Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Swollen micelles and alcohol-surfactant co-adsorption: Structures and mechanisms from liquid- and solid-state ^1H-^1H NMR spectroscopy

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This PDF includes:

- SDS solubility in 1-Heptanol
- Additional ^2H spectra and simulations
- ^{13}C NMR spectra and chemical shifts
- DQ MAS spectra

SDS solubility in 1-Heptanol

In order to evaluate the solubility of SDS in 1-heptanol in the absence of water, 1-heptanol was mixed with SDS in large excess at room temperature for 24h. The solution was then centrifuged and the clear solution was inserted into a 5mm NMR sample tube and analysed. A ^{13}C NMR spectrum is displayed below in Figure S1, which gives the molar ratio between SDS and 1-heptanol. The ^{13}C NMR spectrum is recorded quantitatively, using inverse-gated proton decoupling and 40s relaxation delay. A 30° excitation pulse is used.

The spectrum indicates that **5.7 mol%** of the solution is SDS.

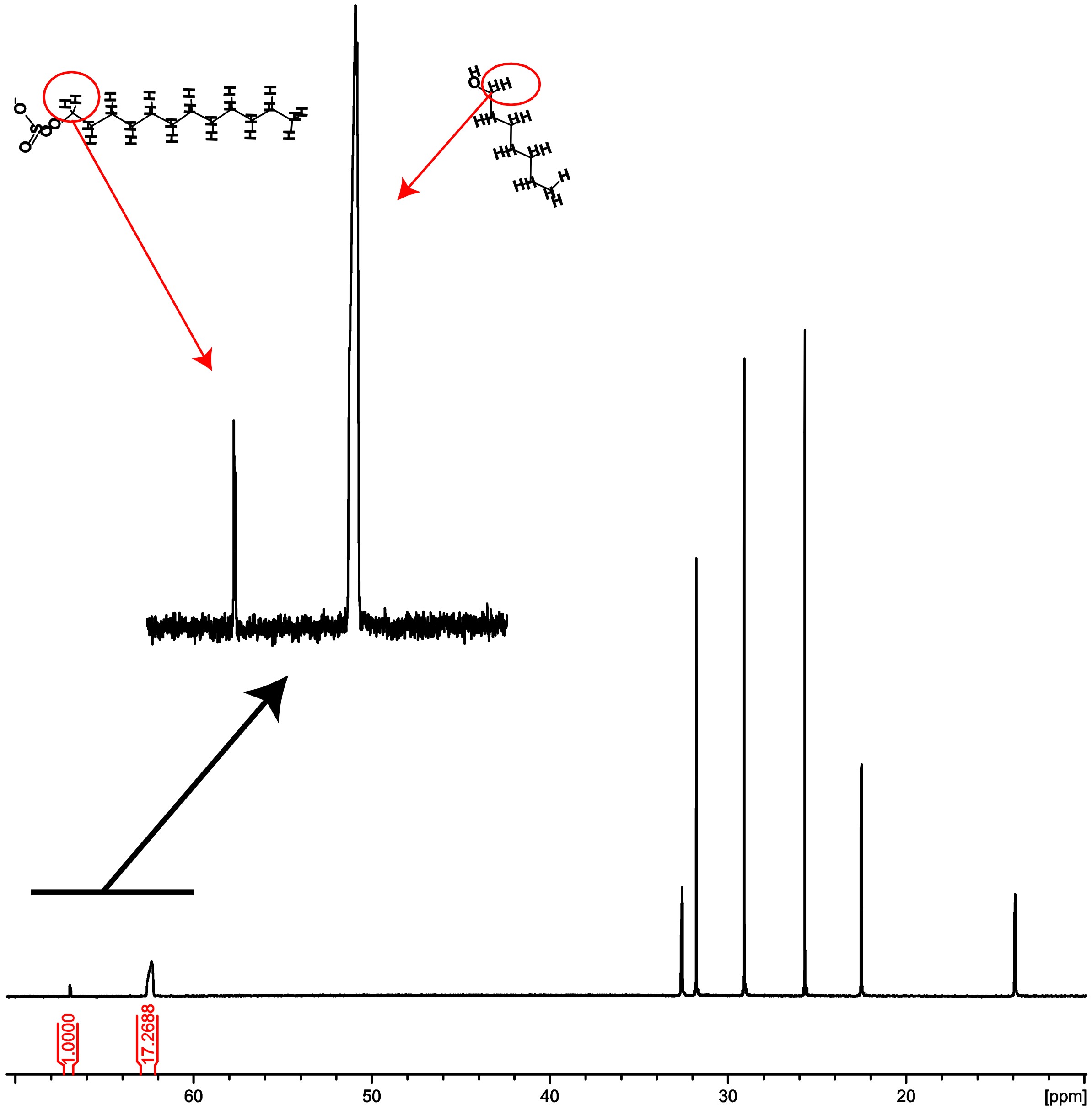

Figure S1. ^{13}C NMR spectrum of SDS dissolved at the solubility limit in 1-heptanol. Integrals of the alpha-methylene proton resonances of SDS and 1-heptanol are displayed, giving a solubility of SDS in 1-heptanol of about 5.7 %.

Additional ^{2}H spectra and simulations

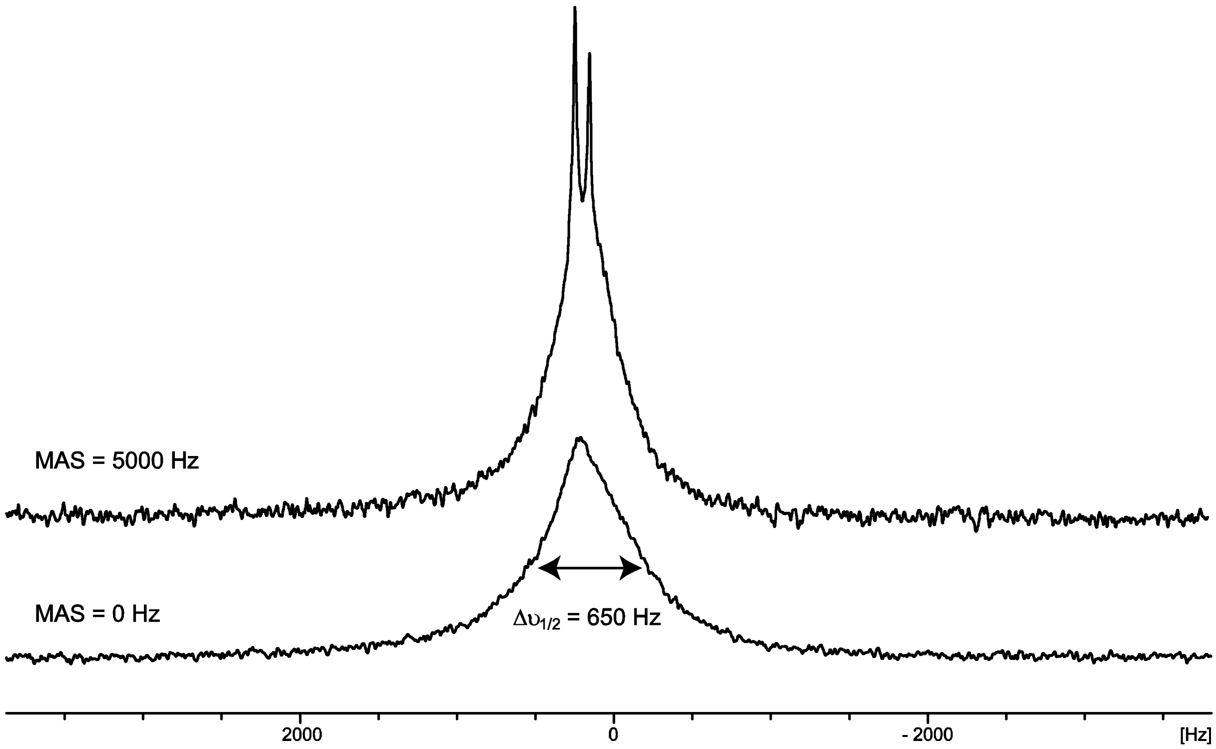

Figure S2. Static (bottom) and MAS (top) ^{2}H NMR spectra of ^{2}H labelled (α-methylene) 1-heptanol and (non-labelled) SDS adsorbed on alumina at a mole ratio of about 2:1.

