Competitive adsorption of HFBII hydrophobin and surfactant: Sequential vs. parallel adsorption and effect of surfactant micelles

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Summary

Parallel adsorption:

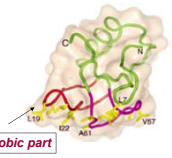
- Below CMC of SDS: irreversible HFBII adsorption; SDS molecules penetrate and fluidize the adsorption layer of HFBII;
- Above CMC of SDS: not detected HFBII at the water – air surface (probably SDS modifies HFBII aggregates in the bulk).

Sequential adsorption (SDS after HFBII):

- Irreversible adsorption of HFBII;
- SDS cannot displace HFBII both below and above CMC.

Materials

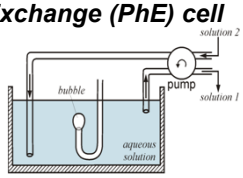
HFBII – M_w=7.2 kDa
~ 70 amino acids
4 disulfide bonds
Dimensions:
24 × 27 × 30 Å



SDS
$CH_3(CH_2)_{11}OSO_3Na$ M_w=288.34 g / mol

Methods

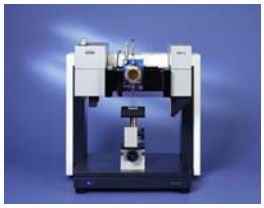
Phase Exchange (PhE) cell



Simultaneous injection and sucking out of liquid at a volumetric flow-rate of 150 mL/min.
The volume of the used cuvette is 15 mL.
For 1 minute work, the pump exchanges 10 times the contents of the container.

Drop Shape Analysis & Oscillating bubble method

(DSA 100R, Krüss GmbH, Hamburg, Germany)



Measured parameters:

Surface tension, $\sigma(t)$;
Surface area, A;
Fit error.

Surface dilatational modulus: E' and E''

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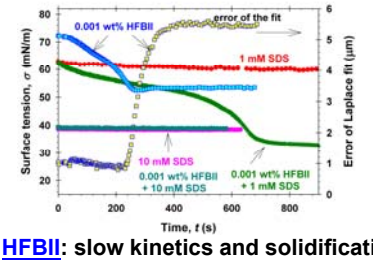
Relaxation kinetics and dilatation rheological properties



T = 2s; ω = 3.14 rad/s

№	Solution composition	σ, mN/m	*E'*, mN/m	*E''*, mN/m
1	0.001 wt% HFBII	70	143.2	5.0
2	1mM SDS	60	2.7	1.2
3	0.001 wt% HFBII +1mM SDS	51	35.7	5
4		35	155.6	0
5	10 mM SDS	38	0.4	0.7
6	0.001 wt% HFBII + 10 mM SDS	38	0.3	0.4

HFBII: slow kinetics and solidification

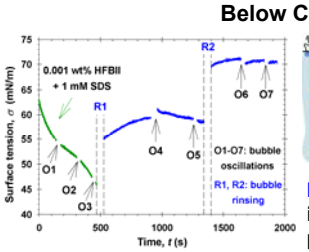
SDS: Fast adsorption and fluid surface

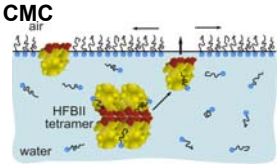
HFBII + 1 mM SDS: The surface is first occupied by SDS and then the slower HFBII adsorbs.

HFBII + 10 mM SDS: The surface tension σ with and without HFBII is the same

Parallel adsorption of HFBII and SDS

Below CMC

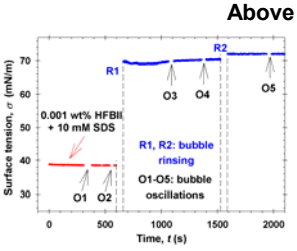


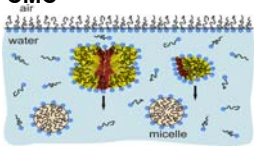


HFBII adsorbs at the interface and displaces a part of the already adsorbed SDS

Stage / System	σ, mN/m	*E'*, mN/m	*E''*, mN/m
1) 0.001 wt% HFBII + 1mM SDS (O1)	55	20.6	3.2
2) Rinsing with water (R1)	61	239.7	0
3) Rinsing with water (R2)	69	152.1	8.5

Above CMC

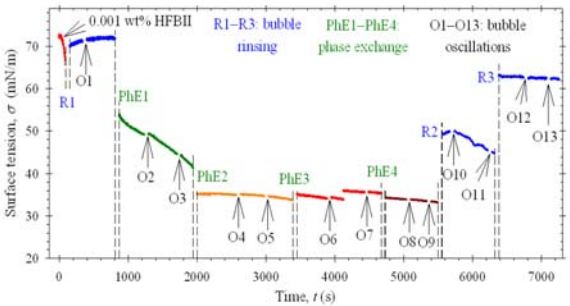




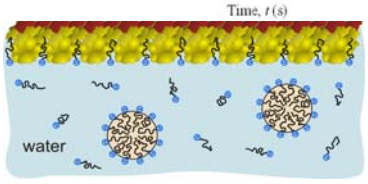
Hypothesis: SDS brings negative charge to HFBII aggregates, i.e. the aggregates are hydrophilic.

Stage / System	σ, mN/m	*E'*, mN/m	*E''*, mN/m
1) 0.001 wt% HFBII + 10 mM SDS (O1 and O2)	38	0	0.4
2) Rinsing with water (R1)	70	6.5	1.4
3) Rinsing with water (R2)	72	0	0

Sequential adsorption of SDS after HFBII



Stage / System	σ, mN/m	*E'*, mN/m	*E''*, mN/m
0.001 wt% HFBII (O1)	70	139	5.7
PhE1 with 1 mM SDS (O3)	43.9	102.2	17.3
PhE2 with 10 mM SDS (O4 and O5)	34	30.8	3.6
PhE3 with 20 mM SDS (O6 and O7)	35	29.7	2.7
PhE3 with 50 mM SDS (O8 and O9)	33.6	28.5	3.6
Rinsing with water R2 (O10 and O11)	45.5	134	1
Rinsing with water R3 (O12 and O13)	63	227.8	3.3

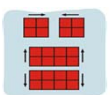


HFBII molecules irreversibly adsorb on water/air surface and cannot be displaced by the molecules of SDS at concentrations both below and above the CMC.

Stanimirova et al., *Colloids Surf. A* (2014) just appeared.

Surface Dilatational Elasticity

55 < σ < 65 mN/m (B)
– smaller aggregates merge first;
– bigger aggregates coalesce at greater π_s values because the electrostatic barrier is higher for them.



σ≈ 53 mN/m
the interfacial HFBII layer solidifies. The protein becomes the continuous phase forming an elastic protein network.

Maximum of $E(\sigma)$ ↔ surface phase transition.

(A)

65 < σ < 72 mN/m
protein molecules and small protein aggregates (oligomers) are present at the interface.