Electronic Supplementary Information

CₙTAB / Polystyrene Sulfonate Mixtures at Air-Water Interfaces: Effects of Alkyl Chain Length on Surface Activity and Charging State

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A.   Description of the experimental set-up for vibrational sum-frequency generation

Our Münster Ultra-fast Spectrometer for Interfacial Chemistry (MUSIC) consists of a Solstice-Ace regenerative amplifier (Spectra-Physics) which is seeded by a Mai Tai SP fs-oscillator (Spectra Physics, 84 MHz, 770 mW) centered at a wavelength of 794 nm with a bandwidth of 22 nm and a pumped Q-switched laser (Ascend 60, 1 kHz, > 35 W). The amplifier delivers an average power of approximately 7 W (1 kHz, at 795 nm), which is divided (50:50) by an internal beam splitter and guided into an internal and an external compressor. The former (3.2 W, 796 nm and 18 nm bandwidth) pumps the optical parametric amplifier (Light conversion, TOPAS Prime) with the NDFG non-collinear configuration to generate broadband femtosecond IR pulses, which are tunable from 2.7 to 20 µm. The broadband IR has approximately 300 cm⁻¹ FWHM bandwidth. An air-spaced etalon (SLS Optics LTD, FSR 12.4 nm at 735 nm, R=94.5%) is inserted into the external compressor to generate the narrowband VIS pulse centered at 804.1 nm with 4 cm⁻¹ bandwidth. Etalon side bands are removed by beam blocks placed inside the external compressor.

For the generation of the SFG, VIS and IR pulses overlap temporally and spatially at incidence angles of 54° and 60°, respectively. The mean circularized beam diameters ($1/e^2$) were 530 µm (VIS) and 260 µm (IR). The SFG photons are directed into a spectrograph (Kymera-328i-D2-SIL, Andor) with an electron multiplying charge-couple device EMCCD (Andor Newton, Du97P-BVF).

B. Additional electrophoretic mobility measurements

The following figures show the effect of the choice of batch and the total concentration (for constant mixing ratios).
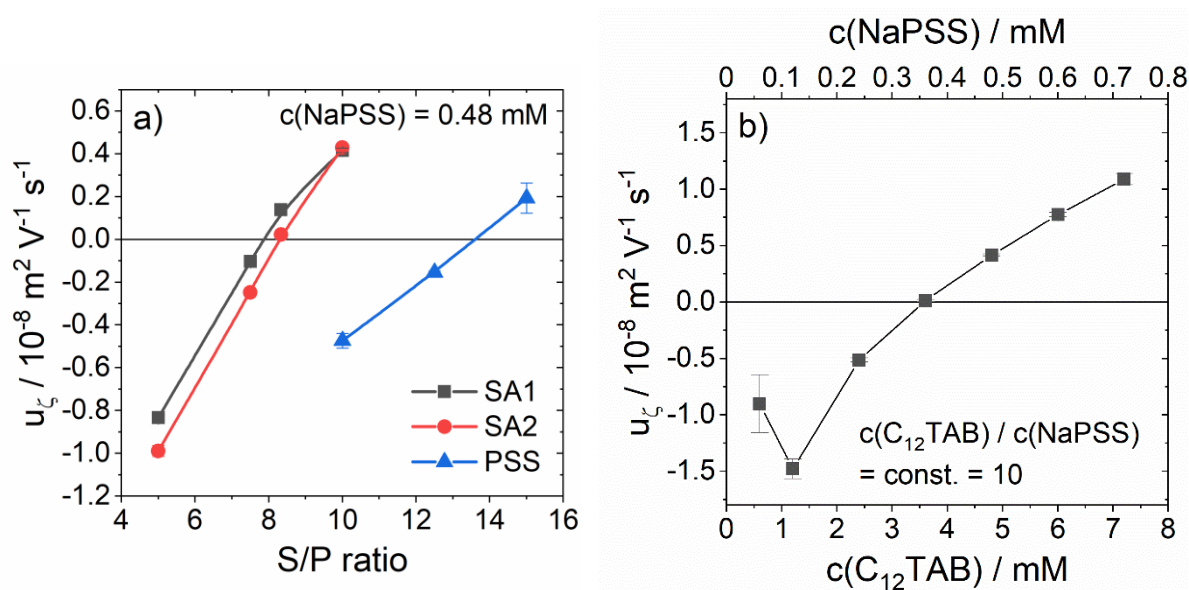

