Experimental report

25/01/2024

Proposal: 9-12-668 **Council:** 10/2022

Title: Tuning mechanical properties of spread polypeptide/surfactant films by specific interactions. Relationship with their structure and dynamics

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Sodium Dodecyl Sulfate
Poly-L-lysine
D25-Sodium Dodecyl Sulfate
poly-L-arginine

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	3	3	02/07/2023	05/07/2023

Abstract:

The work carried out over the last years on spread polyelectrolyte/surfactant (P/S) films at the air/water interface has resulted in important outcomes. The important role of polymer rigidity and compensation of interfacial charges on the stabilization of extended structures has recently been demonstrated. Besides, control over the formation of 2D vs 3D structures in poly-L-Lysine (PLL) and sodium dodecyl sulfate (SDS) films has also been shown. However, control over the interfacial properties and structure of the films by tuning specific P/S interactions is missing. To study the influence of such interactions between SDS headgroups and different polypeptides, we have used poly-L-arginine (PLA)/SDS films. In addition, the use of high compression ratios showed interesting film mechanical properties. This proposal aims to resolve the composition (low-Q approach) and structural changes (mid-Q approach) taking place during dynamics, as well as the structure of PLA/SDS films and complete the study of PLL/SDS films. This work can show for the first time the possibility to tune the mechanical properties and structure of P/S films through the design of specific P/S interactions.

Experimental report on FIGARO #9-12-668 (30 June – 02 July 2023)
Tuning mechanical properties of spread polypeptide/surfactant films by specific interactions. Relationship with their structure and dynamics

Experimental details

The main objective of this experiment was to determine the structure of PLA/SDS and PLL/SDS films at different compression ratios, as well as the compositional and structural kinetics during several compression/expansion cycles. First, it is important to mention that due to problems with the FIGARO anti-vibration table we lost part of our beamtime and the experimental objectives were not completed. We decided to focus then on the structural measurements, recording the full Q_Z reflectivity profiles at 6 compression ratios during compression and 2 ratios during expansion, while we recorded the missing x10 ratio for PLL/SDS films and 1 ratio during expansion. It is planned in the future to submit a continuation proposal to record low Q_Z data during compression/expansion cycles to determine the surface excess of polyelectrolyte and surfactant during kinetics. On the other hand, since the structure of these films is very complex at high compression ratios (as detailed below) we do not plan to make the structural measurements during compression/expansion cycles, since using a single contrast only in the mid Q_Z range it will be difficult to obtain accurate structural information.

Results

The main results obtained in this experiment are shown in Figure 1, where the reflectivity profiles collected using 3 isotopic contrasts for each of the indicated compression ratios are shown.

