Structures of interfaces and foam films of (poly)electrolyte / surfactant mixtures

vom Fachbereich Physik der Technischen Universität Darmstadt zur Erlangung des Grades

Doktor der Naturwissenschaften (Dr. rer. nat.)

genehmigte Dissertation von Larissa Caritina Braun geboren in Berlin

Erstgutachter: Prof. Dr. Regine v. Klitzing Zweitgutachter: Prof. Dr. Emanuel Schneck

Darmstadt 2022



TECHNISCHE UNIVERSITÄT DARMSTADT

Braun, Larissa: Structures of interfaces and foam film of (poly)electrolyte/surfactant mixtures Darmstadt, Technische Universität Darmstadt Jahr der Veröffentlichung der Dissertation auf TUprints: 2023 URN: urn:nbn:de:tuda-tuprints-230499 Tag der mündlichen Prüfung: 19.12.2022

Veröffentlicht unter CC-BY-SA 4.0 International https://creativecommons.org/licenses/

Promotionsausschuss:

Referentin: Prof. Dr. Regine v. Klitzing Koreferent: Prof. Dr. Emanuel Schneck Prüfer: Prof. Dr. Michael Gradzielski Prüfer: Prof. Dr. Jens Braun

Tag der Disputation: 19.12.2022

Erklärung gemäß § 9 Promotionsordnung

Hiermit versichere ich, Larissa Caritina BRAUN, dass ich die vorliegende Dissertation selbstständig angefertigt und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe. Alle wörtlichen und paraphrasierten Zitate wurden angemessen kenntlich gemacht. Die Arbeit hat bisher noch nicht zu Prüfungszwecken gedient.

Datum und Unterschrift

Wissenschaftlicher Werdegang

03/2017 - heute	wissenschaftliche Mitarbeiterin am Institut für konden-
	sierte Materie an der Technischen Universität Darmstadt
	in der AG von Prof. Dr. Regine v. Klitzing
02/2016 - $02/2017$	wissenschaftliche Mitarbeiterin am Institut für Chemie
	an der Technischen Universität Berlin in der AG von
	Prof. Dr. Regine v. Klitzing
11/2013 - $12/2015$	Studium der Chemie (M. Sc.) an der Technischen Uni-
	versität Berlin. Titel der Masterarbeit: Surface grafted
	crosslinkers as surface agents and photo initiators in
	liquid crystal test devices
10/2010 - $11/2013$	Studium der Chemie (B. Sc.) an der Technischen Univer-
	sität Berlin. Titel der Bachelorarbeit: Einfluss der ther-
	mischen Stabilität von vanadiumsubstituierten Keggin-
	Heteropolyoxomolbdaten auf die katalytische Aktivität bei
	der Propenoxidation

Wissenschaftliche Veröffentlichungen

Publikationen als Erstautorin

"Polymers and surfactants at fluid interfaces studied with specular neutron reflectometry" L. Braun, M. Uhlig, R.A. Campbell, R. v. Klitzing, *Adv. Colloid Interface Sci.*, **2017**, 247, 130-148.

"Stability of aqueous foam films and foams containing polymers: Discrepancies between different length scales" L. Braun, M. Kühnhammer, R. v. Klitzing, *Current Opinion in Colloid and Interface Science*, **2020**, 50, 101379.

"Insights into extended structures and their driving force: Influence of salt on polyelectrolyte/surfactant mixtures at the air/water interface" L. Braun, M. Uhlig, O. Löhmann, R.A. Campbell, E. Schneck, R. v. Klitzing, *ACS Applied Materials & Interfaces*, **2022**, 14, 27347-27359.

"When bulk matters: Disentanglement of the role of polyelectrolyte/surfactant complexes at surfaces and in bulk of foam films" L. Braun, R. v. Klitzing, *Langmuir*, **2022**, accepted

Ausstehende Publikation als Erstautorin

"Insights into the non-ionic foam stabilization mechanism by chaotropic nano-ions" L. Braun, M. Hohenschutz, O. Diat, R. v. Klitzing, P. Bauduin.

Publikationen als Co-Autorin

"Gold nanoparticle distribution in polyelectrolyte brushes loaded at different pH conditions" D. Boyaciyan, L. Braun, O. Löhmann, L. Silvi, E. Schneck, R. v. Klitzing, *Journal of Chemical Physics*, **2018**, 149(16).

"A new model to describe small-angle neutron scattering from foams" M. Kühnhammer,
L. Braun, M. Ludwig, O. Soltwedel, L. Chiappisi, R. v. Klitzing, *Journal of Applied Crystallography*, 2022, 55(4), 758–768.

"Untangling effects of proteins as stabilizers for foam films" K. Gräff, S. Stock, L. Mirau, S. Bürger, L. Braun, A. Völp, N. Willenbachder, R. v. Klitzing, *Frontiers*, **2022**, 2, 1–18.

Abstract

Foam films are the building blocks of macroscopic foams and thus, crucial for their performance. The present thesis studies the interactions between surfactants (Ss) and (poly)electrolytes at interfaces and inside foam films. Mixtures of oppositely charged polyelectrolytes (Ps) and Ss are able to stabilize foam films depending on the ratio between the two components. Even though salt appears in many applications of P/S mixtures, its impact on foam films formed by these mixtures is barely studied. To obtain a general understanding of foam films, their different components are studied in this thesis individually and in combination: from bulk solutions, over a single air / liquid interface to foam films.

The first part of this thesis focuses on the air / liquid interface of two P / S mixtures: PSS / C_{14} TAB and sPSO₂-220 / C_{14} TAB. Tensiometry and neutron reflectometry are used to investigate their surface activity, interfacial composition, and interfacial structures. While PSS / C_{14} TAB mixtures only form monolayers, sPSO₂-220 / C_{14} TAB mixtures form extended structures *around* the bulk stoichiometric mixing point (BSMP), which are suppressed with increasing ionic strength. The main driving force for the formation of extended structures is to maximize the gain of entropy by reaching an interfacial P/S ratio of 1. Increasing the flexibility of the P (*via* increasing the ionic strength or using the more flexible PSS) enables almost reaching this ratio within a monolayer structure.

In the second part, foam films of $sPSO_2-220/C_{14}TAB$ mixtures and the effect of LiBr are studied using a Thin Film Pressure Balance (TFPB). Below the BSMP, unstable foam films form irrespective of c_{LiBr} , while *above* the BSMP, the foam films are stable. A low amount of added LiBr destabilizes the foam films, whereas a high amount stabilizes them. The stabilization results from a steric repulsion of $sPSO_2-220 / C_{14}TAB$ complexes inside the foam film bulk. The complexes contribute to the *apparent* surface potential Ψ_{app} between the interfaces. The foam film stability framework is extended, now including the bulk complexes: a minimal charge of the P/S complexes is necessary to stabilize foam films. Additionally, it is observed that the P/S mixtures aren't equilibrated and phase separate on the time scale of months. The last part focuses on the foam films of the non-ionic S BrijO10 and the Keggin polyoxometalate $H_4SiW_{12}O_{40}$. $SiW_{12}O_{40}^{4-}$ adsorbs at the BrijO10 and charges the foam film interfaces. BrijO10 micelles trapped inside the foam film lead to an additional long-range steric stabilization. These micelles act as a reservoir for excess S in the subinterfacial region making the foam films more resistant to disturbances and thus, leading to stable foams.

