Experimental report

16/10/2020

Proposal: 9-12-614 **Council:** 4/2020

Title: Structural characterisation of spread polyelectrolyte/surfactant films: new insight into tuneable reservoir formation

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

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	3	3	17/08/2020	20/08/2020

Abstract:

The 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 over numerous previous observations of monolayer versus multilayer adsorption. It was achieved by tuning the charge of aggregates used in film preparation, which nucleate reservoirs of material upon spreading or surface area compression. Even so, the nature of the extended structures, in terms of loops, attached vesicles or multilayers, remained unresolved. We have now started to work on more a biologically relevant system - poly-l-lysine with sodium dodecyl sulfate (PLL/SDS) - with potential pharmaceutical applications in mind, which exhibits very different squeeze out dynamics to the system studied previously. This proposal aims to resolve the interfacial composition during film dynamics for the PLL/SDS system (low-Q approach) and perform the first structural characterisations of films formed using aggregates of different charge for both systems (full-Q approach). This work can represent a significant step towards finally resolving why extended structures form in certain P/S mixtures but not others.

Experimental report on FIGARO #9-12-614 (17–20 August 2020)

Structural characterisation of spread polyelectrolyte/surfactant films: new insight into tuneable reservoir formation

Scientific Background

The study of oppositely charged polyelectrolyte/surfactant (P/S) mixtures has received a lot of attention during the last century due to their widespread use in numerous applications.[1-3] Specifically, during the last decade, strong efforts have been devoted to understanding the influence that non-equilibrium (kinetically-trapped) states have on the association of P/S mixtures both in the bulk and at interfaces.[4-6] Recently, a method to prepare P/S trapped films at the air/water interface by spreading and consequently dissociating kinetically-trapped aggregates that have been self-assembled in solution has been developed.[7] In addition, it has been demonstrated that it is possible to control the formation of extended structures (reservoirs) during compression/expansion of poly(sodium styrene-sulfonate) (NaPSS)/dodecyltrimethylammonium bromide (DTAB) films by tuning the charge/structure of the aggregates.[8] Furthermore, a certain analogy can be found between these systems and the dynamics of lung surfactant, where nucleation of lipid reservoirs by lung surfactant protein B occurs during respiration.[9] Despite the progress made, the structure of the reservoirs has not yet been resolved and the materials used were not biocompatible. These limitations motivated the current neutron reflectometry (NR) study on FIGARO.

Experimental details

This study has focused on: (i) extending the spreading methodology to more biocompatible systems of potential use in pharmaceutical applications, and – potentially – to see if the gap can be bridged into the physicochemical processes occurring during nucleation of extended lipid reservoirs by lung surfactant protein B during respiration, and (ii) resolving the structure of both NaPSS/DTAB and poly(L-lysine) (PLL)/sodium dodecyl sulfate (SDS) films at the maximum compression.

After a characterisation of the zeta potential of 100 ppm PLL/SDS mixtures varying the concentration of the surfactant, we performed surface pressure and ellipsometry measurements during compression/expansion cycles of films spread from undercharged ([SDS] = 0.5 mM) and overcharged aggregates ([SDS] = 0.8 mM). This preliminary characterisation of the system showed the need to perform NR experiments to understand the various structural transformations taking place.

It is worth mentioning how the COVID-19 crisis has affected the experimental plan, especially with regard to the preparation of the experiment. During the two weeks before the experiment, a lot of work was required to check the sample environment and perform different tests on the materials to see if we could reproduce the surface pressure behaviour of the system in the Langmuir trough used in FIGARO, which has a different size to the one used in recording the preliminary data. Work was also required to interface the Langmuir trough to the NOMAD software. This work was completed just as the ILL reopened following its closure, and access was granted only for 2 or 3 days per week. Therefore, unfortunately, whilst of course we had planned to do so under normal working conditions, there was no time remaining to check the surface pressure behaviour of PLL/SDS mixtures using the deuterated surfactant before the experiment.

