Supporting Information: Surface Adsorption of Oppositely Charged SDS:C$_{12}$TAB Mixtures and the Relation to Foam Film Formation and Stability

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Supporting Information

Table 1 displays the surface tension measured for SDS:C$_{12}$TAB mixtures of varying mixing ratio at total surfactant concentrations of 10^{-5}, $5 \cdot 10^{-5}$ and 10^{-4} mol/l. In all cases the concentration of catanionic SDS:C$_{12}$TAB complexes is calculated, assuming quantitative 1:1 complex formation. The surface tension values are compared with the surface tension measured for equimolar SDS:C$_{12}$TAB mixtures (doted line in Figure 2 in the main text). The concentration of the equimolar SDS:C$_{12}$TAB mixtures is chosen to exactly match the concentration of the formed catanionic complexes of the respective SDS:C$_{12}$TAB mixtures.

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Table 1: Comparison between surface tension measured at different SDS:C_{12}TAB mixing ratios and concentrations, with the surface tension of the equimolar SDS:C_{12}TAB mixtures (doted line in Figure 2).

mixing ratio (SDS:C_{12}TAB)	surface tension [mN/m]	concentration of catanionic complex if quantitatively formed [mol/l]	surface tension equimolar mixture at the same concentration [mN/m]
$c=10^{-5}mol/l$			
9:1	66.5	10^{-6}	66.9
8:2	58.0	$2 \cdot 10^{-6}$	58.8
7:3	49.8	$3 \cdot 10^{-6}$	50.4
6:4	46.3	$4 \cdot 10^{-6}$	46.4
5:5	45.4	$5 \cdot 10^{-6}$	45.0
4:6	46.6	$4 \cdot 10^{-6}$	46.4
3:7	50.2	$3 \cdot 10^{-6}$	50.8
2:8	58.5	$2 \cdot 10^{-6}$	58.8
1:9	66.7	10^{-6}	66.9
$c=5 \cdot 10^{-5}$mol/l			
9.6 : 0.4	54.0	$2 \cdot 10^{-6}$	58.8
9.4 : 0.6	40.4	$3 \cdot 10^{-6}$	50.8
9:1	31.5	$5 \cdot 10^{-6}$	42.0
8:2	27.7	10^{-5}	29.8
7:3	28.2	$1.5 \cdot 10^{-5}$	28.2
6:4	28.3	$2 \cdot 10^{-5}$	28.2
5:5	28.1	$2.5 \cdot 10^{-5}$	28.2
4:6	28.2	$2 \cdot 10^{-5}$	28.2
3:7	27.9	$1.5 \cdot 10^{-5}$	28.2
2:8	28.0	10^{-5}	29.8
1:9	31.3	$5 \cdot 10^{-6}$	42.0
0.6 : 9.6	40.4	$3 \cdot 10^{-6}$	50.8
0.4 : 9.6	54.0	$2 \cdot 10^{-6}$	58.8
$c=10^{-4}$mol/l			
9.7:0.3	34.1	$3 \cdot 10^{-6}$	50.8
9.5:0.5	30.5	$5 \cdot 10^{-6}$	42.0
9.3:0.7	30.2	$7 \cdot 10^{-6}$	35.0
9:1	28.2	10^{-5}	29.8
8:2	28.3	$2 \cdot 10^{-5}$	28.2
7:3	28.1	$3 \cdot 10^{-5}$	28.2
6:4	28.3	$4 \cdot 10^{-5}$	28.2
5:5	28.2	$5 \cdot 10^{-5}$	28.2
4:6	28.1	$4 \cdot 10^{-5}$	28.2
3:7	28.2	$3 \cdot 10^{-5}$	28.2
2:8	28.3	$2 \cdot 10^{-5}$	28.2
1:9	28.2	10^{-5}	29.8
0.7:9.3	30.1	$7 \cdot 10^{-6}$	35.0
0.5:9.5	30.5	$5 \cdot 10^{-6}$	41.8
0.3:9.7	33.8	$3 \cdot 10^{-6}$	50.9