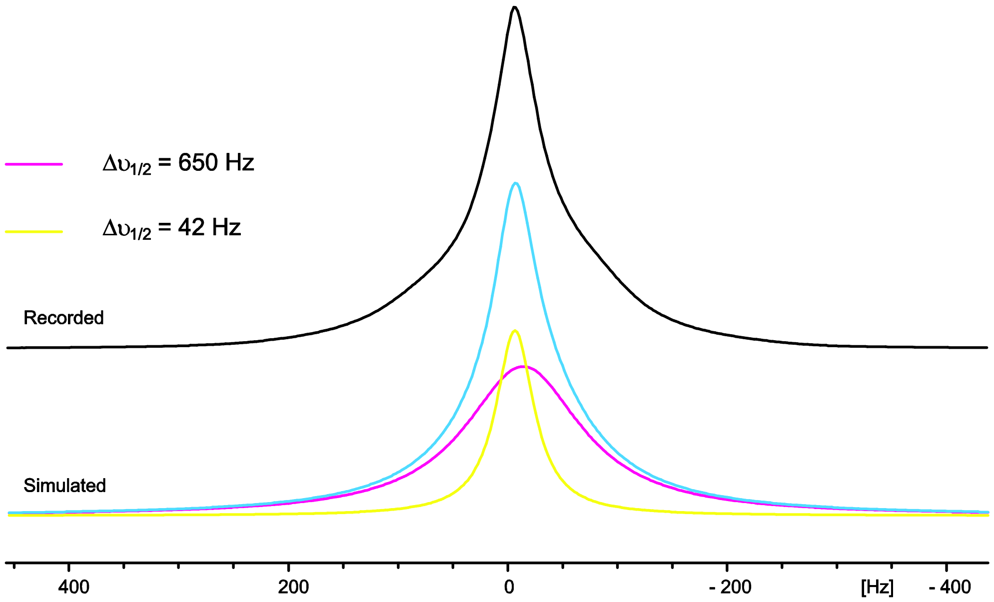

Figure S3. Static recorded (top) and simulated (bottom) ^{2}H NMR spectrum of ^{2}H labelled (α-methylene) 1-heptanol adsorbed on alumina in the absence of SDS. The simulation shows that the 1-heptanol peak consists of one narrow and one broad resonance originating form a mobile and a more immobile molecular environment, respectively. It is likely that the latter refers to 1-heptanol bound directly to the surface. The narrower resonance still has a line width of 42 Hz which is a factor 10 broader than the line width observed for bulk 1-heptanol. This peak is therefore interpreted to be molecules more loosely bound to the first layer of adsorbed 1-heptnaol.

