Experimental report

10/03/2017

Proposal: **9-12-461** **Council:** 4/2016

Title: Interfacial stoichiometry of polyelectrolyte/surfactant films spread from aggregates: effects of aggregate charge and ionic strength

Research area: Soft condensed matter

This proposal is a continuation of 9-12-408

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Samples:
Sodium Bromide
Poly(sodium styrene sulfonate)
h25 & d25 - dodecyltrimethylammonium bromide

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	5	5	25/06/2016	27/06/2016
			15/02/2017	17/02/2017
			06/03/2017	07/03/2017

Abstract:

The non-equilibrium nature of polyelectrolyte/surfactant mixture has received due attention over the last few years. Very recently we have exploited the dissociation and Marangoni spreading at the air/water interface of aggregates formed in the bulk to generate highly efficient membranes with a much higher surface excess than can be achieved from equilibrium adsorption. The NaPSS/DTAB films measured to date are present in a kinetically-trapped state and, thanks to resolution of the dynamic interfacial composition using a novel application of FIGARO, we have shown that they are durable with a faithful surface stoichiometry of 1:1 binding. Following our initial conceptual study last September, we propose now to go on to deliver a thorough characterization of the system with respect to the charge of the aggregates spread and the ionic strength of the subphase. Prior ellipsometry and surface pressure isotherm measurements clearly motivate the need for us to gain a deeper understanding of these parameters. The results should not only generate a comprehensive full paper but also lead to final-year work on encapsulation and deposition-based applications for the PhD student involved.

Report for 5-Days Experiment #9-12-461 on FIGARO:

Interfacial stoichiometry of polyelectrolyte/surfactant films spread from aggregates: effects of aggregate charge and ionic strength

Abstract

The aim of the following experiments is to exploit the phase behaviour of aggregate dispersions composed of oppositely charged polyelectrolyte and surfactants to prepare surface loaded membranes out of equilibrium conditions at the air-water interface, through an all-in-water approach. Our method is based on the Marangoni spreading of polyelectrolyte/surfactant (P/S) colloidal dispersion containing aggregates of different charge, i.e. prepared at fixed [P] = 100 ppm and varying [S] over a broad range. In order to investigate the effect of the sample history on the membranes chemical composition as well as on the overall surface excess, two different sample preparation methods will be compared: spreading from aliquots of P/S dispersion vs. adsorption from solutions with equivalent total bulk composition. A systematic investigation of the effect of the ionic strength of the aqueous subphase (pure water and 100 mM NaCl water solution) on the stoichiometry and mechanical properties of the films has been carried on using surface tensiometry, ellipsometry (PSCM) and specular neutron reflectometry (NR; FIGARO).

Preliminary Investigation

Our studies have focused on spread films from aggregate dispersions, formed in the system poly(sodium styrene sulfonate) and dodecyltrimethylammonium bromide (NaPSS/DTAB). In order to investigate the effect of the charge of the aggregates on the properties of the films, the dispersions were produced at a fixed [P] = 100 ppm while varying [S] over a broad range (from 0.43 mM to 25 mM). First, we prepared stock solutions of each component at double their final bulk concentration (200 ppm of PSS; 0.86 to 50 mM DTAB), then we mixed them fast at mid-air using two pipettes. Figure 1 contains information about the charge of the aggregates produced with this approach. The turbidity data are shown as well.

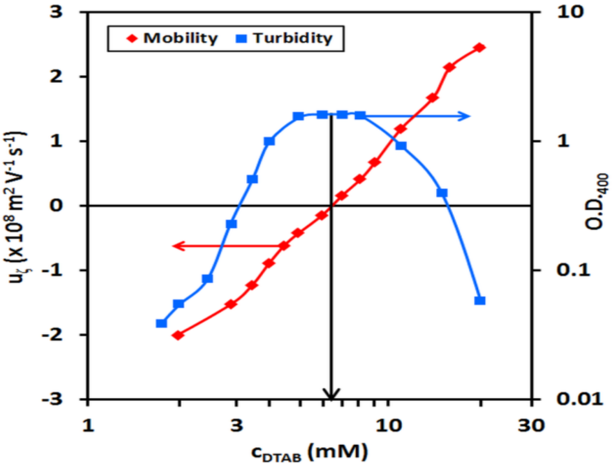

Figure 1- Electrophoretic mobility data of freshly mixed NaPSS/DTAB samples, and optical density data measured at 400 nm. Lines joining the data are to guide the eye.

