Electronic Supporting Information

Mixtures of isobutyric acid and water confined in cylindrical (silica)nanopores revisited, a combined solid-state NMR and molecular dynamics simulation study

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SBA-15 and H_2O~SBA-15

For comparison a blank sample of SBA-15 was prepared by drying the material for 3 days at 120°C under vacuum and packing the sample in the rotor in a glovebox. To investigate the behavior of the material in presence of water, an additional sample H_2O~SBA-15 was prepared where the whole pore volume was filled with water. For this ca.13 mg of the SBA-15 material was wetted with ca. 10µl H_2O.

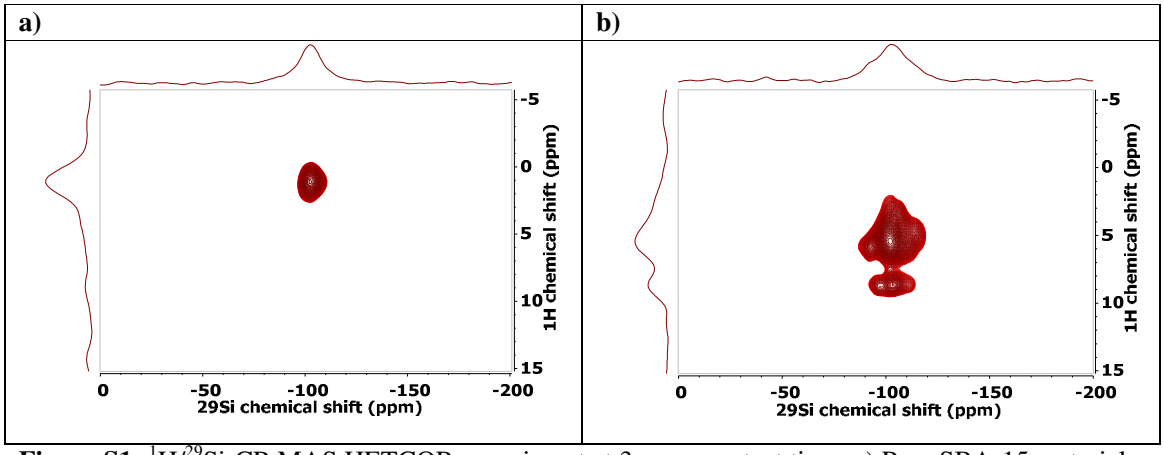

Figure S1: $^{1}H/^{29}Si$-CP-MAS HETCOR experiment at 3 msec contact time: a) Pure SBA-15 material. b) H_2O~SBA-15.

Liquid state NMR of iBA/H_2O mixtures

To get information on the differences of the ^{1}H chemical shifts of a water enriched phase containing iBA, and an iBA enriched phase containing water, two iBA/water mixtures were prepared. Mixture 1 (water enriched) contained 260µl iBA + 750µl H_2O which corresponds to a mass fraction of iBA (w%iBA) of 0.25. Mixture 2 (iBA enriched) contained 430µl iBA + 100 µl H_2O which corresponds to w%iBA=0.8.

From the spectra (Fig. S2) measured at 283K, it is clearly visible that the -OH peak originally at 5.1 ppm in the water enrich phase is shifted by ca 1.5 ppm to lower field in the iBA enriched phase. This observation refers to exchange processes of protons between the COOH group of iBA and H_2O.

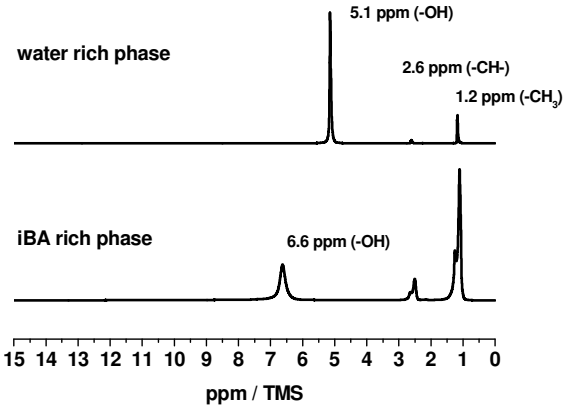

Figure S2: ^{1}H liquid state NMR at 11.4 Tesla of a water rich phase containing iBA, and an iBA rich phase containing water.
Note: Both spectra were measured at 283K. The spectra were referenced employing the signal of the CH_3 groups of the iBA (δ=1.2 ppm) as standard.

The following calculation will illustrate this. Here it is assumed that the pure COOH has a chemical shift of 11.5 ppm and pure H_2O has a chemical shift of 5 ppm, M(iBA)=88.11 g/mol, ρ(iBA)=0.95g/cm^3, M(H_2O)=18.02 g/mol and ρ(H_2O)=1 g/cm^3.