Kurzzusammenfassung

Schaumfilme bilden die Grundbausteine von Schäumen und sind entsprechend von entschiedener Bedeutung für deren Verhalten. Mischungen von entgegengesetzt geladenen Polelektrolyten (P) und Tensiden (engl.: surfactants, S) stabilisieren Schaumfilme unterschiedlich gut, je nach Mischungsverhältnis von P und S. Viele technische Anwendungen dieser Mischungen enthalten Salze, jedoch ist der Einfluss von Salz auf die Schaumfilme der Mischungen kaum untersucht. In dieser Arbeit werden die verschiedenen Komponenten von Schaumfilmen sowohl einzeln wie auch in Kombination untersucht: von einer einzelnen Wasser / Luft-Grenzfläche über die Volumenphase bis hin zu den Schaumfilmen. Mit diesen Untersuchungen soll ein generelles Verständnis von Schaumfilmen und insbesondere des Einflusses von Salz auf die P/S Mischungen erreicht werden.

Der erste Teil dieser Arbeit fokussiert sich auf die einzelne Wasser / Luft-Grenzfläche. Es wurden zwei P/S Mischungen miteinander verglichen. Das kationische Tensid Tetradecyltrimethylammoniumbromid ($C_{14}TAB$) wurde zum einen mit einem anionischen Polyelektrolyten, dem sulfoniertem Polyphenylsulfon (sPSO₂-220), gemischt und zum anderen mit dem anionischem Polystyrolsulfonat (PSS) gemischt. Um die Oberflächenaktivität der Mischungen sowie deren Komposition und Struktur an der Grenzfläche zu untersuchen, wurden Tensiometrie und Neutronenreflektometrie verwendet. $sPSO_2-220 / C_{14}TAB$ Mischungen bilden ausgedehnte Strukturen senkrecht zur Grenzfläche um den stöchiometrischen Mischpunkt (engl.: bulk stoichiometric mixing point, BSMP). Diese werden durch eine Erhöhung der Ionenstärke, sei es durch die Zugabe von Salz oder durch Erhöhung der Polyelektrolytenkonzentration, unterdrückt. Hingegen bilden $PSS/C_{14}TAB$ Mischungen nur Monolagen an der Grenzfläche aus. Der Hauptgrund für die Ausbildung dieser ausgedehnten Strukturen ist der Entropiegewinn bei der Freisetzung der Gegenionen durch Erreichen eines 1:1 Verhältnisses von P und S an der Grenzfläche. Durch die Verringerung der Steifigkeit des Polyelektrolyten - sei es durch Zugabe von Salz oder aufgrund der Verwendung des flexibleren PSS - wird dieses Verhältnis innerhalb einer Monolage nahezu ermöglicht. Im zweiten Teil der Arbeit wurden Schaumfilme der $sPSO_2-220 / C_{14}TAB$ Mischungen und der Einfluss von Salz (LiBr, Kombination der entsprechenden Gegenionen) auf diese näher analysiert. Hierzu wurde als Methode eine Thin Film Pressure Balance (TFPB) eingesetzt. Unterhalb des BSMP bilden sich nur instabile Schaumfilme unabhängig von der LiBr Konzentration. Oberhalb des BSMP kommt es zu stabilen Schaumfilmen. Hier sorgt eine geringe Konzentration an LiBr (bis zu 10^{-3} M) für eine Destabilisierung der Schaumfilme, während eine hohe Konzentration an LiBr (10^{-2} M)

die Schaumfilme stabilisiert. Diese Stabilisierung beruht auf einer sterische Abstoßung der $sPSO_2-220 / C_{14}TAB$ Komplexe im Schaumfilmvolumen. Diese P/S Komplexe spielen auch für das gemessene *scheinbare* Oberflächenpotential eine entscheidende Rolle. Das vorhandenen Modell zum Verständnis der Schaumfilmstabilität wurde in dieser Arbeit erweitert: es bezieht nun auch die P/S Komplexe mit ein. Für einen stabilen Schaumfilm sind Komplexe mit einer gewissen Mindestladung notwendig. Weiterhin wurde der Einfluss des Probenalters der Mischungen untersucht. Es zeigte sich, dass frisch hergestellte Proben sich nicht im Gleichgewicht befinden und im Verlauf von Monaten zur Phasentrennung neigen.

Der letzten Teil der Arbeit beschäftigt sich mit Schaumfilmen des nicht ionischen Tensids BrijO10. Hierbei wurde der Einfluss des Keggin Polyoxometallats $H_4SiW_{12}O_{40}$ auf die Schaumfilme näher untersucht. Si $W_{12}O_{40}^{4-}$ adsorbiert an den BrijO10 Molekülen und lädt so die Schaumfilmgrenzflächen elektrostatisch auf.

Mizellen innerhalb des Schaumfilms sorgen für eine langreichweitige sterische Stabilisierung der Schaumfilme. Diese Mizellen fungieren als Reservoir von zusätzlichen BrijO10 Molekülen unmittelbar unterhalb der Grenzfläche. Dadurch wird der Schaumfilm beständiger gegenüber Störungen, was zu stabileren Schaumfilmen und somit zu stabileren Schäumen führt.

Contents

Ei	gens	ändigkeitserklärung	iv
\mathbf{A}	bstra	ct	vii
K	urzzu	sammenfassung	viii
Co	onter	\mathbf{ts}	x
1	Intr	oduction	1
2	Scie	ntific background	5
	2.1	Foam films	5
		2.1.1 Historical review	5
		2.1.2 Forces inside thin foam films	6
		2.1.3 Surfactants and their foam films	11
	2.2	Polvelectrolyte / surfactant mixtures	14
		2.2.1 Bulk properties of P/S mixtures	14
		2.2.2 P/S mixtures at the air / liquid interface	15
		2.2.3 Foam films formed by P/S mixtures	18
	2.3	Polyoxometalates	20
3	Exp	erimental section	23
3.1 Materials and sample preparation		Materials and sample preparation	23
		Methods	25
		3.2.1 Thin Film Pressure Balance	25
		3.2.2 Specular Neutron Reflectometry	29
		3.2.3 Tensiometry	36
		3.2.4 Additional techniques	37
4	Effe	ct of salt on interfacial structures of P / S mixtures	39
	4.1	Abstract	39
	4.2	Introduction	40
	4.3	Results	41
		4.3.1 $sPSO_2-220 / C_{14}TAB$ mixtures	41
		4.3.2 $PSS/C_{14}TAB$ mixtures	50
	4.4	Discussion	54