Figure S1: *Electrophoretic mobility u_ζ a) as a function of the S/P ratio; comparison of different batches at a fixed NaPSS concentration of 0.48 mM. SA1 indicates batch no. BCBP3081V from Sigma-Aldrich, SA2 batch no. BCBT0737 from Sigma-Aldrich and PSS batch no. pss9029n-2 from PSS (Polymer Standard Solutions). b) as a function of $C_{12}TAB$ concentration; comparison of mixtures with different total concentration but constant $C_{12}TAB/NaPSS$ ratio of 10.*

The measured electrophoretic mobility and with this the binding behavior of the surfactant to the polyelectrolyte is strongly dependent on the structure and conformation of the used NaPSS, which origins from the respective synthesis route and may result in intramolecular sulfone bridges and different degrees of sulfonation. We find a point of zero charge at a surfactant concentration of 3.8, 4.0 and 6.5 mM for our batches (literature: 4.8 mM – 6.0 mM). Not only the mixing ratio alone is important, but also the total used concentration, as can be seen from the right hand figure.

C. Surface tension kinetics

Some chosen dynamic surface tension results are shown in Figure S2.
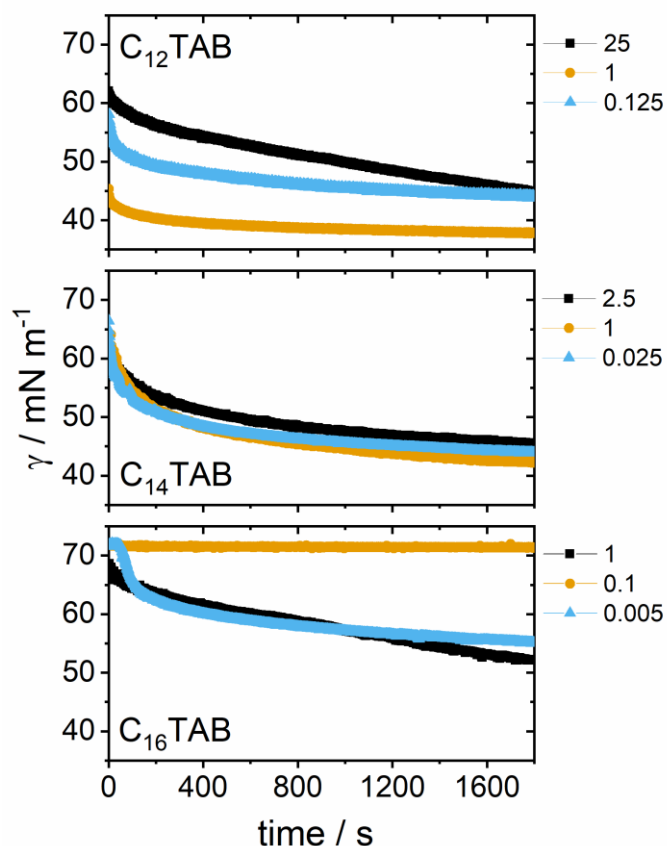
Figure S2: *Dynamic surface tension of C_nTAB/NaPSS mixtures at the air-water interface. S/P ratios and the surfactants chain length (n = 12, 14 and 16) are indicated in the figure. Surfactant concentrations are 2.5, 0.5 and 0.1 mM for C_{12}TAB, C_{14}TAB and C_{16}TAB, respectively.*

One interesting feature that cannot be seen from the surface tension data in Fig. 1c is the effect of polyelectrolyte addition to the surfactant on the surface activity. While for C_{12}TAB and C_{14}TAB addition of polyelectrolyte always leads to a lowered surface tension compared to the surfactant only (at least for the investigated concentrations), the opposite is the case for C_{16}TAB, meaning that the complexes of NaPSS with C_{16}TAB are in general less surface active in the displayed time period compared to pure C_{16}TAB. In general it can clearly be seen that mixtures around the PZC (around S/P = 1, 2.5 and 25 for C_{16}TAB, C_{14}TAB and C_{12}TAB, respectively) lead to dynamic surface tension curves that still have a considerable slope after 30 minutes. It follows from this that especially the surface tension of these mixtures will be notably lower if measured for longer times. Considering the effect of the minimum surface tension at equimolar mixing ratios, there are several effects that have to be considered for a possible explanation. In all three cases, at S/P = 1 there are negatively charged P/S complexes and additionally there is a considerable amount of free surfactant in case of the shorter surfactants but only little free C_{16}TAB. Therefore, a co-adsorption of NaPSS to C_{16}TAB seems unlikely and can be ruled out as a general explanation for all three systems. Remarkable is that

equimolar mixing leads in all cases to mixtures that are just at the margin of the equilibrium two-phase region (see Fig. 1b) – therefore, lower S/P ratios lead to stable samples and increased surface tension, while the increase for higher S/P ratios can be rationalized by the time scale of the measurement. However, complete understanding of the relation between the mixing ratio and the corresponding kinetics definitely merits further work.

