Experimental report

05/09/2022

Proposal:	**9-12-631**	**Council:**	10/2020

Title: Continuation of "structural characterisation of spread polyelectrolyte/surfactant films: new insight into tuneable reservoir formation"

Research area: Soft condensed matter

This proposal is a continuation of 9-12-614

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Samples: Poly(sodium styrene sulfonate)
Poly-L-lysine
h- and d25-sodium dodecyl sulfate
h- and d25-dodecyltrimethylammonium bromide

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	2	2	03/02/2021	05/02/2021

Abstract:

Our recent discovery of how to control the formation of extended structures in spread polyelectrolyte/surfactant (P/S) films at the air/water interface marked an exciting advance. It was achieved by tuning the charge of aggregates used in film preparation, which nucleate reservoirs of material upon surface area compression. Even so, the nature of the extended structures (loops, attached vesicles, multilayers) and the aggregate properties required for their nucleation (charge, hydration, size) remain unresolved. We performed a FIGARO experiment in August 2020 on the poly-l-lysine/sodium dodecyl sulfate system. Interestingly, reservoirs were shown to be nucleated by aggregates of different charge, with patches of surfactant bilayer or hemimicelles adhered to the primary P/S structure. Additional time of 2 days is required to record missing data as well as complete a short extension to provide optimal insight into the nature and underlying reasons for extended structure formation. This work will result in a high quality standalone publication and represents a key step towards finally resolving why extended structures form in certain P/S mixtures of broad interest to materials science.

Experimental report on FIGARO #9-12-631 (03–05 February 2021)

Continuation of "structural characterisation of spread polyelectrolyte/surfactant films: new insight into tuneable reservoir formation"

Scientific background

Oppositely charged polyelectrolyte/surfactant (P/S) mixtures have been studied extensively for decades because of their use in everyday life products,[1] as well as their varied applications from pharmaceuticals[2] to energy harvesting.[3] In recent years, efforts have been invested into understanding the relation between the interfacial properties of P/S mixtures and their bulk phase behaviour.[4,5] Recently, a method to prepare P/S trapped films at the air/water interface has been developed. The spread film formation is driven by Marangoni flow from the dissociation of the aggregates as they contact the water and trapping of the material due to entropy of counterion release.[6] It has also been demonstrated that extended structures can be formed at the air/water interface upon surface area compression beyond the surface pressure (Π) collapse of the film, but only when they are nucleated by aggregates overcharged with an excess of surfactant. While observations about the presence of monolayer vs multilayer structures have been made for P/S films previously,[7] this was the first time a methodology to control and tune extended structure formation had been developed. Even so, important questions remained about the structures (e.g. loops, attached vesicles, multilayers…) and the optimal physicochemistry of the aggregates that can nucleate their formation (e.g. charge, size, hydration…). Hence, we aim to resolve the extended structures for the first time using NR.

Experimental details

This experiment was focused on completing the study on the composition during dynamics and the structure of films spread from poly(L-lysine) (PLL)/sodium dodecyl sulfate (SDS) started in experiment #9-12-631. Besides, NR data from PLL/SDS films spread from overcharged aggregates was recorded before the collapse of the film. The low-Q_z approach was used to perform a compositional analysis of the PLL/SDS films during consecutive compression/expansion cycles. Besides, we recorded the missing full-Q_z measurements that we needed to complete the data set from the experiment #9-12-631.

Results

Figure 1 shows the results obtained in the experiment #9-12-614 from the compositional analysis of PLL/SDS films spread from overcharged aggregates (A) as a function of the area together with the surface pressure data and

(B) as a function of time. The results show that, while the surface pressure data reached a limiting value around 28mN/m, the surface excess (Γ) of both SDS and PLL continued to increase from 4.0 ± 0.1 μmol/m^2 to 5.5 ± 0.1 μmol/m^2 during the compression of the film beyond its collapse. This demonstrates that the material expelled from the surface monolayer remains bound in the form of extended structures. Assuming that Γ_{SDS} in the surface monolayer does not change beyond the collapse, a 27 ± 1 of the SDS would be in the extended structures. Besides, Γ_{SDS} and Γ_{PLL} were reproducible over successive cycles, confirming that there is not loss of material between cycles.