		4.4.1 sPSO ₂ -220 / C_{14} TAB mixtures	54
		4.4.2 PSS / C_{14} TAB mixtures	56
		4.4.3 Comparison of polyelectrolytes	57
	4.5	Conclusions	59
5	Effect of salt on foam films of $sPSO_2-220 / C_{14}TAB$ mixtures		
	5.1	Abstract	61
	5.2	Introduction	62
	5.3	Results and discussion	63
		5.3.1 Foam film stability and type of foam film	63
		5.3.2 Disjoining pressure isotherms	65
	5.4	Conclusions	70
6	Effe	Effect of time on $sPSO_2$ -220 / $C_{14}TAB$ mixtures	
	6.1	Abstract	73
	6.2	Introduction	74
	6.3	Results	75
	6.4	Discussion	80
	6.5	Conclusion	82
7	7 Effect of HSiW on BrijO10 foam films and foams		85
	7.1	Abstract	85
	7.2	Introduction	86
	7.3	Results and discussion	87
		7.3.1 Macroscopic foams	87
		7.3.2 Foam films	89
		7.3.3 Combining SANS and TFPB results with a stabilization mech-	
		anism \ldots	97
	7.4	Conclusion	101
8	General conclusion and future perspectives		103
A	A Scientific appendix		107
	A.1	Fluctuations of the foam film stability	107
	A.2	Effect of LiBr on foam films formed by $C_{14}TAB$	108
	A.3	Optical density of freshly mixed P / S mixtures	109
	A.4	Appendix for chapter 4	111
	A.5	Appendix for chapter 5	120
	A.6	Appendix for chapter 6	124
	A.7	Appendix for chapter 7	125

CONTENTS	xiii
Abbreviations	153
Danksagungen	155

Chapter 1

Introduction

Foams are ubiquitous in our daily life: from shampooing your hair in the morning¹, over fire-fighting² and sophisticated separation techniques (froth flotation³) to enjoying a freshly tapped beer⁴ in the after-work hours. All these foams depict a dispersion of gas (mostly air) bubbles in a liquid (mostly an aqueous solution). Pure water is not able to stabilize the overall large interfacial area of foams, thus foaming agents are needed to form at least temporarily stable foams.⁵ Surfactants⁶, polymers⁷, proteins⁸ or mixtures of them⁹ are frequently used for this purpose.

Foams are hierarchical materials that display various structures at different length scales (Fig. 1.1): From the metric scale of the soft and opaque solid, over the millimetric scale of the individual air bubbles and the submicron scale of the liquid films separating the air bubbles (foam films) to the nanometric scale of a single air / liquid interface and the molecules stabilizing it. The foam films intersect at liquid channels (Plateau borders) forming the basic structure of a foam. Thus, they are considered as the building blocks of foams.

Once a foam is produced, it has a high liquid volume fraction ϕ_1 . With time the liquid flows down through the foam films and Plateau borders due to gravity (drainage) and the foam dries out. Besides drainage, coarsening (gas transfer between bubbles of different sizes) and bubble coalescence (rupture of foam films) lead to the collapse of foam.¹⁰ During drainage, the foam films thin and once they are around 100 nm thin, surface forces come into play and stabilize them. One differentiates between two types of foam films: Common Black Films (CBFs) are mostly stabilized by electrostatic repulsion. While a CBF still contains free water, in a Newton Black Film (NBF) the free water between the two interfaces has completely drained out and only surfactants



FIGURE 1.1: Schematic drawing of the different length scales of foams: macroscopic foam, air bubbles, foam film and the single air / liquid interface. As foaming agent a mixture of oppositely charged polyelectrolyte and surfactant is shown.

and hydration water remain. Thus, NBFs are mostly stabilized by entropic steric forces. For low molecular weight surfactants, the thickness of CBFs ranges from 100 nm to 10 nm. In contrast, NBFs have a thickness below ~ 10 nm depending of the size of the surfactant.

This thesis aims to contribute to a more general understanding of foam films. It focuses on the interactions (mainly electrostatic) between S and charged components and how they impact foam films. The factors (de)stabilizing foam films are studied. The first type of charged components are polyelectrolytes (Ps). Mixtures of oppositely charged Ps and Ss exhibit versatile applications ranging from cosmetics and pharmaceutics^{9,11-13} to oil recovery^{14,15}. Due to the complexation of P and S, an interplay between the S's surface activity and the P's bulk properties leads to new properties of the mixtures. In this thesis, the influence of salt on P/S mixtures and their foam films is studied. The addition of salt does not only affects the individual components but also their interaction. The question arises how salt influences P/S mixtures at the different length scales of foam films.

The second type of charged components are Keggin polyoxometalates (POMs). POMs are nanometer sized, structural discrete metal oxide clusters. They find applications in redox-catalysis¹⁶, in rechargeable batteries¹⁷ or as agent for protein crystallization¹⁸. Due to their highly chaotropic character, they accumulate at charge-neutral soft matter interfaces like S micelles or S loaded air / liquid interfaces. POMs are found to stabilize non-ionic S foams¹⁹, but the question remaining, which will be addressed in this thesis, is what happens inside the foam films.

Chapter 2 provides the scientific background for the thesis. The forces stabilizing foam films are presented. P/S mixtures' properties (in bulk solution, at the air/liquid interface and in foam films) and the characteristics of POMs are described. The

experiments performed for this thesis are described in chapter 3 along with a brief introduction to the used methods.

Chapter 4 deals with the single air / liquid interface of P/S mixtures. Two different Ps (a stiffer and a more flexible one) are compared to study the impact of P's flexibility. Furthermore, salt is added to both mixtures to analyze its impact. The surface activity is studied with tensiometry, but the main focus of chapter 4 is on the interfacial structures formed by the P/S mixtures, which are resolved by specular neutron reflectometry. Different structures (compact or swollen monolayers and extended layers) are found. By considering the impact of the P's flexibility, the driving force for the formation of the different structures are elucidated.

Chapter 5 focuses on the impact of salt on the foam films of one P/S mixture. Salt affects both the foam film thickness and stability: added salt always leads to thinner foams films, but low amounts destabilizes the films while high amounts stabilize them. The electrostatic repulsion between the two foam film interfaces is studied in detail. Based on the finding of chapter 4, the contribution of the interfacial complexes and the bulk complexes to both the foam film stability and the electrostatic repulsion are disentangled.