D.   Sedimentation behavior
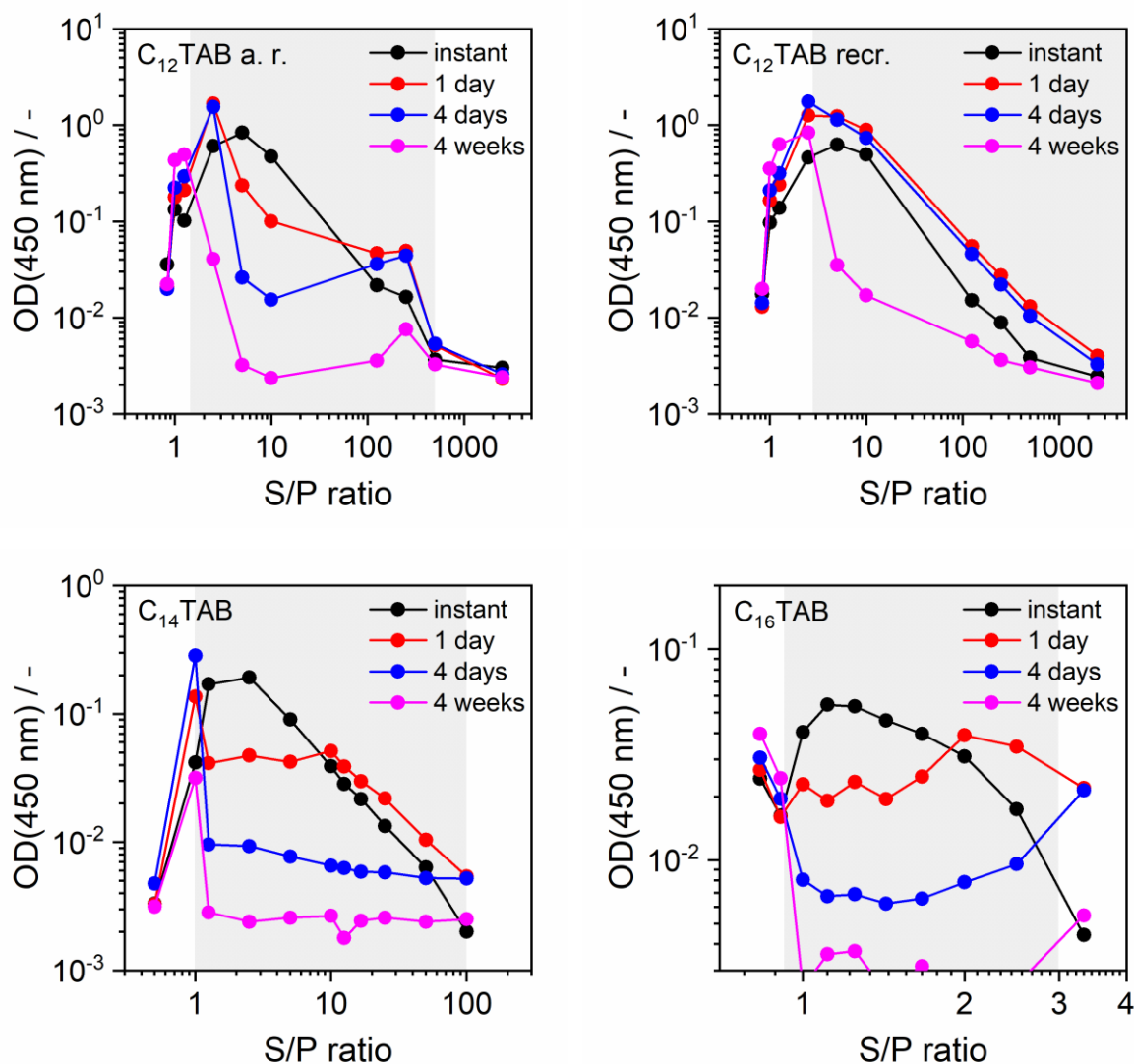
Figure S3: *Optical density at 450 nm of C_nTAB/NaPSS mixtures (n=12, 14 and 16 as indicated in the figure) with respect to the sample age (as indicated). Grey shaded areas indicate the equilibrium two-phase region.*