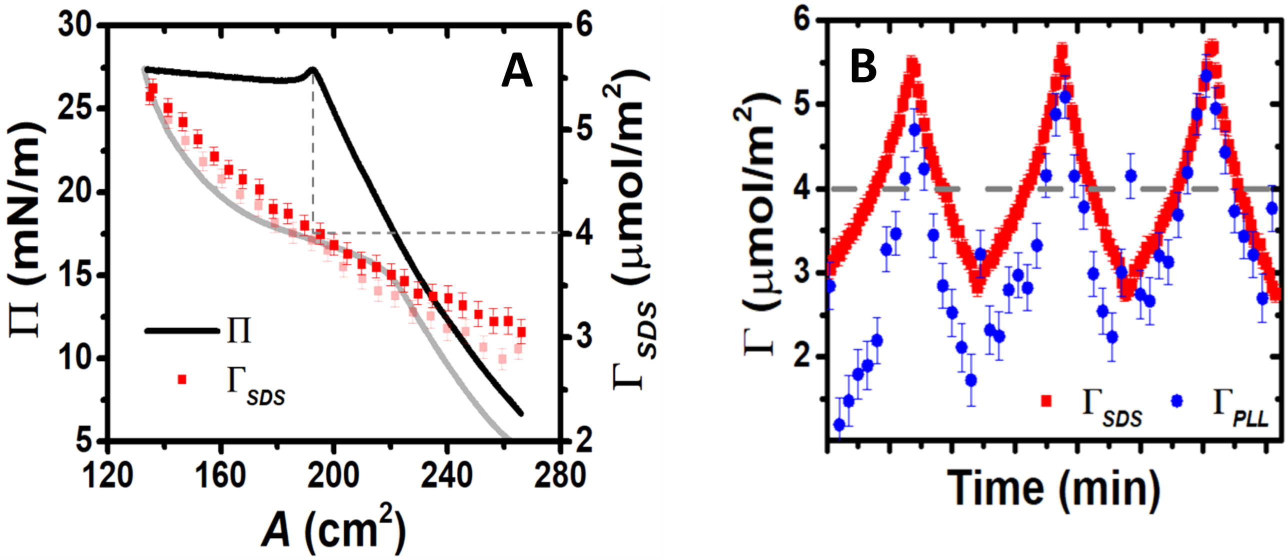

Figure 1. (A) Γ_{SDS} and surface pressure of PLL/SDS films spread from overcharged aggregates as a function of the area and (B) Γ_{SDS} (red squares) and Γ_{PLL} (blue circles) as a function of time over three consecutive compression/expansion cycles.

The NR profiles recorded for PLL/SDS films spread from overcharged aggregates (A) before the collapse and (B) at a x2 compression ratio are shown in Figure 2. Firstly, PLL/SDS layers at 23 mN/m, i.e. before collapse, present a NR profile typical of a monolayer. The analysis of the data confirms that the structure of the film consists of a monolayer of SDS at the air/water interface with PLL bound to the headgroups layer. The NR profile of the same film but compressed x2 clearly shows a Kiessig fringe in the d-SDS/ACMW and h-SDS/D2O isotopic contrasts, which are the ones presenting a greater scattering difference between the chains and the solvent, revealing the presence of extended structures. Indeed, the analysis of the data showed that the optimum layer structure involves 4 different layers: 1) surfactant tails, 2) surfactant headgroups with PLL electrostatically bound and solvent, 3) PLL layer and solvent, and 4) the extended structures formed by the surfactant molecules expelled from the interface. A roughness of 3.5 Å consistent with the presence of capillary waves was applied. Three different constraints were introduced in the fit: (1) the thickness of the surfactant chains in the monolayer was constrained to the surface excess obtained from the low-Q_z analysis at the collapse of the in surface pressure, i.e., 8.5 Å; (2)