After, a small aliquot (100 µl) of the dispersion is spread onto pure water, the overall surface excess is monitored by mean of dynamic ellipsometry (figure 2), i.e. following the evolution of the phase shift of the membranes with respect to the bare interface, as a function of time. The effect of sample history has been investigated by comparison with previously diluted solutions of PSS and DTAB matching the total final bulk concentration of the spread ones. Moreover, we have extended characterization to the effect of the ionic strength of the subphase. To do so, we have repeated all the above mentioned measure onto 100 mM NaCl aqueous solution.

These results suggest that the sample history has a strong effect on film formation: a trapped layer with higher surface excess is produced by spreading rather than bulk adsorption. Furthermore, the films are stable over almost the entire range of concentration tested so far. A deviation is observed when spreading at relatively high concentration of DTAB. In this case, we observe a rapid decay of the signal, probably related to the solubilisation of material from the interface to the bulk of the subphase.

The mechanical features of the spread films have been evaluated by performing 5 consecutive compression/expansion cycles of the interface. The surface pressure was followed through the Wilhelmy method; the surface excess has been derived *in situ* by performing NR measurements only at low Q_z on FIGARO.

Results

The effect of the ionic strength was investigated by using pure water or 100 mM NaCl solution as the subphase, contained in FIGARO's Langmuir trough with a volume of 125 ml. The high flux of the FIGARO instrument combined with the TOF analysis allowed us to resolve the surface composition of each system in less than eight hours. This approach consists of measuring the reflectivity profile only at low Q using just two contrasts: hydrogenous PSS + deuterated DTAB (d-DTAB) in air contrast match water (ACMW) and hydrogenous PSS + contrast match DTAB (cm-DTAB) in ACMW. Measurements at low Q are insensitive to the structure of the layer and depend only on the scattering excess, which itself is a convolution of the amount of material and its scattering properties. The scattering excess is then converted to surface excess by solving the linear equations:

$$(\sigma \cdot d)_1 = \mathrm{N_A}.(\Gamma_{\mathrm{surf}} \cdot b_{\mathrm{i,d-surf}} + \Gamma_{\mathrm{poly}} \cdot b_{\mathrm{i,poly}})$$
$$(\sigma \cdot d)_2 = \mathrm{N_A}.\Gamma_{\mathrm{poly}} \cdot b_{\mathrm{i,poly}}$$

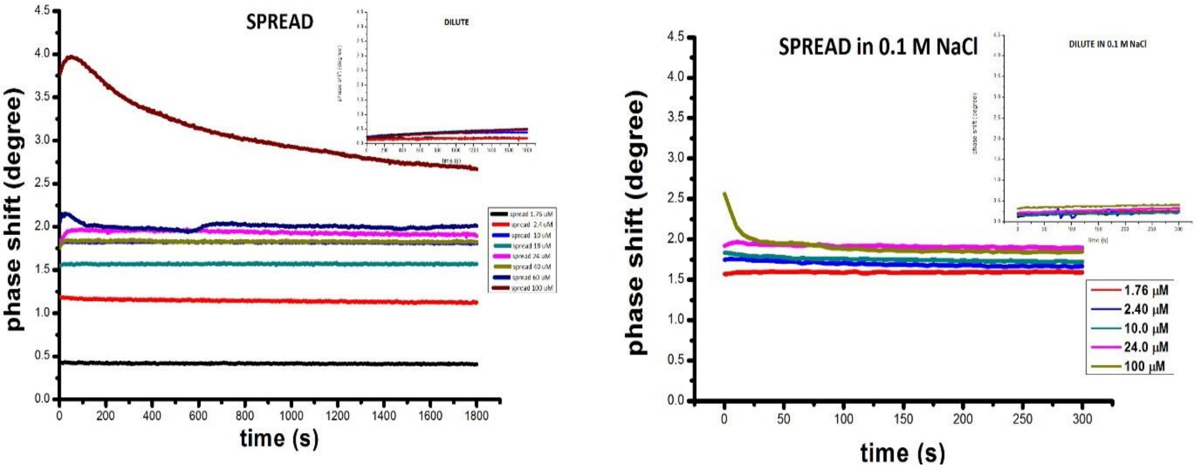

Figure 2- Ellipsometry measurements of the surface excess of NaPSS and DTAB spread film varying the DTAB concentration in the spreading dispersion onto: pure water (left); 100 mM NaCl (right).the small square in the two sets of data are relative to the surface excess of previously diluted sample matching the final bulk concentration. Spread films were prepared using 100 µL aliquots of 100 ppm, 17k NaPSS on 20 mL of pure water in a static trough.