Chapter 6 investigates the impact of time on P/S mixtures regarding their adsorption, bulk and foam film properties. Aged P/S mixtures are compared to the P/Smixtures from chapter 5. A phase separation due to agglomerated P/S complexes lacking sufficient electrostatic stability and the consequences for the P/S mixtures are discussed.

Chapter 7 focuses on the impact of a Keggin POM on foam films of a non-ionic S. The addition of POM increases the foam film stability and changes the type of stabilization of the foam film: from sterically stabilized by S molecules, over electrostatically stabilized by charged foam film interfaces to sterically stabilized by S micelles. These findings are discussed in the context of the stability of macroscopic foams to elucidate the foam stabilization mechanism of POMs.

Chapter 8 provides a summarizing conclusion on how the interaction between S and charged components (either Ps or POMs) affects the foam film stability and what this means for the structure of the foam films. Moreover, further perspectives for this research area are discussed.

Chapter 2

Scientific background

2.1 Foam films

2.1.1 Historical review

Foam films attract the attention of scientists for centuries: On the one hand because they are the building blocks of macroscopic foam and on the other hand, because they fascinate us due to their colorful iridescence and their fragile nature. Isaac Newton (1643 - 1727) studied the different colors of foam films and related them to different thicknesses of the foam films. He also found two different kinds of black spots in foam films (that are nowadays called Common Black Film and Newton Black Film).²⁰ Joseph Plateau (1801 - 1883) studied the impact of film tension and the role of pressure on the size and shape of soap bubbles. Later on, Edwin Johonnott used a modified interferometer to systematically study vertical foam films and their thicknesses.¹⁰ He was the first to demonstrate a temperature induced transition between the two black films described by Newton. Jean Baptiste Perrin (1870 - 1942) observed flakes of different color - hence thicknesses - in foam films and attributed this phenomenon to layers of elementary sheets.²⁰

Most of these early studies of foam films were phenomenological but a general theoretical description of foam films was lacking. This changed in the 1930s. Boris Derjaguin (1902 - 1994) introduced the concept of disjoining pressure Π , which he defined as the negative derivative of the Gibbs free energy G by the film thickness

 h^{10} :

$$\Pi(h) = -\left(\frac{dG}{dh}\right)_{T,p,A,n} \tag{2.1}$$

 Π expresses an excess pressure with respect to the bulk liquid that acts normal to the film interface. In its mechanical definition, Π equals the pressure difference between the pressure inside the film P_{film} and the pressure inside the initial bulk liquid P_1^{10} :

$$\Pi = P_{\rm film} - P_{\rm l} \tag{2.2}$$

In the 1940, Boris Derjaguin and Lev Landau $(1908 - 1968)^{21}$ as well as Evert Verwey (1905 - 1981) and Theodoor Overbeek (1911 - 2007)²² independently used the concept of Π to rationalize the stability of lyophobic colloids. It resulted in the nowadays renowned DLVO theory describing the stability of colloidal systems as well as foam films in terms of two acting forces: van der Waals forces (Π_{VdW}) and electrostatic forces ($\Pi_{\rm el}$). Next to these two, non-DLVO forces contribute to Π in foam films. These forces are discussed in detail in the following section. Studies of foam films gained precision and sophistication in 1959, when Alexei Scheludko (1920 - 1995) and Dotchi Exerowa (1935 - 2017) invented a special measuring cell to study horizontal microscopic foam films under defined pressure.²³ The setup and measuring procedure was refined in the following years leading to a device called Thin Film Pressure Balance (TFPB), allowing the detailed investigation of foam films.²⁴⁻²⁶ The development continues. Nowadays, with interferometry digital imaging optical microscopy the kinetics of nanostructures²⁷ inside the foam film as well as hydrodynamic aspects²⁸ became resolvable and with a microfluidic TFPB²⁹ even solidifying foam films are suitable for studying.

2.1.2 Forces inside thin foam films

As mentioned Π is composed of different forces acting between the two air / liquid interfaces. Depending on the foaming agent, the strength and importance of each component differs.

Electrostatic force An electrostatic component Π_{el} arises once the electric double layers of charged interfaces (air / liquid interfaces for foam films) overlap. In the following, first the origin of the electric double layer of a single interface and later the force arising between two interfaces are described.

One charged interface Most interfaces are charged in water due to different reasons. Ionization or dissociation of surface groups (*e.g.* bound hydroxyl group dissociate into H^+ and bound O⁻ groups) or adsorption of charged molecules (*e.g.* dissociated S or P) can lead to interfacial charges.³⁰ These interfacial charges form an electric flied, which attracts counterions and change the ion distribution around the interface. The combination of interfacial charges and counterions is called electric double layer.

Hermann Helmholtz (1821 - 1894) provided a first model of the electric double layer where the counterions are directly bound to the interface.³¹ Later Louis Gouy (1854 -1926) and David Chapman (1869 - 1958) improved the model by taking into account the thermal motion of the ions resulting in a diffusive layer of counterions.³² Otto Stern (1888 - 1969) combined the two ideas.³³ The Stern model divides the electric double layer into two parts: the inner part (Stern layer) contains hydrated counterions bound to the interface, whereas the outer part (Gouy-Chapmann layer) contains mobile ions (Fig. 2.1). The distance between the interface and the center of the hydrated ions is called outer Helmholtz plane and separates the Stern layer from the Gouy-Chapman layer. The potential of the Helmholtz plane is called zeta potential Ψ_{ζ} .



FIGURE 2.1: Schematic Stern model of the electric double layer. The distribution of ions near a positive charged interface together with the potential Ψ is shown. (adapted from Ref. 34)

To calculate the potential near a charged interface the Poisson-Boltzmann equation (PB eq.) is used. It contains two parts. The Poisson equation relates the potential Ψ to the charge density ρ :

$$\frac{\mathrm{d}^2 \Psi}{\mathrm{d}x^2} = -\frac{\rho}{\epsilon_0 \epsilon} \tag{2.3}$$

where x is the distance to the interface, ϵ_0 is the vacuums dielectric constant, and ϵ the dielectric constant of water. The charge density can be described by the Boltzmann

equation:

$$\rho = e \sum_{i} z_{i} c_{i,\infty} \cdot \exp\left(\frac{-z_{i} e \Psi(x)}{kT}\right)$$
(2.4)

with e being the elementary charge, z the ion valency, c_{∞} the concentration of ion, k being the Boltzmann constant, and T the temperature. Note that a Boltzmann distribution is only the case for the mobile ions outside the outer Helmholtz plane and therefore the zeta potential is considered as the interfacial potential in the PB eq. and will be named surface potential Ψ_s in the following ($\Psi(x = 0) = \Psi_{\zeta} = \Psi_s$). By combining eq. 2.3 and eq. 2.4 one obtains the PB eq.:

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} = -\frac{e}{\epsilon_0\epsilon} \cdot \sum_{\mathbf{i}} z_{\mathbf{i}}c_{\mathbf{i},\infty} \cdot \exp\left(\frac{-z_i e\Psi(x)}{kT}\right) \tag{2.5}$$

The PB eq. can be analytically solved for z:z electrolytes by integration and the use of some mathematical identities. One obtains:

$$\Psi(x) = \frac{4kT}{ze} \cdot \tanh\left(\frac{ze\Psi_s}{4kT}\right) \cdot \exp\left(-\kappa x\right).$$
(2.6)

With increasing distance x the potential decays exponentially with a decay length κ^{-1} - called Debye length:

$$\kappa^{-1} = \sqrt{\frac{\epsilon_0 \epsilon kT}{\sum_{i} z_i^2 c_{i,\infty} e^2}} = \sqrt{\frac{\epsilon_0 \epsilon kT}{2e^2 N_A I}}$$
(2.7)

where $N_{\rm A}$ is Avogadro's number. The Debye length corresponds to the characteristic decay length of the diffuse ionic atmosphere and provides an approximate range of the electrostatic force. It is sensitive to the ionic strength $(I = \frac{1}{2} \sum_{i} z_{i}^{2} c_{i,\infty})$ and decreases with increasing electrolyte concentration.

For low potentials $(z_i e |\Psi| \ll kT)$, at room temperature for $\Psi_s \leq 25 \text{ mV}$ but often valid up to 50 -- 80 mV³⁴) an linearisation can be used solve the PB eq.:

$$\Psi(x) = \Psi_s \cdot \exp\left(-\kappa x\right) \tag{2.8}$$

By assuming that the total charge within the electric double layer (interface + counterions) must be zero, one can calculate the surface charge q_0 . The Grahame eq. correlates the potential to the interfacial charge:

$$q_0 = -\int_0^\infty \rho \mathrm{d}x = -\epsilon\epsilon_0 \frac{\mathrm{d}\Psi}{\mathrm{d}x} = \sqrt{8\epsilon\epsilon_0 kT} \sinh\left(\frac{ze\Psi_s}{2kT}\right)$$
(2.9)

Two charged interfaces When two charged interfaces approach each other, their electric double layer overlap. Furthermore, liquid (solvent) is expelled from the gap between the interfaces, but the counterions are forced to stay inside the gap. This situation gives an osmotic pressure difference between the gap and the bulk liquid, leading to a disjoining pressure Π :

$$\Pi_{\rm el}(h) = \Pi_{\rm osmotic, \ midplane} - \Pi_{\rm osmotic, \ bulk} \tag{2.10}$$

where h is the distance between the two interfaces. For symmetric interfaces (as in foam films), the two interfacial potentials are identical. This symmetry simplifies the calculation. Between the interfaces the potential decreases. Due to the symmetry the gradient of the potential at the midplane ($\Psi_{\rm mid}$) must become zero (Fig. 2.2).



FIGURE 2.2: Potential distribution between two identical charged interfaces. (adapted from Ref. 34)

The disjoining pressure is now giving by 35 :

$$\Pi_{\rm el} = kT \sum_{\rm i} c_{\rm i,\infty} \left(\exp\left(\frac{-z_i \Psi_{\rm mid}}{kT}\right) - 1 \right).$$
(2.11)

If one assumes only weakly overlapping double layers, the midplane potential can be considered as the sum of the two undisturbed interfaces (linear superposition approximation):

$$\Psi_{\rm mid} = 2\Psi'(h/2) \tag{2.12}$$

with Ψ' being the undisturbed potential of one interface.

For low potentials eq. 2.8 can be used to calculate the undisturbed potential. Therefore, the disjoining pressure is:

$$\Pi_{\rm el}(h) = 2\epsilon\epsilon_0 \kappa^2 \cdot \Psi_s^2 \cdot \exp(-\kappa/h). \tag{2.13}$$

For high potentials eq. 2.6 is used for calculating the potential and the disjoining pressure is:

$$\Pi_{\rm el}(h) = 64c_{\rm i,\infty}kT \cdot \tanh\left(\frac{ze\Psi_s}{4kT}\right)^2 \cdot \exp\left(-\kappa h\right).$$
(2.14)

When the two interfaces approach each other, the interfacial charges may change e.g. due to adsorbing / desorbing ions or due to rearrangements of the charges. To account for this situation, one of two boundary conditions is usually used. Either a constant charge or a constant potential is assumed upon approaching.³⁵

In the PB theory, assumptions were made leading to some limitations.³⁴ For example the ions' size was neglected. Close to the interface the ion concentration may become high and their distance low. In this case, the size of the ion should become relevant. The PB theory is a mean field theory. The ions only interact with an averaged electrostatic field and any ionic correlations are neglected. Furthermore, the interfaces are assumed to be thin and flat on a molecular scale.

Even if some errors due to the limitations compensate each other³⁴, the applicability of PB to foam films can be questionable in some cases. $\Pi_{\rm el}$ prevents the further approach of the two interfaces.

Van der Waals forces A van der Waals component Π_{VdW} arises from the interaction of induced and permanent dipoles. Most prominent are the London dispersion forces between two induced dipoles. In each atom (molecule) the electrons circulate around the nuclei and thus create instantaneous dipoles. These dipoles generate a field to which the electrons of a second atom (molecule) respond.³⁵ After integration over all molecules, Π_{VdW} can be written as⁵:

$$\Pi_{\rm VdW} = -\frac{A}{6\pi h^3}.$$
(2.15)

A is the Hamaker constant. For symmetric foam films A has a positive value which leads to an attraction of the two air / liquid interfaces. Due to their h-dependency $(\Pi_{\rm VdW} \propto \frac{1}{h^3})$, van der Waals forces are rather short ranged compared to electrostatic forces. When the electrostatic barrier is overcome and the air / liquid interfaces are close to each other $(h \approx 10 \text{ nm})$, $\Pi_{\rm VdW}$ comes into play and may lead to film rupture.

Steric forces A repulsive steric contribution Π_{steric} arises due to steric interactions of the adsorption layers of the air / liquid interfaces. Depending on the foaming agent,

these can be short ranged (small molecules) or long ranged (macromolecules).¹⁰ Π_{steric} stabilizes foam films.

Structural forces A structural or oscillatory contribution $\Pi_{\text{structual}}$ arises from structuring of the liquid inside the foam film. Confined between the two air / liquid interfaces, a layering of molecules or particles may occur close to the interfaces. The layering relates to an damped oscillatory concentration profile of the molecules or particles from the interface towards the film bulk³⁶:

$$\Pi_{\text{structural}} = A \cdot \exp\left(-\frac{h}{\zeta}\right) \cdot \cos\left(2\pi\frac{h}{\lambda} + \psi\right)$$
(2.16)

where A is the amplitude of the oscillation corresponding to the strength of the oscillatory force. ζ is the correlation length, λ is the oscillation wavelength and ψ is a phase shift. When the two air / liquid interfaces approaches, the molecules or particles are pushed out layer by layer, resulting in a stepwise thinning of the foam films. This process is called stratification.