^{13}C NMR spectra and chemical shifts

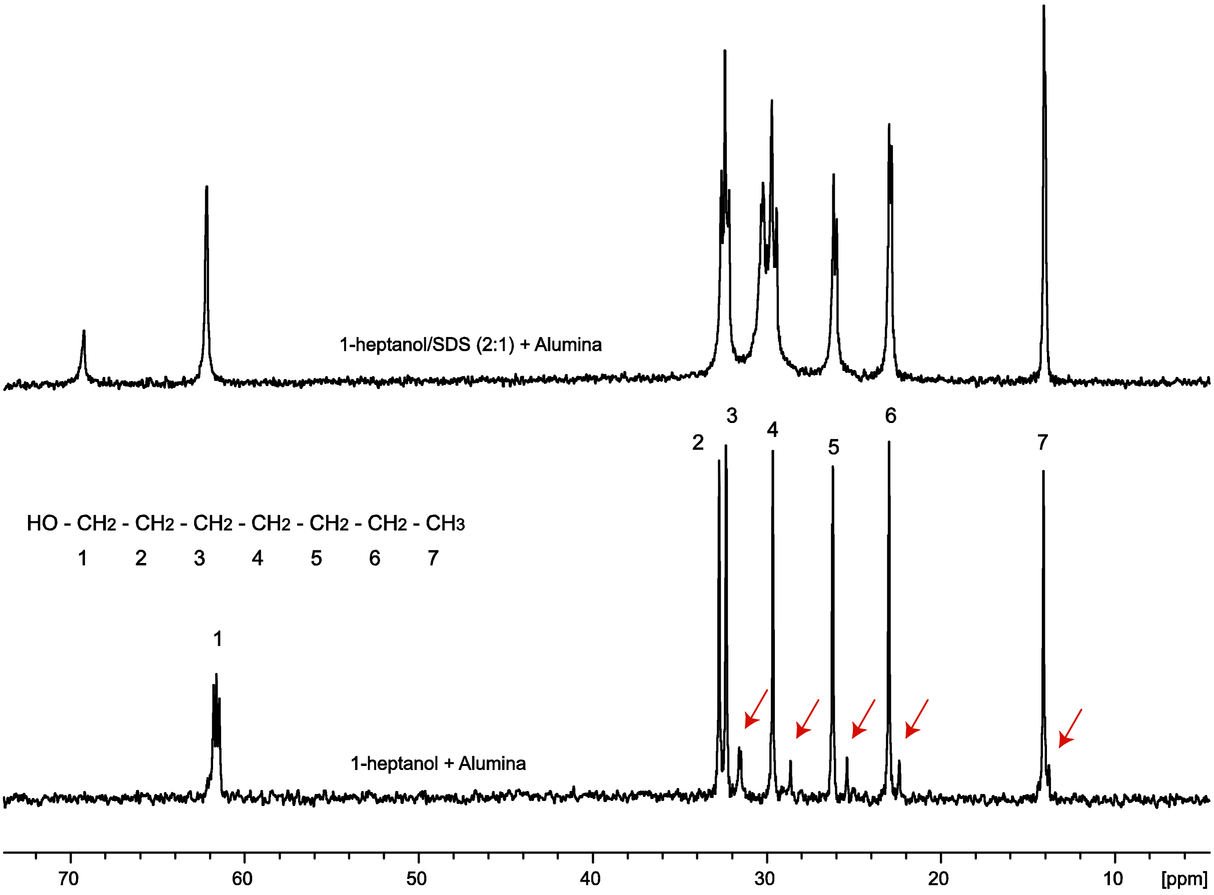

Figure S4. ^{13}C MAS (5000 Hz) NMR spectra of: Top; SDS and 1-heptanol adsorbed on alumina, and bottom; 1-heptanol adsorbed on alumina (from a 100 mM 1-H in water solution). Red arrows indicate resonances from a small amount of 1-heptanol in a different molecular environment. The occurrence of two sets of peaks suggests that the exchange between the respective molecular environments is slow. The higher chemical shift of the larger peaks (Table S1) suggests more C-C *trans* conformers in the alkyl chain of these molecules, indicative of a more ordered adsorbed phase. The smaller peaks may thus refer to 1-heptanol dissolved in the small bulk phase of the sample.

Table S1. Chemical shifts (ppm) from the spectra shown in Figure S4. (B) refers to the smaller peaks (red arrows) of Figure S4, and (A) to the larger main peaks. The difference in ppm is shown.

carbon	**1-H+Alumina (A)**	**1-H+Alumina (B)**	**(B) - (A)**	**1-H/SDS + Alumina**	**(1-H/SDS) - (A)**
1	61.612	-	-	62.200	0.588
2	32.732	31.632	-1.10	32.633	-0.099
3	32.333	31.483	-0.85	32.183	-0.150
4	29.655	28.635	-1.02	29.737	0.082
5	26.213	25.393	-0.82	26.192	-0.021
6	22.978	22.378	-0.60	23.003	0.025
7	14.100	13.780	-0.32	14.100	0

Alkyl chain ^{13}C chemical shifts are not sensitive to changes in the chemical environment of the nucleus, such as is the case for protons, but has been shown to almost exclusively reflect the ratio of C-C *gauche* and *trans* conformers. One exception is the first carbon adjacent the 1-heptanol hydroxyl, where the chemical shift is also sensitive to changes in polarization of the H-O-C-H bonds, e.g. as a result of interactions or adsorption. It is therefore noteworthy that this 1-heptanol chemical shift is as much as 0.588 ppm lower in the absence of SDS (Table S1), indicating stronger surface association of the hydroxyl when SDS is not present. As mentioned in the main text, the corresponding proton chemical shift is higher in the absence of SDS. A combined reduction and increase in ^{13}C and ^{1}H chemical shifts, respectively, indicate a change in polarization in this segment that originates from a surface interaction where the hydroxyl O and H interact with surface Lewis acid and base cites, respectively (see main text).