Here the product $\sigma \cdot d$ is the fitted product of the scattering length density and layer thickness of a uniform layer at the air-water interface, b_i is the scattering length of the molecule and N_A is Avogadro's number. The results are given in figure 3 and they are in good agreement with Langevin's prediction of equimolar binding for dilute systems involving flexible polyelectrolytes and our previous measurements on films spread from neutral aggregates. Surprisingly, the surface excess of both P and S does not vary within the two phase region, when large aggregates are produced. As soon as we increase the concentration of DTAB outside this region, the two quantities start increasing, but still their ratio stays very close to the one-to-one molar charge binding.

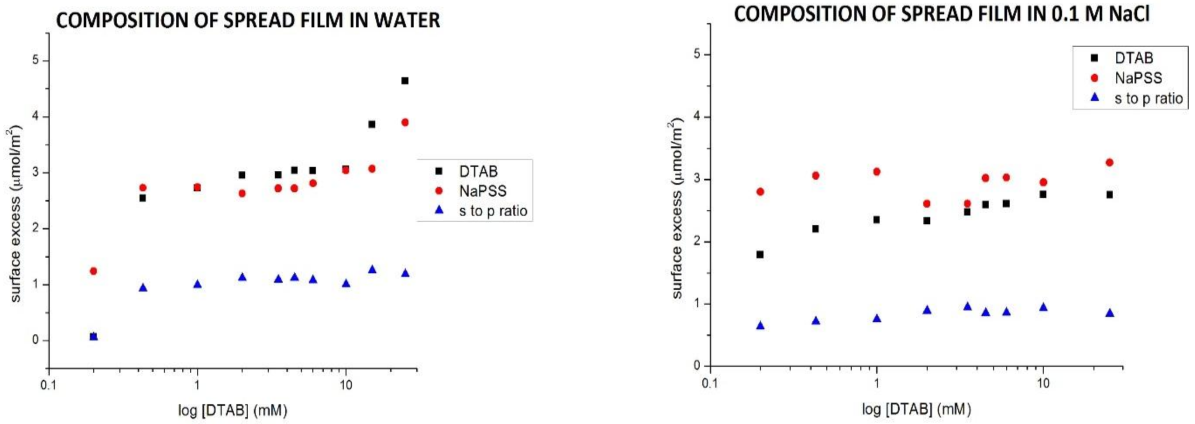

Figure 3- stoichiometry of the air/water interface and surfactant to polymer ratio after the first compression. The surface excess is plotted vs the logarithm of the DTAB concentration in the spreading solution.

The ionic strength has a more marked effect on the film composition: at all the concentrations measured, the surface excess of P is almost constant and it exceeds that of S. As consequence the S-to-P stays always below unity. At the same time, a small increase in the surfactant surface excess is observed. The higher polyelectrolyte surface excess than the corresponding spread film in pure water can be explained by the increase in the number of loops of the adsorbed chain at the surface, thus increasing the effective monomer density at the air-water interface. We moved to characterize the physical properties P/S spread films at different charge of the aggregates, from slightly negatively charged to positively charged aggregates. The surface excess has been followed *in situ*, using NR again. The results are contained in figure 4.

These results shows that these P/S films behave like perfectly insoluble membranes in both ionic strength regimes, which is rather surprising as we had imagined that the higher ionic strength would have reduced the entropy gain of counterion release rendering them more soluble, i.e. closer to an equilibrium system. In fact, the maxima and the minima of the surface excess, which mark full compression and full expansion of the trough, respectively, do not vary during the consecutive cycles. The one-to-one molar charge ratio is also still observed in pure water and it is kept in all the cycles. This situation however is different at high ionic strength since in this condition the polyelectrolyte can form loops at the surface, increasing its monomer density.

