Experimental report

05/09/2022

Proposal: **9-10-1656** **Council:** 4/2020

Title: First direct exploitation of non-equilibrium aggregate effects in polyelectrolyte/surfactant mixtures totune emulsion stability

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Hexadecane
Poly(diallyldimethylammonium chloride)
Oleic acid
d34-hexadecane
d34-oleic acid

Instrument	Requested days	Allocated days	From	To
FIGARO User-supplied	3	3	06/07/2021	09/07/2021

Abstract:

This proposal extends for the first time advances on the strong influence of non-equilibrium effects in polyelectrolyte/surfactant (PE/S) mixtures at the air-water interface made using neutron reflectometry (NR) to tuning emulsion stability at the oil-water interface. While PE/S mixtures exhibit high surface activity and are commonly used to stabilise emulsions, aggregates produced in the aqueous phase can contact and modify the properties of the oil-water interface, resulting in droplet coalescence and reduced stability. This work concerns a comparison of the structures created at the oil-water interface as a function of the strength of the PE/S interaction and the presence versus absence of bulk aggregates in the aqueous phase. While the former factor is tuned through the solution pH, the latter is tuned through a unique comparison of mixing both PE/S components in the aqueous phase versus introducing surfactant in the oil phase and polyelectrolyte in the aqueous phase. Only NR can deliver a direct characterisation of the interfacial structure and composition. The work will mark the first study of its kind to tune non-equilibrium effects to influence future emulsion technologies.

Experimental report on FIGARO #9-10-1656 (05–07 May 2021)

Continuation of "First direct exploitation of non-equilibrium aggregate effects in polyelectrolyte/surfactant mixtures to tune emulsion stability"

With permission of the instrument responsible, this experiment was conducted on a related polyelectrolyte/surfactant system because due to the travel restrictions imposed by the covid-19 pandemic, it was thought not possible to conduct such a challenging oil/water interface experiment remotely.

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…).

Experimental details

In experiments #9-12-614 and #9-12-631 a comprehensive characterization of the dynamic behaviour of PLL/SDS films at the air/water interface spread from undercharged and overcharged aggregates was carried out. The use of neutron reflectometry (NR) showed that extended structures of SDS were formed when the film was compressed beyond its collapse in surface pressure and that the material expelled was reincorporated into the surface monolayer upon expansion. Excitingly, we performed a structural analysis of the films showing for the first time that the extended structures are formed by discrete patches of SDS bilayer wrapped by a small, unresolved amount of PLL or by SDS hemimicelles bound to the PLL layer. With these results we know the compositional dynamics and structure of PLL/SDS films at the air water interface. But, what kind of structural changes are taking place during dynamics? To answer this question we aimed to develop a new NR methodology that allows to follow the structural changes taking place during dynamics measuring the reflectivity in 1 min slices.

In order to develop this methodology, it was necessary to decide which angle of incidence and isotopic contrast were optimal to follow the 3D structural changes. First, we decided to use an angle of incidence of 1.97° and reduce the data over 3.6–20 Å to get Q_z = 0.02–0.12 $Å^{-1}$.The reason for this choice was because the Keissig fringe that reveals the presence of the extended structures appears in this Q_z region and the peak of the neutron flux is found at Q_z = 0.1 $Å^{-1}$ where the Keissig fringe appears. Then, although we measured the d-SDS/ACMW and h-SDS/D_2O isotopic contrasts because they were the ones showing the Keissig fringe symptomatic of the extended structures, the optimum is h-SDS/D_2O. While the reflectivity in the d-SDS/ACMW contrast is dominated by the d-SDS monolayer, in the h-SDS/D_2O contrast it is dominated by the subphase and its sensitivity to the presence of the monolayer is much lower. Thus, the penetration of h-SDS molecules into the D_2O subphase when the extended structures are formed causes a large modulation of the reflectivity due to the very high scattering difference between the surfactant chains and the solvent.

