Experimental report

06/11/2023

Proposal: **9-12-460**

Council: 4/2019

Title: Equilibrium and non-equilibrium structures of a polyelectrolyte/surfactant mixture at the oil/water interface

Research area: Soft condensed matter

This proposal is a new proposal

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

Instrument	Requested days	Allocated days	From	To
FIGARO User-supplied	4	6	03/03/2017	05/03/2017
			27/06/2018	29/06/2018
			29/09/2018	01/10/2020

Abstract:

While oppositely charged polyelectrolyte/surfactant mixtures, present in many of the product formulations we use on a daily basis, have been well studied at the air/liquid and solid/liquid interfaces using neutron reflectometry, such work at the liquid/liquid interface has not been attempted to date. Equally, there has been a recent focus on the non-equilibrium properties of these systems both in the bulk and at interfaces due to the presence of kinetically-trapped states. In this work we will make a comparison of the equilibrium and non-equilibrium properties of such a mixture at the oil/water interface for the first time. The former aim will be accessed through adsorption of molecular components from one-phase solutions. The latter aim will be accessed through the dissociation and spreading of material from neutral aggregates with films both transferred from the air/water interface and formed in situ at the oil/water interface. A starting point for the prediction of any of the resulting interfacial structures does not even exist, and our intention is that these measurements will lay the foundation for future work on controlled delivery applications at different fluid interfaces.

FINAL EXPERIMENTAL REPORT: #9-12-460

Equilibrium and non-equilibrium structures of a polyelectrolyte/surfactant mixture at the oil/water interface

Richard Campbell, Andrea Tummino & Imre Varga

FIGARO, 3–5 March 2017 & 27–29 June 2018 & 29 September–1 October 2018

Abstract

The mechanism of formation of interfacial multilayers in oppositely charged polyelectrolyte/ surfactant systems has recently come under scrutiny. Typically the rationalization of the presence of a Bragg peak in neutron reflectivity data of such systems is surface induced self assembly. However, for the system Pdadmac/SDS we demonstrated on FIGARO that the underlying process is related to the self assembly of bulk aggregates with internal molecular structure combined with their transport towards a given interface under gravity. We have recently extended this work to the PEI/SDS system, which is much more widely studied in this respect, and critically we have shown that the same mechanism is dominant. A conundrum remains however, as the bulk aggregates are more ordered at higher polyelectrolyte charge density where no such surface structure has yet been observed. Logically the surface structure must exist under certain conditions, and we believe that we can solve this conundrum by the application of the same novel methodology to the problem. With this beam time award, we will be able to deliver a thorough characterization of multilayer formation in the PEI/SDS system by next summer.