We faced problems with the d-SDS during the experiment since from the surface pressure behavior it seemed that the amount of it in the sample was significantly less than what we had added. Zeta potential measurements were performed to determine qualitatively the amount of SDS bound to PLL chains. While a 100 ppm PLL/0.5 mM h-SDS sample gave a zeta potential value of ~ 17 mV, the same sample using d-SDS gave a value of ~ 40 mV. Therefore, since the batch was new, the differences were attributed to the presence of impurities. Finally, another batch was provided to us and we obtained a zeta potential value of ~ 20 mV. Unfortunately, this lost us about 1 day of beam time, which meant that measurements on films prepared from neutral aggregates were not completed.

Results

Dynamic interfacial composition analysis of PLL/SDS films spread from undercharged and overcharged aggregates was measured using the low Q approach.[7] For that purpose, measurements on FIGARO during compression/expansion cycles were performed using 2 isotopic contrasts: h-SDS/PLL and d-SDS/PLL in air contrast matched water (ACMW). The results of the interfacial composition analysis during 3 cycles for PLL/SDS films spread from undercharged and overcharged aggregates are shown in Figure 1 together with the corresponding Langmuir isotherms. While the surface pressure data reached a limiting value around 28 mN/m in both cases, the surface excess of SDS and PLL continued to increase in each cycle. Moreover, the surface excess corresponding to a full monolayer of SDS determined by NR is 4.2 μmol/m^2, which coincides with the surface excess of the system when the collapse is reached. Since the surface excess of surfactant after the collapse increases reproducibly above 4.2 μmol/m^2, the results obtained by NR strongly suggest that extended structures (i.e. more surfactant than in the surface monolayer) are formed beyond the collapse of the films. Furthermore, the presence of the same amount of material for each cycle suggests that the material sequestered into the extended structures during the compression is efficiently reincorporated to the surface monolayer during the expansion.