In order to determine the margins of the equilibrium two-phase region and the precipitation rates, the turbidity of the supernatant of the mixtures was measured directly on the freshly mixed samples and then after one day, four days and four weeks. In case of sufficient electrostatic repulsion of the complexes, the turbidity of the samples is constant or even increases a little bit

over time. If complexes are not electrostatically stabilized, they aggregate and precipitate. In these mixtures, the turbidity of the supernatant decreases with time and a sediment can be observed at the bottom of the vessel. Therefore, the margins of the equilibrium two-phase region can be found between two S/P ratios where the optical density after four weeks is for one ratio constant or higher and for the other ratio considerably lower than the instantly measured optical density. From these results, the margins of the equilibrium two-phase region can be observed at the following S/P ratios:

Table S1: *Margins of the equilibrium two-phase region of $C_nTAB/NaPSS$ mixtures.*

|	Lower boundary (S/P)	Upper boundary (S/P)
2.5 mM C_{12}TAB a. r.	~ 1 to 1.5	~ 500
2.5 mM C_{12}TAB recr.	~ 3	none
0.5 mM C_{14}TAB	~ 1	~ 50
0.1 mM C_{16}TAB	~ 0.9 to 1	~ 3 to 3.5

E.   Surface cleaning by aspiration

Nonequilibrium aggregates are known to be possibly trapped at the interface,[1] which can have a substantial effect on the macroscopic properties of the respective interface. The applied mixing protocol of simultaneous mixing of equal volumes of surfactant and polyelectrolyte solutions with double their intended final bulk concentration should in general minimize the formation of such aggregates. However, we made checks to see if indications of aggregates like this can be found at the surface. We therefore aspirated the surfaces as probed with SFG spectroscopy in the middle of the petri dish to remove surface-trapped aggregates or particles. A clean pipette was used to carefully remove liquid directly from the surface. Here it is of great importance to check that no measurable depletion of surface active material results from this. Afterwards, the surface was equilibrated and another spectrum was recorded. The spectra are presented in Figure S4.
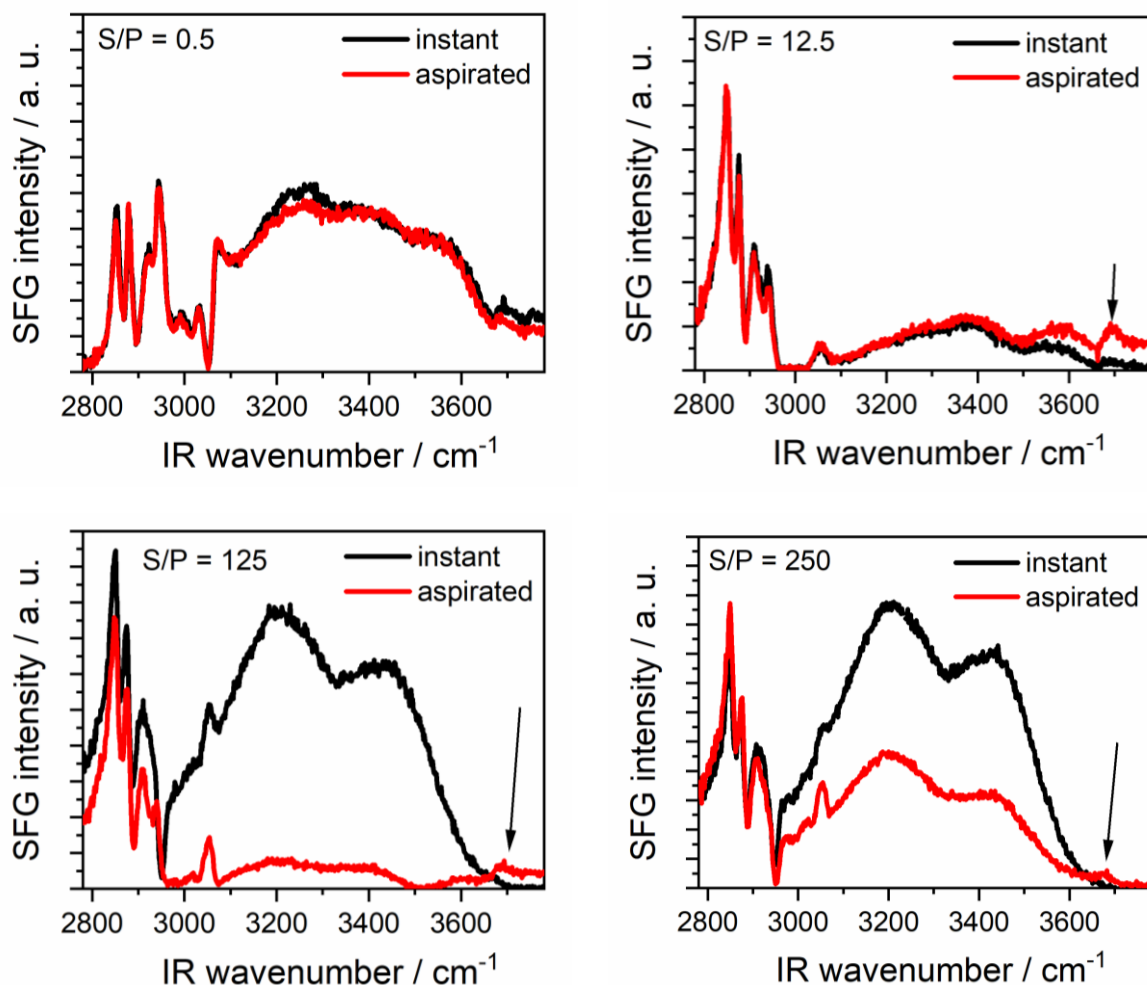
Figure S4: *SFG spectra of aspirated surfaces of $C_{12}TAB/NaPSS$ mixtures.*