2.1.3 Surfactants and their foam films

An important class of foaming agents are surface active agents - short: surfactants (Ss).³⁷ Ss are characterized by their amphiphilic character; they contain a hydrophobic part (mostly an aliphatic alkyl chain) and a hydrophilic part (called head group). The head group can be cationic, anionic, non-ionic, or zwitterionic S.³⁸ Ss accumulate at interfaces, where the chain is exposed to the hydrophobic phase (*e.g.* air) and the head group is directed towards the hydrophilic phase (*e.g.* water). In doing so, they reduce the surface tension of *e.g.* water because air / water interface (having a high surface tension) is replaced by air / hydrocarbon interface (having a low surface tension). Once the whole interface is covered with S molecules, the S starts to form aggregates in the bulk -- called micelles. With the formation of micelles the entropy of the whole system maximizes as less water molecules have to arrange around the hydrophobic chains compared to the separated S molecules (hydrophobic effect).³⁰ The concentration at which micelles start to form is called the critical micelle concentration (cmc).

Ionic Ss dissociate in water into charged S ions and the corresponding counterions. By adsorbing at the air / liquid interface, Ss increase or decrease the surface charge - depending on their own charge. The cmc as well as the adsorption of ionic Ss are



FIGURE 2.3: Schematic disjoining pressure isotherm.

sensitive to salt. Salt screens the charges of the head groups leading to less electrostatic repulsion between them. The reduced repulsion results in a higher surface coverage and a lower cmc.

Foam films formed by the different kinds of Ss were widely studied in the last decades: not only due to their importance for industrial application such as detergents¹⁰ or fire-extinguishers³⁹ but also due to the increase of understanding of the fundamental physics of foam films and the forces stabilizing them. To study foam films and gain information about the forces acting inside of them, disjoining pressure isotherms are recorded. Fig. 2.3 schematically shows such a disjoining pressure isotherm. The solid lines correspond to mechanically stable parts, which are accessible by a TFPB. The dashed part is mechanically unstable and thus not accessible by a TFPB. However, full force-distance-curves can be recorded using a colloidal probe atomic force microscopy (CP-AFM) that measures the forces between two solid interfaces.⁴⁰

For ionic Ss and their charged air / liquid interfaces, the electrostatic repulsion is the dominant force inside the foam film leading to the formation of a CBF.¹⁰ With increasing S adsorption, the surface charge increases until a saturation is reached due to binding of counterions at the interface.³⁶ Here, studies on foam films offer the ability to obtain insights on surface charge, surface coverage and on the dissociation degree of the S.⁴¹ The effect of salt on S stabilized foam films has been studied quite intensively.⁴²⁻⁴⁴ Two key effects have been identified for these foam films: First, salt vertically screens the electrostatic repulsion between the two opposite air / liquid interfaces leading to thinner foam films and a larger adsorption of counterions, which lowers the surface potential. Second, salt horizontally screens the electrostatic repulsion between neighboring S molecules. Screened repulsion leads to a higher amount of adsorbed surfactants (higher surface excess) and increases the surface potential and surface elasticity. The vertical screening favors a CBF -- NBF transition (low surface potential), while the horizontal screening favors a stable NBF (high ordering of adsorbed S). The amount of salt required for the CBF -- NBF transition depends on the S itself and its concentration. In general, more salt is needed at lower S concentration to induced the CBF--NBF transition as more salt is required to sufficiently increase the S's adsorption and obtain an NBF.⁴³ For example, the anionic sodium dodecyl sulfate (SDS) needs $\sim 0.5 \,\mathrm{M}$ NaCl for the CBF -- NBF transition at $0.15 \,\mathrm{mM} \,\mathrm{SDS} \,(< 1/40 \,\mathrm{cmc})$ but only $0.18 \,\mathrm{M} \,\mathrm{NaCl}$ at $1 \,\mathrm{mM} \,\mathrm{SDS} \,(\sim 1/8 \,\mathrm{cmc})$. For the cationic tetradecyltrimethylammonium bromide ($C_{14}TAB$), studied in this thesis, 1 M NaCl induces the NBF -- CBF transition at 3.5 mM C_{14} TAB (~ cmc).⁴³ Concerning high salt concentration ($\sim 1 \,\mathrm{M}$ and higher), an additional aspect has to be considered: underscreening. As mention in section 2.1.2, the PB theory has some limitation that become relevant at high concentration: as the distance between the ions become small, their sizes and the granularity of the solvent are relevant and the applicability of the theory breaks down.⁴⁶ The electrostatic interactions have a larger range than the expected Debye length. This effect leads to a thickening of the foam films.⁴⁶

If micelles are present in the foam film bulk, structural forces ($\Pi_{\text{structural}}$) appear. The foam film thins discontinuously and steps in the disjoining pressure isotherm are detected (stratification) caused by layer-wise exclusion of layers of micelles.⁴⁷ The addition of salt decreases both the number of steps and their thickness as salt influences the number density of the micelles.^{48,49}

For low concentrations of non-ionic S, CFB are found as well. Among others, this finding suggests that the pure air / water interface itself is charged. The most reasonable explanation for this charge is an excess of OH⁻ molecules at the interface.⁵⁰ With increasing concentration of the non-ionic S, more and more charges of the air / liquid interface are replaced by non-charged S molecules and a NBF forms.⁵¹ For the stability of foam films formed by pure S, the surface elasticity turned out to be a crucial parameter.⁵²

Beside the head group charge and chain length⁵³ or simple salts, the use of additives - $organic^{54}$ or inorganic - highly influences foam films formed by S. In the last chapter of this thesis, the effect of the polyoxometalate HSiW on foam films formed by a non-ionic S is studied. Thus, this class of inorganic additive will be shortly introduced

in the last section of this chapter. One class of prominent and important organic additives are polyelectrolytes (Ps). Mixtures of P and S are introduced in the next section.

2.2 Polyelectrolyte / surfactant mixtures

Ps are charged polymers which dissociate in water into charged macroions (charged polymer chains) and the corresponding counterions. The properties of Ps in solution are governed by several parameter such as *e.g.* pH, molecular weight or ionic strength (c_{salt}) . The stiffness of a P is described by its persistence length l_{t} , which gives an estimate for the typical radius of curvature.⁵⁵ The total persistence length l_{t} is the sum of an intrinsic contribution (intrinsic persistence length l_{P}) and an electrostatic contribution (electrostatic persistence length l_{e}).⁵⁶ For comparing the stiffness of different Ps, the intrinsic persistence length is usually used as the electrostatic one is highly influenced by external parameters *e.g.* c_{salt} .