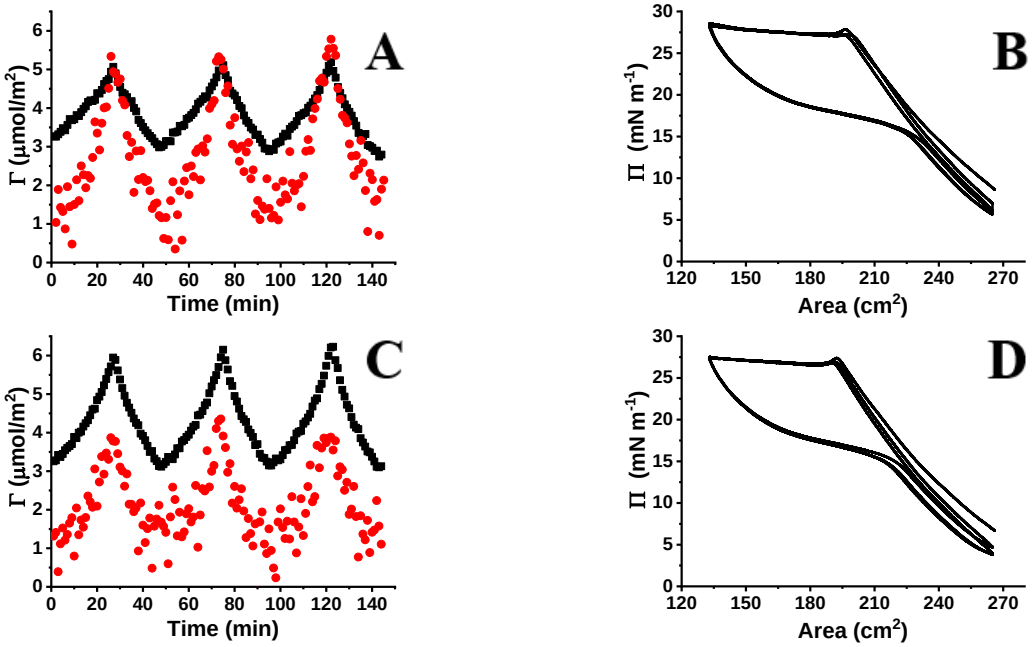
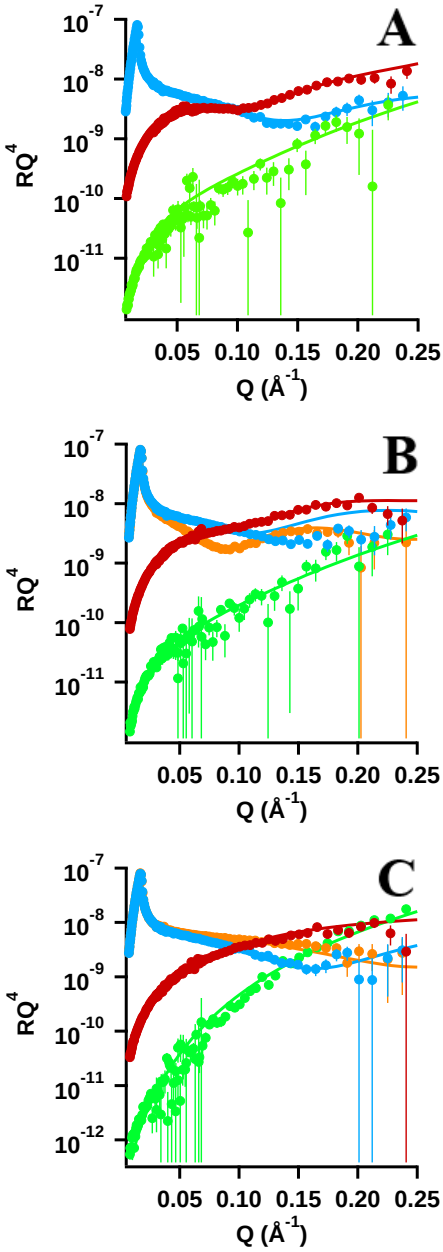


Figure 1. Surface excess of PLL (red circles) and SDS (black squares) obtained using NR for PLL/SDS films spread from (A) undercharged and (C) overcharged aggregates; corresponding Langmuir isotherms in panels B and D, respectively.

Following the dynamic interfacial compositional analysis of PLL/SDS films, full Q measurements were performed to determine the structure of films spread from PLL/SDS overcharged and undercharged aggregates, and NaPSS/DTAB overcharged aggregates, which have already been shown to form reservoirs during compression/expansion cycles.[8] 4 isotopic contrasts (h-SDS/PLL and d-SDS/PLL in ACMW and D_2O) were measured for PLL/SDS undercharged aggregates and NaPSS/DTAB overcharged aggregates, while the h-SDS/PLL on D_2O contrast is missing for PLL/SDS overcharged aggregates due to time limitation. Figure 2 shows the reflectivity profiles of the different contrasts for each sample and the best fittings obtained in the preliminary analysis of the data. Both PLL/SDS films spread from overcharged and undercharged aggregates requires a 4-layer model: surfactant chains/surfactant heads/polyelectrolyte/surfactant bilayer. This is consistent with the results obtained from the low Q analysis where the surface excess of surfactant after the collapse suggests the formation of extended structures. Moreover, interestingly the same approach was used to resolve the structure of poly(phenylene sulfone)/tetradecyltrimethylammonium bromide mixtures in which the surfactant surface excess was greater than monolayer coverage.[10] Although films spread from NaPSS/DTAB overcharged aggregates were demonstrated to form reservoirs during compression/expansion cycles, there is no evidence of an extended

structure in the reflectivity profiles of the film at the maximum compression and after the equilibration. Indeed, the best fit obtained so far suggests that the film is composed of 3 layers: surfactant chains/surfactant heads/polyelectrolyte. It should be noted that these are initial fits as the experiment was performed shortly before the next proposal deadline, and work is required still to optimize the models to obtain the best fit of the data to get the structure of the P/S films.