It has been reported that aggregates may become inherently trapped at the interface during its creation. This irreversible process is most pronounced for aggregates with the lowest charge. In case of the $C_{12}TAB$, the PZC is not crossed – however, there are still aggregates with low charge, and at the surface even overcharged aggregates seem to be present (e. g. S/P = 12.5). However, even the removal of small liquid volumes such as 100 µl from the surface seems to leads to a distinct depletion of surface active material, which is corroborated by the arising of the dangling O-H vibration (indicated by the arrows). As it must be a precondition for the cleaning of the surface that there is no measurable depletion of surface active material (see also the mentioned reference), in our case it does not seem suitable to perform such a cleaning. For the higher S/P ratios, it seems that free surfactant is removed, leaving low charged aggregates with low coverage. For the low S/P ratio of 0.5, the recorded spectra are very much alike. Additional measurements on $C_{14}TAB/PSS$ layers can be found in the following figure.
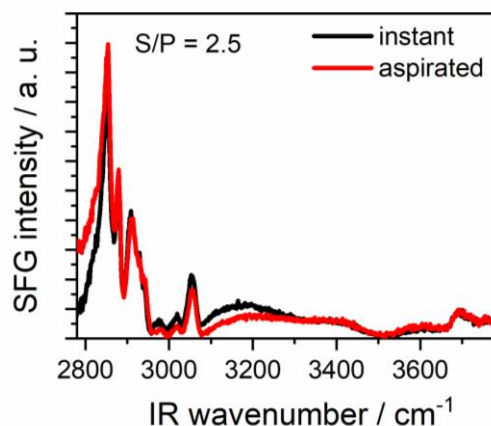
Figure S5: *SFG spectra of aspirated surfaces of C₁₄TAB/NaPSS mixtures.*

In this case, we performed the aspiration on a mixture which forms nearly uncharged complexes. There are small differences in the spectra, however no hints that would indicate that trapped aggregates were removed are found. In fact, the observable differences might as well be related to the time difference between the measurements, since these low-charge mixtures are not very stable (compare Fig. S3).

F.   Surface tension isotherms of the used surfactants
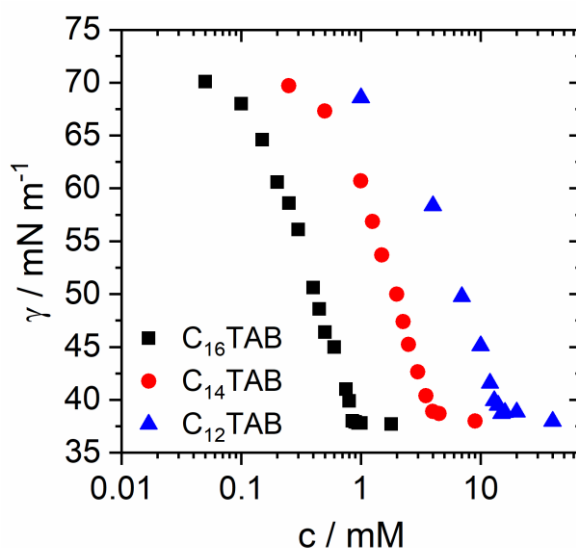
Figure S6: *Surface tension isotherms of the use surfactants. C₁₆TAB was used as received while C₁₄TAB and C₁₂TAB were recrystallized.*

Reference

(1)   Campbell, R. A., Yanez Arteta, M., Angus-Smyth, A., Nylander, T., Noskov, B. A., Varga, I. Direct impact of nonequilibrium aggregates on the structure and morphology of Pdadmac/SDS layers at the air/water interface. *Langmuir* **2014**, *30*, 8664–8674.