This thesis deals with oppositely charged P/S mixtures, thus the following section focuses on this kind of mixtures. The versatile applications of P/S mixtures take advantages of the mixtures' different properties. For example, the precipitation of large P/S aggregates due to dilution is a key factor for the performance of hair conditioner and 2-in-1 shampoos. When shampooing your hair, the mixtures dilute and P/S aggregates deposit on the damaged hair fiber, providing a better lubrication.¹² Enhanced oil recovery and mineral flotation are separating techniques based on differences in hydrophobicity. Here, P/S mixtures adsorb *e.g.* on the mineral interface resulting in an increased hydrophobicity and the attachment of the mineral to an air bubble.^{2,15,57} In order to understand foams and foam films of P/S mixtures, different scales and phases have to be considered. Therefore, the characteristics of P/S mixtures in terms of their behavior in bulk, at the air/liquid interface and in foam films are shortly reviewed.

2.2.1 Bulk properties of P / S mixtures

The association of P and S bearing opposite charges exhibit one main driving forces: the entropic gain through the release of counterions when S molecules bind to the P. Moreover, hydrophobic interactions both in between the S chains as well as between S chains and hydrophobic parts of the P are relevant. The bulk binding passes through different states of non-cooperative and cooperative binding, which dictates the formed complexes and their phase behavior.^{12,58} At low S content, S bind to the P leading to charged complexes. With increasing S content, more S binds to the P and due to cooperative binding attached micelles or hemimicelles form. This concentration is called critical aggregation concentration (cac). The complexes are close to neutral charge and they start to form larger aggregates. The aggregates precipitate and the mixtures enter the two-phase regime. Depending on the P charge density either a solid-like phase (highly charged P) or a liquid-like phase (lower charged P) separates off.¹² The precipitation formed has different internal structures (hexagonal, lamellar or cubic) depending on the specific system.⁵⁹ At high S content, S adsorbs to the P/S aggregates and allows their re-solubilization. An electrostatically stabilized colloidal dispersion forms and the mixtures re-enter a one-phase regime.^{60,61}

A phase separation can also be induced by diluting high concentrated mixtures, which is a key feature for their use as shampoos and hair conditioners.^{12,62} The aggregation formation is highly susceptible to non-equilibrium effects, thus kinetically trapped non-equilibrium aggregates may form and modify the mixture properties.^{63,64} Depending on its concentration, salt influences this bulk phase behavior. At moderate concentrations, salt shifts the two-phase regime towards higher S concentration due to suppression of the kinetically stabilized composition range for the dispersion (reduced electrostatic repulsion).⁶⁵ Higher salt concentration may suppress the phase separation entirely due to considerably reduced S binding⁶⁶ and promotes bulk and interfacial properties reaching equilibrium⁶⁷. Salt not only affects the mixtures, but also the P itself. Both hydrodynamic radius in bulk and flexibility of P depend on the ionic strength.⁶⁸ The bulk behavior is relevant for many applications of P / S mixtures but it as well influences their behavior at the air / liquid interface.^{53,69}

2.2.2 P/S mixtures at the air / water interface ¹

The main tool to study P/S mixtures at the air / liquid interface is tensiometry as it allows fast and routinely studying of the surface activity of the mixtures. The drawbacks of this method are that there is no direct correlation with the adsorbed amounts of P and S and it is not sensitive to the structures formed at the air / liquid interface. Methods like X-ray reflectometry^{71,72}, ellipsometry^{73,74} and surface rheology⁷⁵ were

¹Parts of this section are published in "Polymers and surfactants at fluid interfaces studied with specular neutron reflectometry" L. Braun, M. Uhlig, R.A. Campbell, R. v. Klitzing, *Adv. Colloid Interface Sci.*, **2017**, 247, 130-148. Reprinted with permission. Copyright 2017 Elsevier.⁷⁰

used to further characterize the P/S mixtures. However these methods are generally only sensitive to the total adsorbed amount (P+S). Thus, neutron reflectometry (NR) became the method of choice. Using contrast variation *via* isotopic substitution allows to distinguish between adsorbed P and S as well as to resolve the formed structures at the air / liquid interface.

Typical concentration ranges studied are 10^{-4} to 10^{-2} monoM (= molar monomer concentration) for the P and 10^{-6} to 10^{-2} M for the S. In these ranges the Ps themselves are often not surface active whereas the Ss themselves are surface active. Two different approaches are used: changing the S concentration with at a fixed P concentration or the other way around: working with a fixed S concentration and changing the P concentration. The first way is more common. Here, at low bulk S concentrations the adsorption of surface active complexes or the synergistic adsorption reduces the surface tension compared to the pure S solution (Fig. 2.4). At this concentration, only loosely packed monolayers are formed at the interface.^{73,76} With a further increase of the bulk S concentration (above the cac), the surface tension reaches a plateau. Above the plateau the surface tension isotherm resembles that of the pure S, though it can be shifted depending on the specific chemicals properties of P and S.

The surface tension isotherm of a P/S mixture depends on many parameters like the P charge^{72,74} or the S chain length⁷⁷. Also, deviations from that described above were observed. In particular, it was found that a peak in the surface tension isotherm appears close to the two-phase regime.^{78,79} The surface tension peak may result from depletion of material from the interface happening at different time scales (from days to months)⁷⁹. The value is determined by the concentration of free S, that is neither bound to the P nor assembled in micelles. Salt suppresses the peak because it lowers the cmc of the S and accordingly reduces the concentration of free S at a fixed S bulk concentration.⁶⁷



FIGURE 2.4: Schematic surface tension isotherms for an oppositely charged P/S mixture (black) as well as the pure S (gray) as a function of c_S . The dashed line indicate the surface tension peak may appearing close to the two-phase regime.

In this thesis, P / S mixtures are studied in the opposite way: at a fixed S concentration the P concentration is varied. This way, the critical concentration for the adsorption is the bulk stochiometric mixing point (BSMP). At this point the concentration of P monomer equals the S molecules concentration in bulk. Below the BSMP, the addition of P strongly decreases the surface tension compared to the pure S solution (Fig. 2.5). Thus, highly surface active complexes form. Around the BSMP, the mixtures typically show an abrupt increase in surface tension. This phenomena is explained either by a loss of surface activity of the complexes⁸⁰ or a depletion of material from the interface due to precipitation⁸¹. Above the BSMP, the surface activity depends on the hydrophobicity of the P: for rather hydrophobic P like sodium poly(styrenesulfonate) (PSS) mixed with $C_{14}TAB$ the surface tension stays at values close to the pure S solution (indicating a low amount of adsorbed P at the surface).⁸² For more hydrophilic Ps like poly(acrylamido methyl propanesulfonate) (PAMPS) or sulfonated polyphenylene sulfone ($sPSO_2-220$) mixed with $C_{14}TAB$, the surface tension decreases again indicating the re-adsorption of complexes.^{80,83} The comparison of the mentioned Ps revealed as well an influence of the P stiffness on the surface adsorption: the stiffer backbone of sPSO₂-220 ($l_{\rm P} \sim 20 \,\mathrm{nm}$) lead to a flat and more effective adsorption (lower surface tension) compared to the rather flexible PSS and PAMPS ($l_{\rm P} \sim 1 \, \rm nm$), which are supposed to form loops when adsorbing at the interface.⁸³



FIGURE 2.5: Schematic surface tension isotherms for oppositely charged P/S mixtures (black) as well as the pure S (gray) as a function of $c_{\rm P}$. The dashed line indicate the surface tension isotherm for a hydrophilic P.