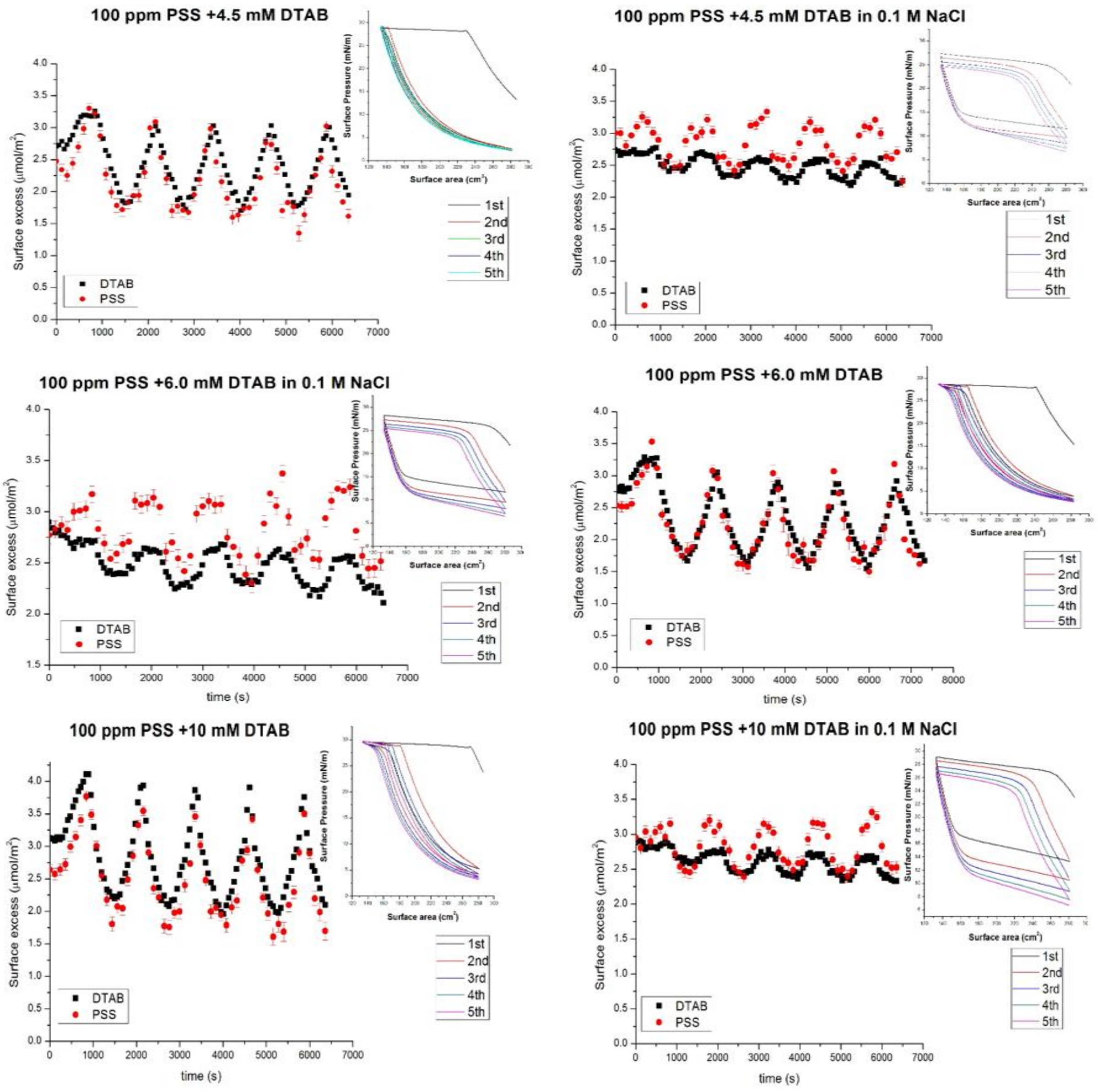

Figure 4- (left) Surface stoichiometry derived from NR during five consecutive compression expansion cycles with correspondent isotherm in pure water (in the small square on the top right); (right) Surface stoichiometry derived from NR during five consecutive compression expansion cycles with correspondent isotherm in 100 mM NaCl subphase. For both high strengths 500 ul containing 100 ppm PSS + 4.5, 6.0 and 10 mM DTAB were spread onto 125 ml of subphase.

Outlook

This work will be written up as a publication during the Spring of 2017 by ILL student Andrea Tummino. The work paves the way for a detailed study later in 2017 on spread films created from aggregates of poly(ethylene imine) and sodium dodecyl sulfate. The strength of interaction in this system depends strongly on the pH and the polyelectrolyte is available commercially in 3 molecular weights. These parameters will be systematically studied in order to gain a better understanding of how to optimize further the production of spread films for efficient use of materials in applications. We believe that our findings can open new possibilities in the production of thin and efficient molecular films at the air-water interface, prior to transfer for technological applications, spacing from coating based technologies to organic photovoltaic (OPV) devices fabrication.