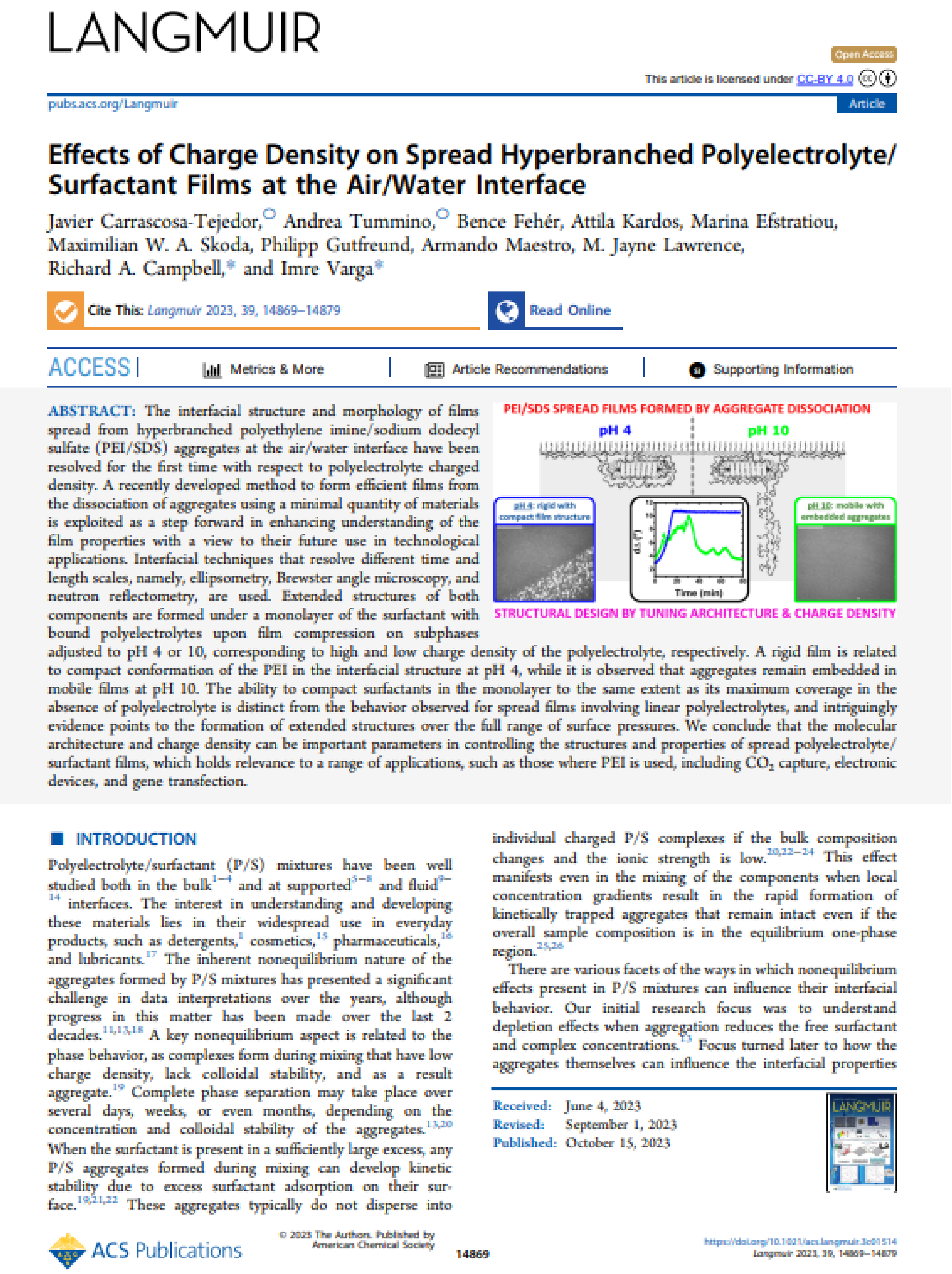
Output

This experiment started as intended but there were significant problems related to the technical challenge of making such a difficult experiment work. Its continuation was written off due to problems with the FIGARO instrument, and the final part shifted focus to spread films. The data were very interesting but incomplete, so the work was extended with an experiment on the INTER reflectometer in December 2018. That timing coincided with the completion of Andrea Tummino's PhD project, and the data lay unexploited for some time. The project was picked up by another student, Javier Carrascosa Tejedor, who completed the data analysis and writing, and the data resulted in a publication: *Langmuir*, **2023**, *39*, 14869–14879.

Publication Abstract

The interfacial structure and morphology of films spread from hyperbranched polyethylene imine/sodium dodecyl sulfate (PEI/SDS) aggregates at the air/water interface have been resolved for the first time with respect to polyelectrolyte charged density. A recently developed method to form efficient films from the dissociation of aggregates using a minimal quantity of materials is exploited as a step forward in enhancing understanding of the film properties with a view to their future use in technological applications. Interfacial techniques that resolve different time and length scales, namely, ellipsometry, Brewster angle microscopy, and neutron reflectometry, are used. Extended structures of both components are formed under a monolayer of the surfactant with bound polyelectrolytes upon film compression on subphases adjusted to pH 4 or 10, corresponding to high and low charge density of the polyelectrolyte, respectively. A rigid film is related to compact conformation of the PEI in the interfacial structure at pH 4, while it is observed that aggregates remain embedded in mobile films at pH 10. The ability to compact surfactants in the monolayer to the same extent as its maximum coverage in the absence of polyelectrolyte is distinct from the behavior observed for spread films involving linear polyelectrolytes, and intriguingly evidence points to the formation of extended structures over the full range of surface pressures. We conclude that the molecular architecture and charge density can be important parameters in controlling the structures and properties of spread polyelectrolyte/surfactant films, which holds relevance to a range of applications, such as those where PEI is used, including CO2 capture, electronic devices, and gene transfection.

Publication First Page Screenshot



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Article

Effects of Charge Density on Spread Hyperbranched Polyelectrolyte/Surfactant Films at the Air/Water Interface

Javier Carrascosa-Tejedor,○ Andrea Tummino,○ Bence Fehér, Attila Kardos, Marina Efstratiou, Maximilian W. A. Skoda, Philipp Gutfreund, Armando Maestro, M. Jayne Lawrence, Richard A. Campbell,* and Imre Varga*

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■ INTRODUCTION

Polyelectrolyte/surfactant (P/S) mixtures have been well studied both in the bulk[1−4] and at supported[5−8] and fluid[9−14] interfaces. The interest in understanding and developing these materials lies in their widespread use in everyday products, such as detergents,[1] cosmetics,[15] pharmaceuticals,[16] and lubricants.[17] The inherent nonequilibrium nature of the aggregates formed by P/S mixtures has presented a significant challenge in data interpretations over the years, although progress in this matter has been made over the last 2 decades.[11,13,18] A key nonequilibrium aspect is related to the phase behavior, as complexes form during mixing that have low charge density, lack colloidal stability, and as a result aggregate.[19] Complete phase separation may take place over several days, weeks, or even months, depending on the concentration and colloidal stability of the aggregates.[13,20] When the surfactant is present in a sufficiently large excess, any P/S aggregates formed during mixing can develop kinetic stability due to excess surfactant adsorption on their surface.[19,21,22] These aggregates typically do not disperse into individual charged P/S complexes if the bulk composition changes and the ionic strength is low.[20,22−24] This effect manifests even in the mixing of the components when local concentration gradients result in the rapid formation of kinetically trapped aggregates that remain intact even if the overall sample composition is in the equilibrium one-phase region.[25,26]

There are various facets of the ways in which nonequilibrium effects present in P/S mixtures can influence their interfacial behavior. Our initial research focus was to understand depletion effects when aggregation reduces the free surfactant and complex concentrations.[13] Focus turned later to how the aggregates themselves can influence the interfacial properties

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