# Experimental report

06/11/2023

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|---|---|---|---|
| **Proposal:** | **9-10-1281** | **Council:** | 10/2019 |
| **Title:** | Solving a surface/bulk conundrum: extending the examination of interfacial multilayer formation in PEI/SDS mixtures to the charge density | | |
| **Research area:** | Soft condensed matter | | |

**This proposal is a continuation of 9-10-1186**

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|---|---|
| **Main proposer:** | **Richard CAMPBELL** |
| **Experimental team:** | Imre VARGA<br>Attila KARDOS |
| **Local contacts:** | Richard CAMPBELL |

**Samples:**
sodium chloride
poly(ethylene imine)
d25-sodium dodecyl sulfate
sodium dodceyl sulfate

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| FIGARO User-supplied | 4 | 4 | 14/07/2013 | 15/07/2013 |
| | | | 15/07/2013 | 17/07/2020 |

## 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.

# FINAL EXPERIMENTAL REPORT: #9-10-1281

## Solving a surface/bulk conundrum: extending the examination of interfacial multilayer formation in PEI/SDS mixtures to the charge density

*Richard Campbell & Imre Varga*

FIGARO, 14–17 July 2013

### 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.

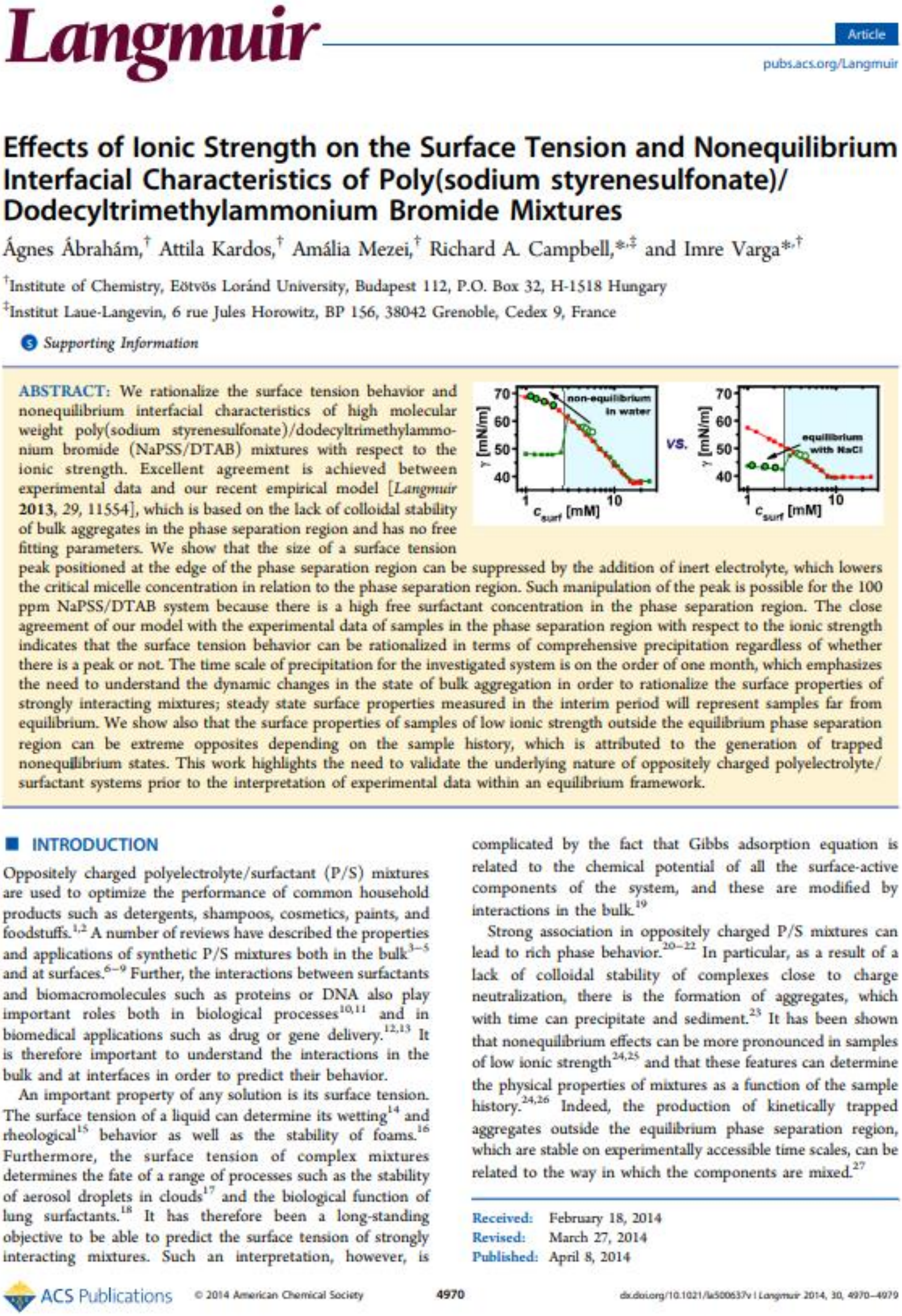
### Output

Although this experiment was intending to focus on the PEI/SDS system, a publication by the same authors on the same year on the same system (*Soft Matter*, **2013**, *9*, 6103–6117) prompted the measurements to focus on the NaPSS/DTAB system instead. This provided to be a good decision, as the data contributed to a publication the following year: *Langmuir*, **2014**, *30*, 4970–4979.