If vesicles are present in the bulk solution phase the formation of an inhomogeneous CBF was detected (Figure 1). Thicker film domains (bright areas), surrounded by a microtubular network were embedded in the film. The dark regions corresponded to 8-10 nm thick film areas, while the light and coloured regions ranged from 100 to several hundreds of nanometers thickness. Thus the long and interconnected strands running through the film were actually thick-film regions (microtubes) suspended in the film. Excess material (water, vesicles) was pushed together and eventually trapped to form a wrinkle. Such behaviour is generally observed for foam films stabilized from vesicular solutions (Bergeron, V.; Journal of Physics: Condensed Matter 1999 (11) R215-R238). The thin films contain highly flexible bilayers and the film surface is densely covered with surfactant molecules. Two bilayers fuse or adhere within an indivual foam film leading to a gelification of the foam film and its typical structure (Figure 1).
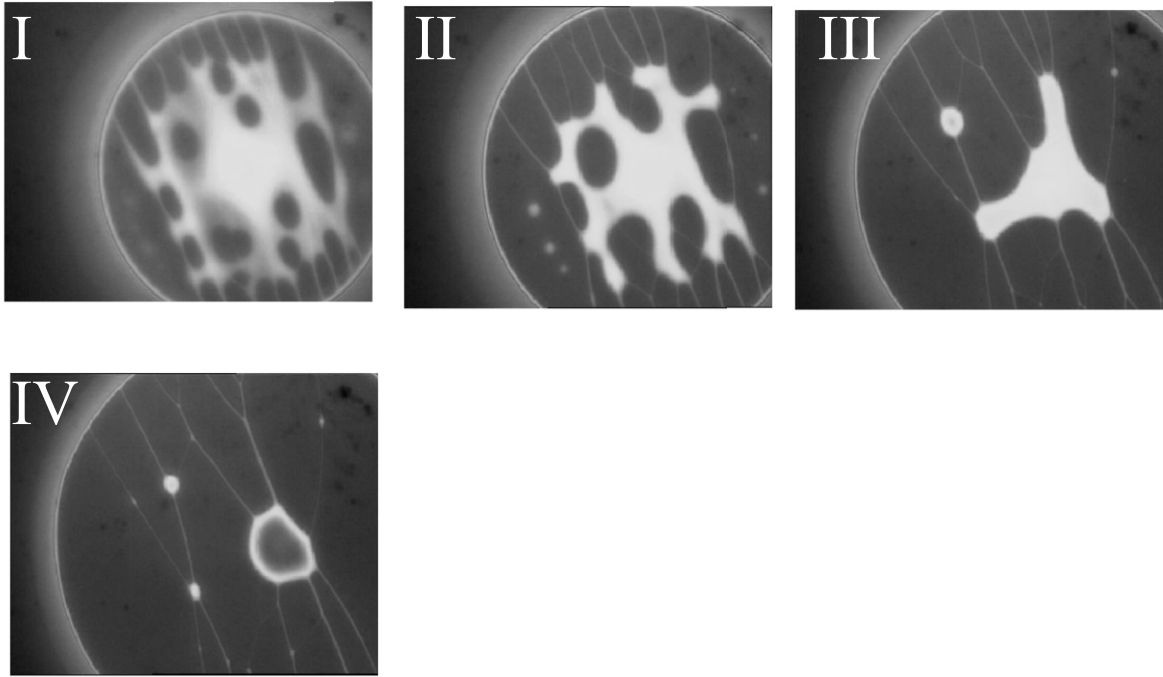
Figure 1: Images of a foam film stabilized from a $3.4 \cdot 10^{-2}$ mol/l 6.5:3.5 SDS:C_{12}TAB mixture (vesicular phase). The roman numbers I-VI depict different moments in time.
I) Formation of an inhomogeneous CBF. Thicker film domains (bright areas) are surrounded by a microtubular network embedded in the film.
II-IV) Excess liquid drained out of the microtubular network. Picture IV displays the final foam film at high disjoining pressure.