Results

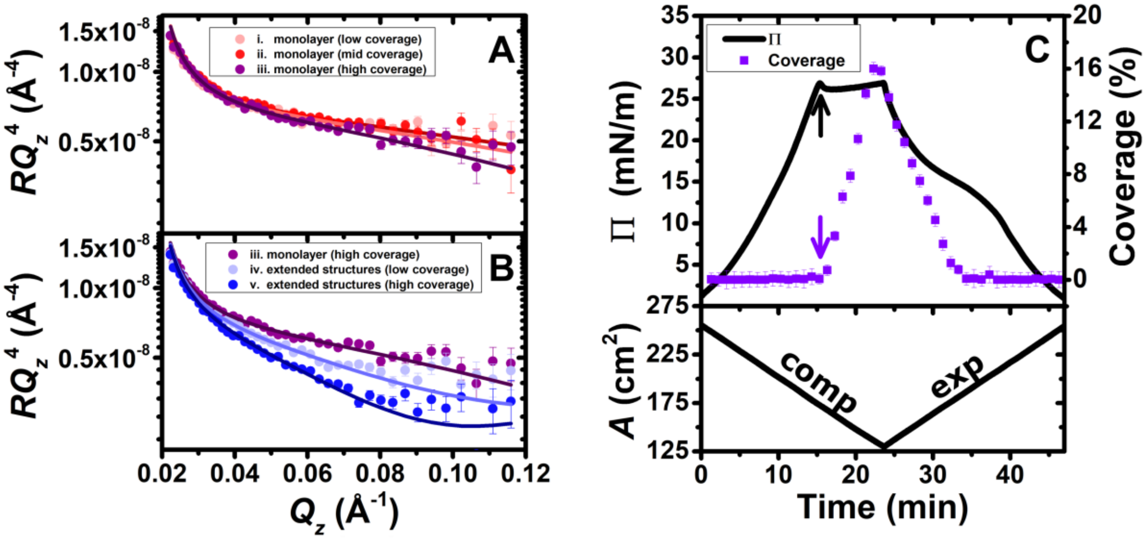
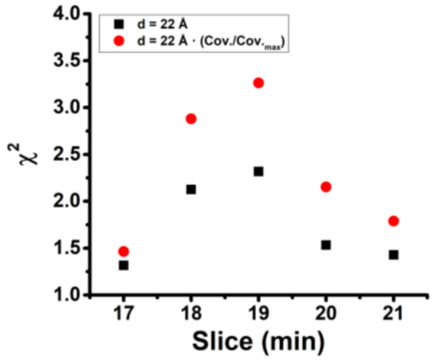


Figure 1. (A) NR profiles of a PLL/SDS spread film using the h-SDS/D_2O contrast at different compression states: (A) monolayer region and (B) extended structure region. The indices i-v indicate different compression states where i and v correspond to the minimum and maximum compression of the film, respectively. (C) Variation of Π (black line) and the coverage of the extended structures (violet squares) with respect to the time. The black and violet arrows indicate the film collapse and the onset of extended structures, respectively. Variation of the area versus time is also shown at the bottom.

Figure 1A shows the NR profiles of A PLL/SDS film spread from overcharged aggregates using the h-SDS/D_2O contrast at different compression states. The NR profiles together with the simulations of the reflectivity profiles based on a surface monolayer (Figure 1A) show that the variation in surface monolayer coverage has a small effect on the reflectivity. On the contrary, the NR together with fits of the volume fraction at a constant extended structure thickness of 21.8 Å show the very high sensitivity of this methods to changes in the coverage of the extended structure layer (Figure 1B). Figure 1C shows the variation of Π and the coverage of the extended structures layer as a function of time during 1 compression expansion cycle. It is clearly shown that the extended structures start to form (violet arrow) only when the surface pressure collapse is reached (black arrow), increasing during the compression beyond the collapse and decreasing back to 0 during the Π pseudo –plateau upon expansion.

The aim of the development of this methodology was to resolve if the changes in reflectivity after the collapse were consequence of changes in the thickness or the coverage of the extended structures. For that reason, Figure 2 shows the comparison of fits of the data after the collapse using two different approaches: (1) constant thickness of the extended structures and variation of its coverage, and (2) changes in the thickness keeping the volume fraction equal to the one obtained using approach 1 for each slice. The results obtained using approach 2 exhibits significant worse agreement. As revealed by an increase of up to 30% in the global χ^2 parameter. Therefore, it can be concluded that the coverage of the extended structures can be controlled by compressing/expanding the films.



	Approach 1 d_4 = 22 Å			Approach 2 d_4 = 22 · (Cov./Cov.$_{max}$) Å		
Slice (min)	d_4 (Å)	Coverage (%)	χ^2	d_4 (Å)	Coverage (%)	χ^2
17	22	3	1.316	4	24	1.463
18	22	6	2.126	9	19	2.880
19	22	8	2.318	11	18	3.263
20	22	11	1.533	15	17	2.153
21	22	14	1.427	19	17	1.788
22	22	16	1.830	22	--	--

Figure 2. Variation of the χ^2 of different 1-min slices fits in the extended structures region (Π collapse) using approaches 1 (black squares) and 2 (red circles). The table shows the values of thickness (d) and coverage used in each case and the correspondent χ^2 values.

The results presented in this experimental report 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. In this manuscript it is shown for the first time the possibility to follow the 3D structural changes in fluid films at the air/water interface taking place during dynamics using NR.

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.