-OH signal for the iBA enriched phase:

430µl iBA + 100 µl H_2O (5.15 mM iBA + 5.55 mM H_2O)

Since two protons of H_2O can exchange with the proton of the COOH group of iBA, the theoretical value for the exchange peak can be approximated by the weighting of the iBA and H_2O fraction.

iBA $\frac{2*5.15}{2*5.15+5.55}$ H_2O $\frac{5.55}{2*5.15+5.55}$

$$\delta_{exchange} = \frac{5.55}{15.85} * 11.5\ ppm + \frac{10.3}{15.85} * 5\ ppm = 7.3\ ppm$$

-OH signal for the water enriched phase:

260µl iBA + 750 µl H_2O (3.11 mM iBA + 41.6 mM H_2O)

Since two protons of H_2O can exchange with the proton of the COOH group of iBA, the theoretical value for the exchange peak can be approximated by the weighting of the iBA and H_2O fraction.

iBA $\frac{2*3.11}{2*3.11+41.6}$ H_2O $\frac{41.6}{2*3.11+41.6}$

$$\delta_{exchange} = \frac{6.22}{47.82} * 11.5\ ppm + \frac{41.6}{47.82} * 5\ ppm = 5.8\ ppm$$

This calculation shows that between the water enriched and the iBA enriched phase a chemical shift difference of approximately 1.5 ppm is found for the exchange signal which is reproduced well by the experimental liquid phase spectra shown in Fig. S2.

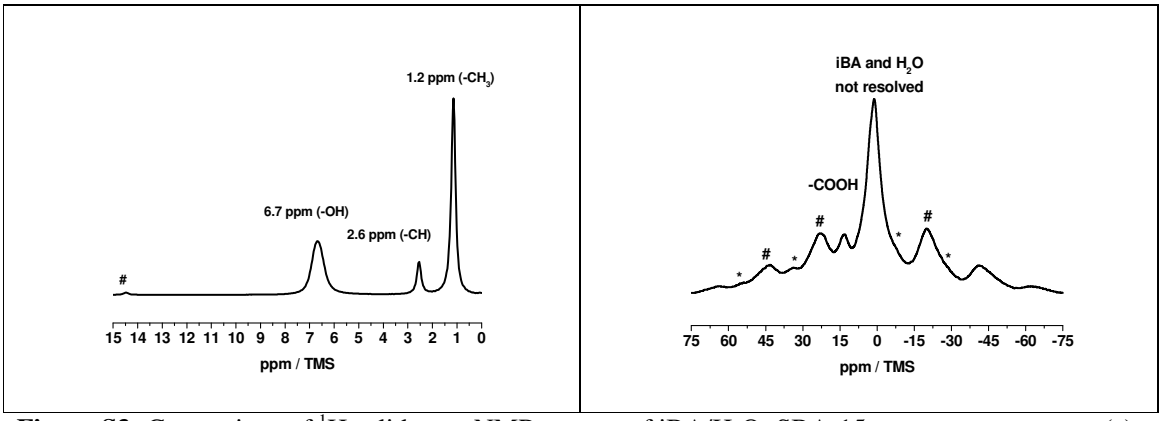

Figure S3: Comparison of ^{1}H solid-state NMR spectra of iBA/H_2O~SBA-15 at room temperature (a) and at nominally 100K. *Note:* Signals marked with # or * are spinning sidebands.

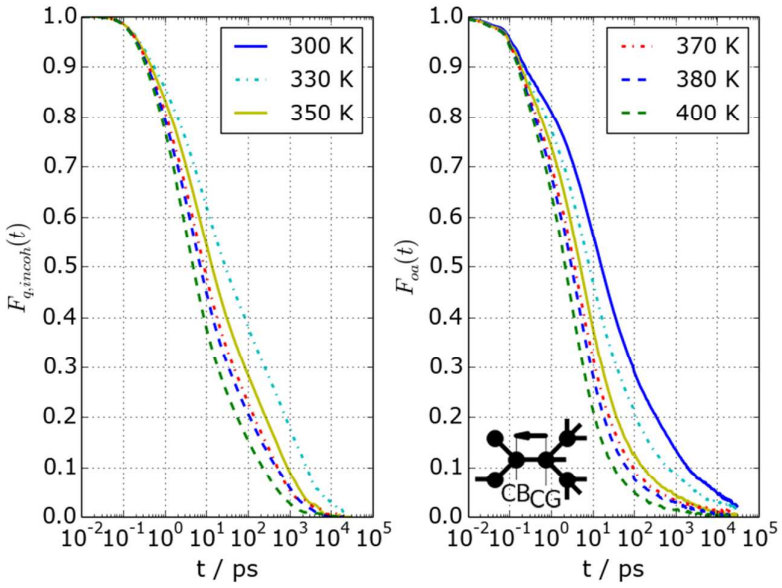

Figure S4: Incoherent intermediate scattering function $F_{q,incoh}(t)$ and orientational autocorrelation function $F_{ao}(t)$ of the iBA.