	d-surf/ACMW	d-surf/D_2O	h-surf/D_2O	h-surf/ACMW
d_1 (Å)	7.5	7.5	-	7.5
ρ_1 (x 10^{-6} Å^{-2})	7	7	-	-0.39
v_{f1}	0	0	-	0
d_2 (Å)	4	4	-	4
ρ_2 (x 10^{-6} Å^{-2})	2.4	3.7	-	2.4
v_{f2}	0	0	-	0
d_3 (Å)	7	7	-	7
ρ_3 (x 10^{-6} Å^{-2})	1.09	3.09	-	1.09
v_{f3}	40	40	-	40
d_4 (Å)	20.271	20.271	-	20.271
ρ_4 (x 10^{-6} Å^{-2})	6.69	6.69	-	0.39
v_{f4}	74	74	-	75

	d-surf/ACMW	d-surf/D_2O	h-surf/D_2O	h-surf/ACMW
d_1 (Å)	8.5	8.5	8.5	8.5
ρ_1 (x 10^{-6} Å^{-2})	7	7	-0.39	-0.39
v_{f1}	0	0	0	0
d_2 (Å)	4	4	4	4
ρ_2 (x 10^{-6} Å^{-2})	4.89	4.89	4.89	4.89
v_{f2}	70	70	70	70
d_3 (Å)	12	12	12	12
ρ_3 (x 10^{-6} Å^{-2})	1.09	3.09	3.09	1.09
v_{f3}	50	50	50	50
d_4 (Å)	20	20	20	20
ρ_4 (x 10^{-6} Å^{-2})	6.69	6.69	0.39	0.39
v_{f4}	90	90	75	75

	d-surf/ACMW	d-surf/D_2O	h-surf/D_2O	h-surf/ACMW
d_1 (Å)	7	7	7	7
ρ_1 (x 10^{-6} Å^{-2})	7	7	-0.39	-0.39
v_{f1}	0	0	0	0
d_2 (Å)	6	6	6	6
ρ_2 (x 10^{-6} Å^{-2})	0.78	0.78	0.78	0.78
v_{f2}	35	35	35	35
d_3 (Å)	5	5	5	5
ρ_3 (x 10^{-6} Å^{-2})	1.85	2	2	1.85
v_{f3}	100	100	50	50

Figure 2. Neutron reflectivity profiles of films spread from (A) PLL/SDS overcharged aggregates, (B) PLL/SDS undercharged aggregates and (C) NaPSS/DTAB overcharged aggregates recorded in (blue) d-surf/D_2O, (orange) h-surf/D_2O, (red) d-surf/ACMW and (green) h-surf/ACMW. The corresponding lines represent the results of a preliminary analysis. The tables show the values of thickness (d_i), roughness (r_i) and volume fraction (v_{fi}) obtained from the correspondent fit for each layer of the system.

References

[1] Guzmán, E. et al. Adv. Colloid Interf. Sci. 2016, 233, 38; [2] Barreiro-Iglesias, R. et al. J. Controlled Release 2003, 93, 319; [3] Sweet, M. L. et al. Appl. Surf. Sci. 2014, 289, 150; [4] I. Varga and R. A. Campbell, Langmuir 2017, 33, 5915; [5] Llamas, S. et al. Adv. Colloid Interface Sci. 2015, 222, 461; [6] Bain, C. D. et al. Adv. Colloid Interface Sci. 2010, 155, 32; [7] Campbell, R. A. et al. Soft Matter 2016, 12, 5304; [8] Tummino, A. et al. Langmuir 2018, 34, 2312; [9] Pérez-Gil, J. et al. BBA – Biomembranes 2008, 1778, 1676; [10] Uhlig, M. et al. Chem. Commun. 2020, 56, 952.