### Publication Abstract

We rationalize the surface tension behavior and nonequilibrium interfacial characteristics of high molecular weight poly(sodium styrenesulfonate)/dodecyltrimethylammonium bromide (NaPSS/DTAB) mixtures with respect to the ionic strength. Excellent agreement is achieved between experimental data and our recent empirical model [Langmuir 2013, 29, 11554], which is based on the lack of colloidal stability of bulk aggregates in the phase separation region and has no free fitting parameters. We show that the size of a surface tension peak positioned at the edge of the phase separation region can be suppressed by the addition of inert electrolyte, which lowers the critical micelle concentration in relation to the phase separation region. Such manipulation of the peak is possible for the 100 ppm NaPSS/DTAB system because there is a high free surfactant concentration in the phase separation region. The close agreement of our model with the experimental data of samples in the phase separation region with respect to the ionic strength indicates that the surface tension behavior can be rationalized in terms of comprehensive precipitation regardless of whether there is a peak or not. The time scale of precipitation for the investigated system is on the order of one month, which emphasizes the need to understand the dynamic changes in the state of bulk aggregation in order to rationalize the surface properties of strongly interacting mixtures; steady state surface properties measured in the interim period will represent samples far from equilibrium. We show also that the surface properties of samples of low ionic strength outside the equilibrium phase separation region can be extreme opposites depending on the sample history, which is attributed to the generation of trapped nonequilibrium states. This work highlights the need to validate the underlying nature of oppositely charged polyelectrolyte/surfactant systems prior to the interpretation of experimental data within an equilibrium framework.

## Publication First Page Screenshot



Langmuir
Article
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# Effects of Ionic Strength on the Surface Tension and Nonequilibrium Interfacial Characteristics of Poly(sodium styrenesulfonate)/Dodecyltrimethylammonium Bromide Mixtures

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*Supporting Information*

**ABSTRACT:** We rationalize the surface tension behavior and nonequilibrium interfacial characteristics of high molecular weight poly(sodium styrenesulfonate)/dodecyltrimethylammonium bromide (NaPSS/DTAB) mixtures with respect to the ionic strength. Excellent agreement is achieved between experimental data and our recent empirical model [*Langmuir* **2013**, *29*, 11554], which is based on the lack of colloidal stability of bulk aggregates in the phase separation region and has no free fitting parameters. We show that the size of a surface tension peak positioned at the edge of the phase separation region can be suppressed by the addition of inert electrolyte, which lowers the critical micelle concentration in relation to the phase separation region. Such manipulation of the peak is possible for the 100 ppm NaPSS/DTAB system because there is a high free surfactant concentration in the phase separation region. The close agreement of our model with the experimental data of samples in the phase separation region with respect to the ionic strength indicates that the surface tension behavior can be rationalized in terms of comprehensive precipitation regardless of whether there is a peak or not. The time scale of precipitation for the investigated system is on the order of one month, which emphasizes the need to understand the dynamic changes in the state of bulk aggregation in order to rationalize the surface properties of strongly interacting mixtures; steady state surface properties measured in the interim period will represent samples far from equilibrium. We show also that the surface properties of samples of low ionic strength outside the equilibrium phase separation region can be extreme opposites depending on the sample history, which is attributed to the generation of trapped nonequilibrium states. This work highlights the need to validate the underlying nature of oppositely charged polyelectrolyte/surfactant systems prior to the interpretation of experimental data within an equilibrium framework.

## ■ INTRODUCTION

Oppositely charged polyelectrolyte/surfactant (P/S) mixtures are used to optimize the performance of common household products such as detergents, shampoos, cosmetics, paints, and foodstuffs.[1,2] A number of reviews have described the properties and applications of synthetic P/S mixtures both in the bulk[3−5] and at surfaces.[6−9] Further, the interactions between surfactants and biomacromolecules such as proteins or DNA also play important roles both in biological processes[10,11] and in biomedical applications such as drug or gene delivery.[12,13] It is therefore important to understand the interactions in the bulk and at interfaces in order to predict their behavior.

An important property of any solution is its surface tension. The surface tension of a liquid can determine its wetting[14] and rheological[15] behavior as well as the stability of foams.[16] Furthermore, the surface tension of complex mixtures determines the fate of a range of processes such as the stability of aerosol droplets in clouds[17] and the biological function of lung surfactants.[18] It has therefore been a long-standing objective to be able to predict the surface tension of strongly interacting mixtures. Such an interpretation, however, is complicated by the fact that Gibbs adsorption equation is related to the chemical potential of all the surface-active components of the system, and these are modified by interactions in the bulk.[19]

Strong association in oppositely charged P/S mixtures can lead to rich phase behavior.[20−22] In particular, as a result of a lack of colloidal stability of complexes close to charge neutralization, there is the formation of aggregates, which with time can precipitate and sediment.[23] It has been shown that nonequilibrium effects can be more pronounced in samples of low ionic strength[24,25] and that these features can determine the physical properties of mixtures as a function of the sample history.[24,26] Indeed, the production of kinetically trapped aggregates outside the equilibrium phase separation region, which are stable on experimentally accessible time scales, can be related to the way in which the components are mixed.[27]

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