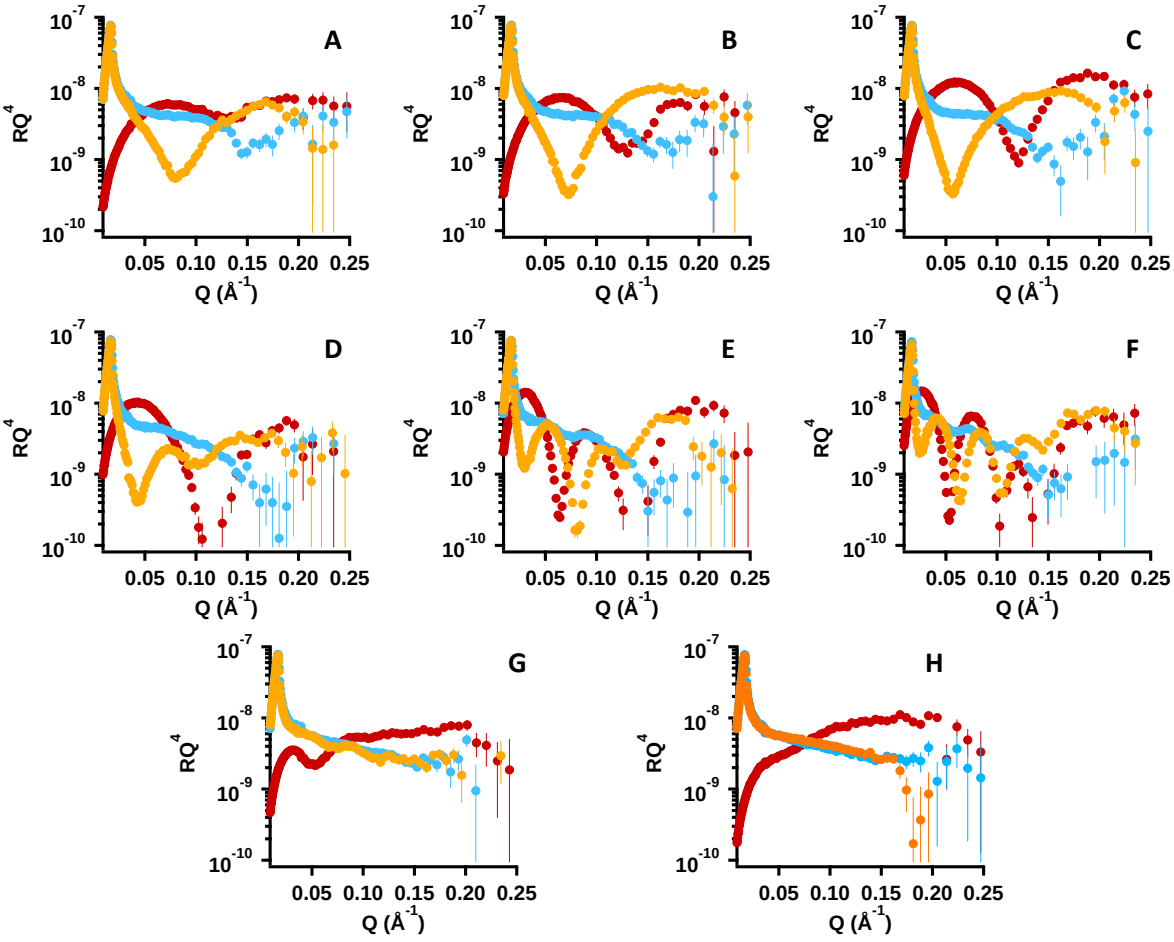

Figure 1. NR profiles of PLA/SDS films during compression (A) x2, (B) x2.5, (C) x3.5, (D) x4.5, (E) x6.5, (F) x10, and expansion (G) x3.5 and (H) x2. The different isotopic contrasts used are d-SDS/ACMW (red), d-SDS/D_2O (blue) and h-SDS/D_2O (orange).

It can be clearly seen how the layer becomes thicker and thicker, showing multiple Kiessig fringes, which indicates the presence of ES multilayers. Although a preliminary analysis of the data has been carried out which confirms the large increase in coverage of the ESs in more than one layer, there is still work to be done to resolve the structure of the films. In fact, future measurements of the surface excess of polyelectrolyte and surfactant during compression/expansion cycles will help to provide a further constraint for the analysis of the full Q_Z data, as we will know the total amount of polyelectrolyte and surfactant for each compression ratio. The large difference in the reflectivity profiles of panels A-H and C-G is very striking. Although measured at the same compression ratio, it is observed that the film structure is significantly different depending on whether the film is compressing or expanding. Therefore, this can give valuable information about the mechanism of the film for the formation of ESs during compression and the re-incorporation of that material into the monolayer during expansion.

Figure 2 shows the reflectivity profiles of PLL/SDS films at x10 compression ratio during compression and x3.5 during expansion. This data complete the dataset recorded at INTER (ISIS Neutron and Muon source) in experiment RB2210138. Contrary to PLA/SDS films, the high compression ratios do not give rise to the appearance of multiple Kiessig fringes, suggesting a film consisting of a monolayer and two PLL-rolled hemimicelles that is probably much denser than PLA/SDS films, as we recently published in a study in which the same systems are studied. (Nanoscale, 2023,15, 11141-11154)

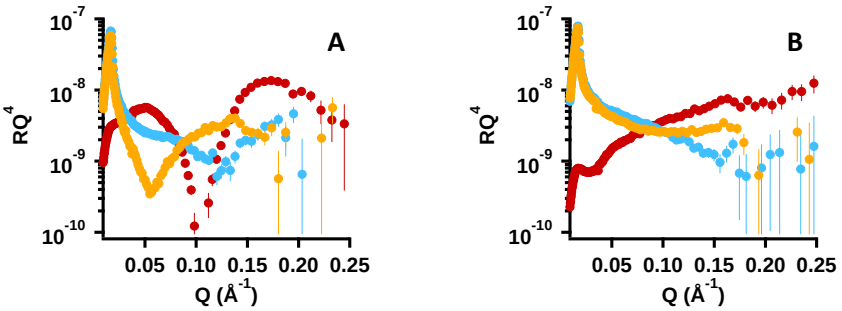

Figure 2. (A) Γ_{SDS} and surface pressure of PLL/SDS films spread from overcharged aggregates as a function of the area and (B) Γ_{SDS} (red squares) and Γ_{PLL} (blue circles) as a function of time over three consecutive compression/expansion cycles.

Outlook

The combination of the results obtained in this experiment with those obtained in the INTER experiment complete a set of measurements that will provide very valuable information about the variation of the structure of these films in a wide range of compression ratios. Furthermore, the difference in the structure during compression and expansion at the same compression ratio will give important information about the formation mechanism of ESs and the reincorporation of the material into the monolayer. Additionally, we plan to deposit these films on solids in the future and study them using AFM to see if the ESs are maintained, lost or rearranged in some way. The latter represents an important step for the possible application of this technology in fields such as antimicrobial coatings or tissue engineering. We therefore plan to publish this work in a high-impact journal by early 2025.