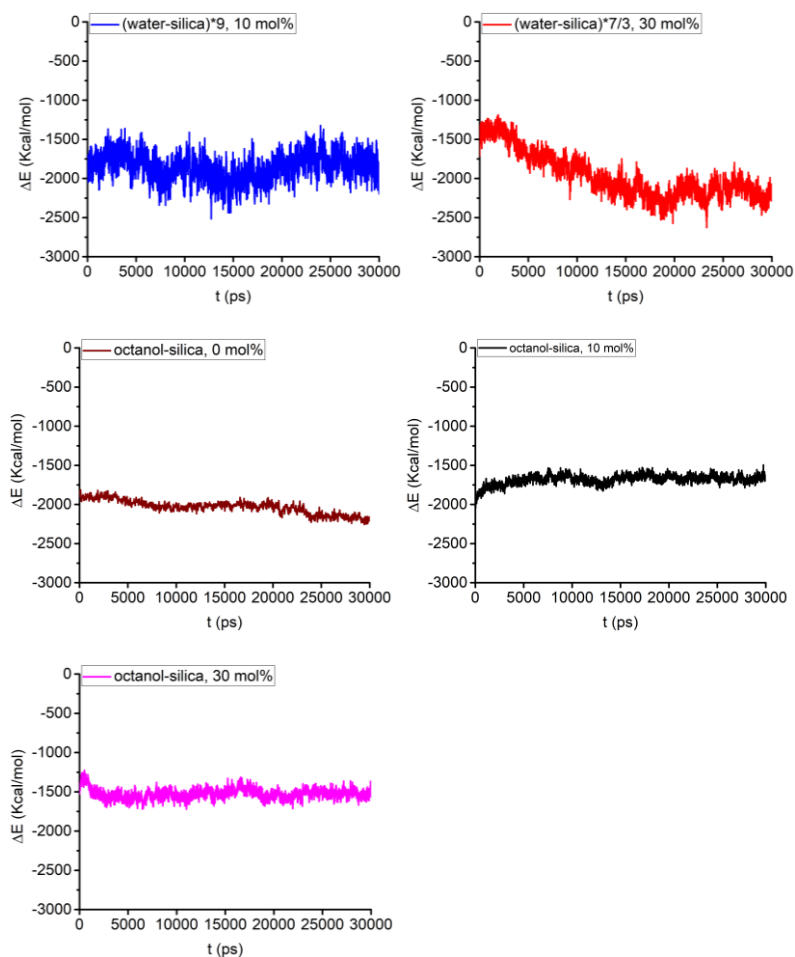


Figure S8a: The comparison of electrostatic energy between water-water, water-silica and octanol-silica. The water-silica energy has been multiplied by the indicated factor for comparison with octanol-silica.

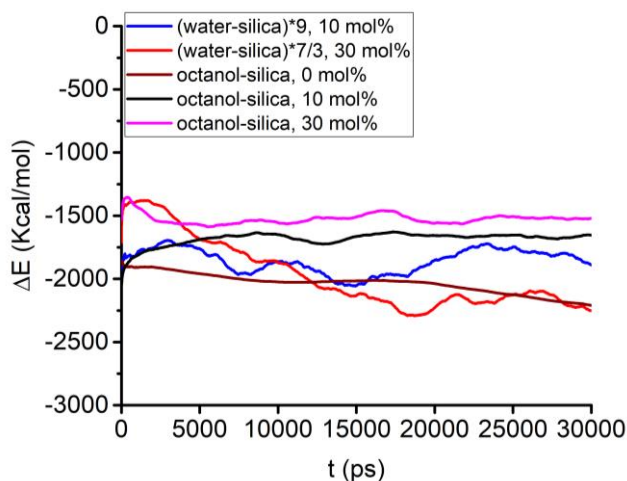


Figure S8b: The comparison of electrostatic energy shown in Figure S8a between water-silica and octanol-silica. For water-silica, the energy tends to increase (in absolute value) with increasing water content. This is in agreement with the H-bond profile in Figure 11b in which one gets slightly more H-bonds between water and silica for 30 mol% compared to 10 mol%. For octanol-silica, the energy is slightly reduced (in absolute) when water is added. This trend is displayed by the H-bond profile octanol-silica in Figure 11a, in which one can notice that for 0 mol %, the number of H-bonds is slightly larger compared to 10 or 30 mol%.

References:

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2. DeBolt, S. E.; Kollman, P. A., Investigation of Structure, Dynamics, and Solvation in 1-Octanol and Its Water-Saturated Solution: Molecular Dynamics and Free-Energy Perturbation Studies. *J. Am. Chem. Soc.* **1995**, *117*, 5316-5340.
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