DQ MAS spectra

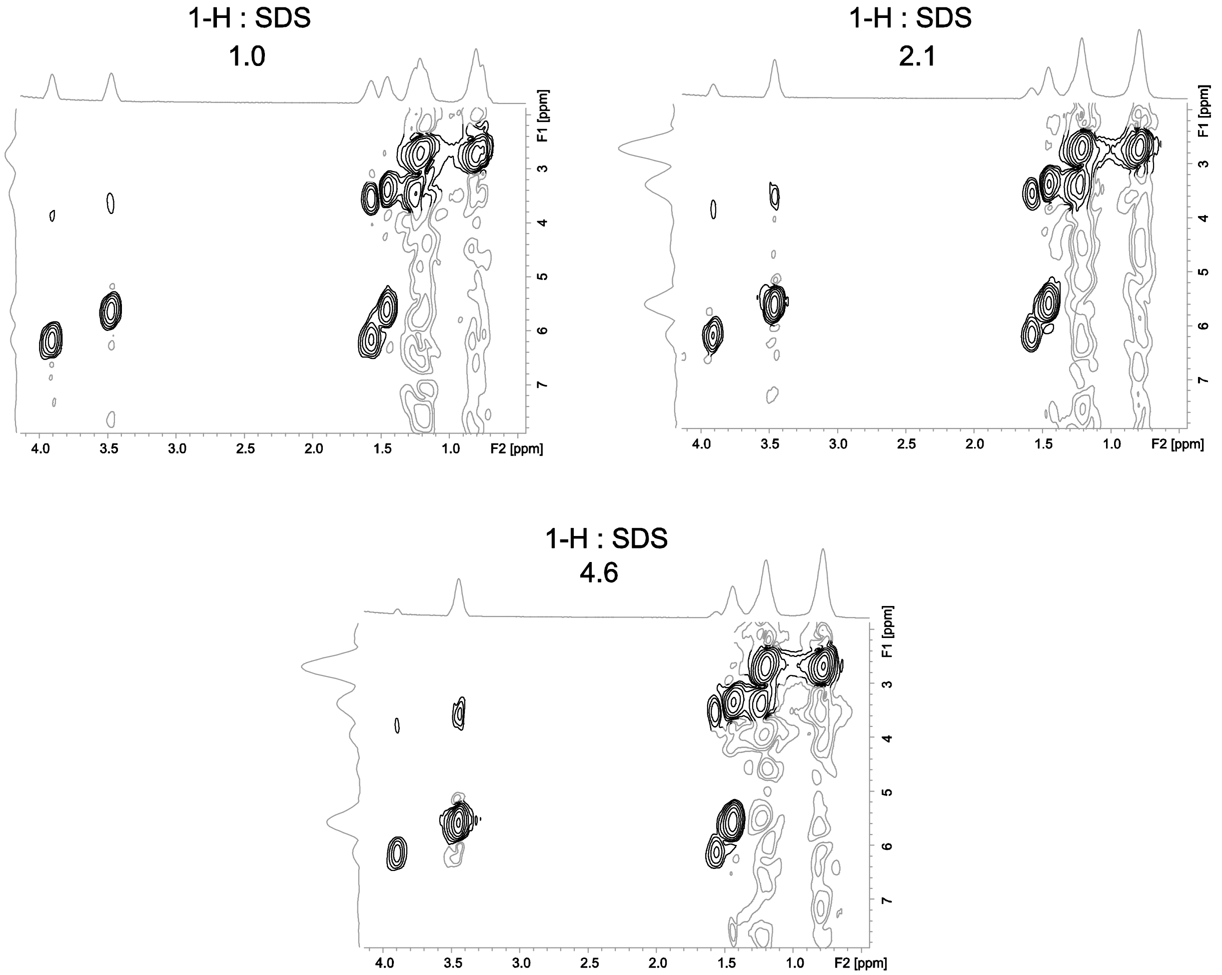

Figure S5. DQ MAS spectra of three samples of 1-heptanol and SDS adsorbed on alumina. The mole ratios in the adsorbed phases are indicated above each spectrum. The noise of the spectra is faded for better clarity.