Table 2 gives the surface charge (q_0) and surface potential (Ψ) obtained from the DLVO model calculations of the disoining pressure isotherms in Figure 3 in the main text. Surface charge and surface potential values are ploted in Figure 4 in the main text.

Table 2: List of surface charge (q_0) values given in mC/m^2 in variation of the SDS:C$_{12}$TAB mixing ratio. The corresponding surface potentials Ψ (in mV) are given in the brakets. All values given were obtained from DLVO model calculations of the experimental $\Pi(h)$ curves in Figure 3 in the main text.

SDS:C$_{12}$TAB	10:0	9.5:0.5	9:1	8:2	7:3	6:4	5:5
$5 \cdot 10^{-5}$ mol/l	1.25 (82)	- (-)	0.92 (63)	0.77 (60)	0.67 (50)	0.64 (45)	0 (-)
10^{-4} mol/l	1.94 (65)	1.64 (58)	1.33 (50)	1.05 (46)	0.98 (45)	0.85 (46)	0 (-)

Table 3 compares the Debye lengths (λ_{fit}), obtained from fitting the $\Pi(h)$-curves of Figure 3 in the main text with an exponential decay function of 1. order, with the Debye lengths theoretically expected (λ_{theo}) if a quantitative formation of catanionic complexes in the bulk solution phase occurs. The respective values are ploted in Figure 5 in the main text.

Table 3: Summary of the Debye lengths λ_{fit} derived from a fit of the experimental data. λ_{theo} corresponds to the Debye length when a quantitative formation of catanionic complexes is assumed. The total concentration of the SDS:C$_{12}$TAB mixtures was 10^{-4} mol/l.

SDS:C$_{12}$TAB mixing ratio	λ_{fit} [nm]	λ_{theo} [nm]
10:0	30.5	30.5
9.5 : 0.5	31.2	30.5
9:1	32.1	32.1
8:2	34.1	35.2
7:3	36.4	36.4
6:4	39.3	43.1
5:5	43.1	43.1

Figure 2 shows the time dependance of the NBF domain growth for the 5:5 SDS:C$_{12}$TAB mixture at a total surfactant concentration of 10^{-4} mol/l. A similar change in the CBF-NBF transition kinetic ($d(t) \propto t^n$) was observed as for the $5 \cdot 10^{-5}$ mol/l 5:5 SDS:C$_{12}$TAB mixture (figure 9 in the main text). The exponent n drops slightly from n = 0.55 (domain growth with Rayleigh instabilities) to n = 0.45 (domain growth without Rayleigh instabilities).
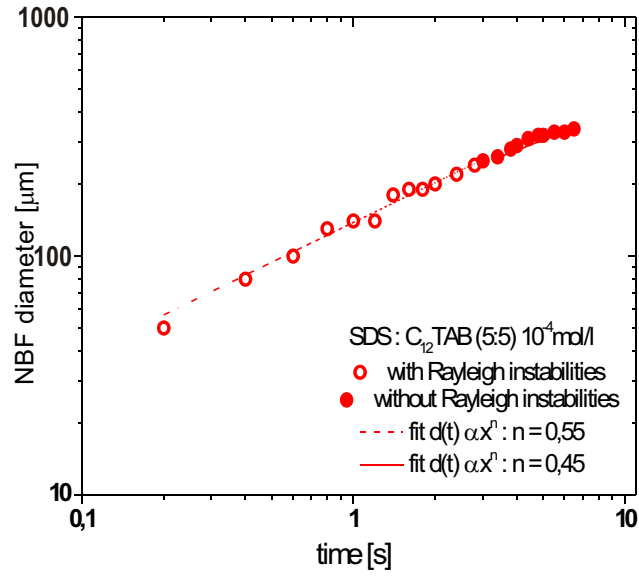
Figure 2: Detailed analysis of the CBF-NBF transition for a SDS:C_{12}TAB (5:5) mixture at a total surfactant concentration of 10^{-4} mol/l.