Γ_{chains} and Γ_{heads} must be equal in the SDS monolayer ; (3) since the SLD of PLL is different in ACMW and D2O due to isotopic substation of labile protons, the SLD of the headgroups layer must be consistent between both contrasts so that the amount of PLL in this layer is the same. The thickness of the extended structures layer obtained from the fit is 21.8 ± 0.8 Å (almost twice that of the SDS monolayer). Since the addition of PLL to this layer did not improve the quality of the film, we conclude that these structures correspond either to discrete patches of SDS bilayer wrapped by a small, unresolved amount of PLL or to SDS hemimicelles bound the layer of PLL. From this analysis it can be concluded that the amount of SDS present in the extended structures is 29 ± 1%, consistent with the 27 ± 1% calculated above. This is the first time that the extended structures formed in spread P/S films is resolved.

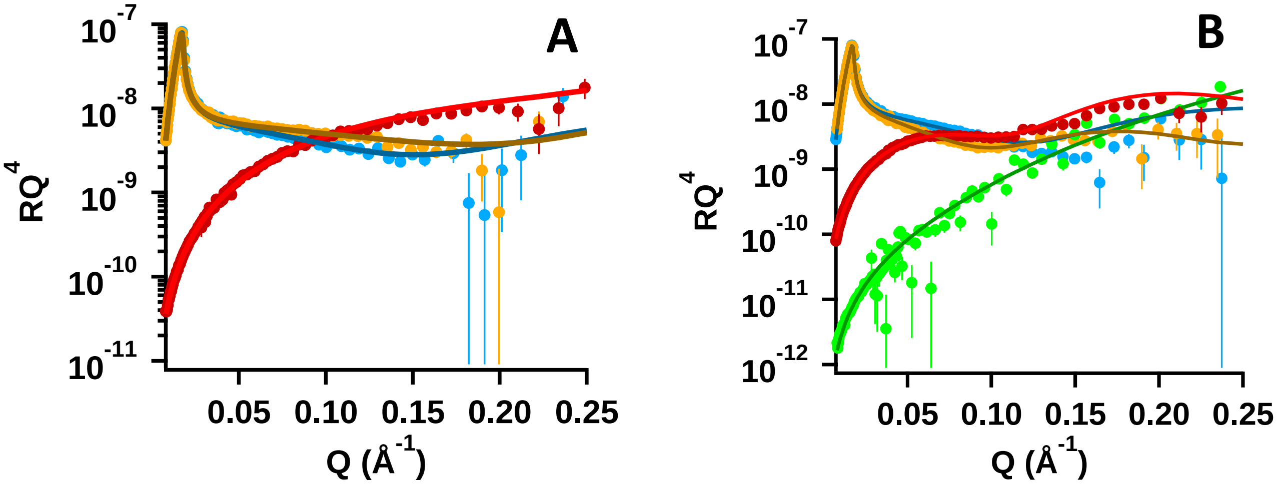

Figure 2. NR profiles of PLL/SDS films spread from overcharged aggregates (A) before the collapse and (B) at x2 compression ratio. The isotopic contrasts used were d-SDS/ACMW (red), d-SDS/D_2O (blue), h-SDS/D_2O (orange) and h-SDS/ACMW (green).

The results presented in Figure 1 and Figure 2B have been included in a manuscript recently accepted for publication in *Chemical Communications* where we demonstrate for the first time the possibility to reversibly control the surface monolayer coverage, switching on/off the extended structures, and control over their coverage.

References

[1] Guzmán, E. … Adv. Colloid Interf. Sci. 2016, 233, 38; [2] Barreiro-Iglesias, R. … J. Controlled Release 2003, 93, 319; [3] Sweet, M. L. … Appl. Surf. Sci. 2014, 289, 150; [4] Campbell, R. A. … Langmuir 2014, 30, 8664; [5] Varga, I. … Langmuir 2017, 33, 5915; [6] Campbell, R. A. … Soft Matter 2016, 12, 5304; [7] Tummino, A. … Langmuir 2018, 34, 2312.