Regarding the composition at the air / liquid interface, NR revealed interesting details. PAMPS / C_{14} TAB mixtures show a depletion of material *around* the BSMP. However, P and S do not deplete at the same P / S bulk ratio: *at* the BSMP, solely C_{14} TAB depletes leading to a roughly three times excess of PAMPS monomers at the interface. With increasing of its bulk concentration, PAMPS depletes as well, but a slight excess of PAMPS remains at the interface.⁸⁴ Recently, the structures of sPSO₂-220 / C_{14} TAB mixtures formed at the air / liquid interface were analyzed.⁸⁵ *Below* the BSMP, a monolayer of S with an attached compact layer of P forms. *Around* the BSMP, a monolayer of S and P forms as well, but underneath an additional extended layer consisting of P and S forms. *Above* the BSMP, a monolayer of S and attached a highly swollen P layer (thickness ~ 80 Å) forms.⁸⁵ The questions arise why these specific structures form and how salt may influence them.

2.2.3 Foam films formed by P/S mixtures ²

For studying foam films of P / S mixtures, the concentration of both components have to be carefully chosen. Regarding the P concentration, its overlap concentration c^* has to be considered. Above c^* , the P chains overlap and start to form a transient network.⁷ This network leads to stratification, which influences the foam film.^{86,87} Below c^* , no stratification is observed. Regarding the S concentration, the cac has to be considered. Above the cac, aggregates are trapped in the foam film and may form

²Parts of this section are published in "When bulk matters: Disentanglement of the role of polyelectrolyte / surfactant complexes at surfaces and in bulk of foam films" L. Braun, R. v. Klitzing, submitted to *Langmuir*, **2022**

are used in this thesis.

The formation of surface active complexes does not necessarily lead to stable foam films of P/S mixtures. For several P/S mixtures^{80,82,83} a quite similar dependency of the foam film stability on the P concentration ($c_{\rm P}$) was found: *Below* the BSMP, the addition of P destabilizes the foam films compared to the ones of the pure S solution at the respective S concentration. *Around* the BSMP, no stable foam film can be formed at all. *Above* the BSMP, the foam film stability increases with $c_{\rm P}$ and exceeds that of the pure S solution.

To rationalize this non-monotonous foam film stability different parameters were used in the past. Surface tension and surface elasticity are suited to explain the higher foam film stability of $sPSO_2-220 / C_{14}TAB$ mixtures compared to PAMPS / $C_{14}TAB$ mixtures: a stronger adsorption of $sPSO_2-220 / C_{14}TAB$ complexes lead to more elastic interfaces and hence to more stable foam films⁸³, but they allow no general conclusions.^{52,89} The surface composition as well failed: PAMPS / $C_{14}TAB$ mixtures with a highly charged interface (due to the depletion of solely $C_{14}TAB$ from the interface *around* the BSMP) should result a high electrostatic repulsion between the two facing air / liquid interfaces. However, here the least stable foam films are found.⁸⁴ The structures formed at a single air / liquid interface of $sPSO_2-220 / C_{14}TAB$ mixtures (see previous section) were able to rationalize the foam film stability.⁸⁵ The extended mixed layer of $sPSO_2-220$ and $C_{14}TAB$ *around* the BSMP results in an unstable foam film due to a minimized electrostatic repulsion of the two facing air / liquid interfaces. Above the BSMP, the swollen $sPSO_2-220$ layer increases the osmotic pressure and leads to a stable foam film.⁸⁵

In all the mentioned studies, a prospective contribution of the foam films bulk was only improperly assumed^{80,82--84}, but no direct proof was found.

In contrast to pure S solutions, the effect of salt on the stability of foam films formed by P/S mixtures was barely studied. Aidarova et. al⁹⁰ investigated the effect of NaCl on foam (films) stabilized by sodium carboxymethylcellulose / SDS and found an increased foam stability, which they rationalized by a more densely packed adsorption layer (similar to what was found for pure S solutions) without proofing it.

P/S mixtures usually form CFBs. Kolaric et. al found that CBFs form if the charge of the foam film interface and of the P in the film bulk have the same sign and repel

each other.⁸⁶ This situation may be giving when P and S have the same charge or when oppositely charged P/S mixtures are used. In the later case, the surface charge could be reversed by the adsorption of P to the S loaded interface. The bulk P is now repelled from the same charged interface. NBFs are only found when non-ionic S and positive P are used. Between these two components no complexation occurs. The slightly negative interface and the positively charged P attract each other and form a NBF.

2.3 Polyoxometalates

The last part of this thesis addresses the impact of the polyoxometalate (POM) $SiW_{12}O_{40}^{4-}$ on foam and foam films of the non-ionic S BrijO10. Hence, in the following POMs are shortly reviewed.

POMs are polyatomic clusters consisting of transition metal cations bridged by oxide anions.⁹¹ The first POM ($[PMo_{12}O_{40}]^{4-}$) was synthesized by Jöns Jakob Berzelius (1776 - 1848) in 1826. In 1933 James Fargher Keggin (1905 - 1993) resolved the structure of the anion with X-ray diffraction, which was afterwards named after him: Keggin anion. Later on, diverse structures of different POMs were resolved (Fig. 2.6). However, the Keggin type remains the most common and used one.



FIGURE 2.6: Structures of different POMs: a) Keggin type, b) Wells–Dawson type, c) Anderson–Evans type and d) Preyssler archetype. The cyan polyhedra correspond to the polyherda around the addendum atom (M), brown polyhedra or brown sphere correspond to the polyhedra or sphere around the central atom (X) and oxygen atoms are shown as small red spheres. Reproduced from Ref. 18

The general formula of the Keggin anion is $[XM_{12}O_{40}]^{n-}$, where X denotes the heteroatom (*e.g.* Si, P or As) and M the addendum atom (e.g. Mo, W or V). The Keggin anion consists of a central XO₄ tetrahedron surrounded by 4 MO₆ triads each formed by 3 MO₆ edge-joined octahedrals (Fig 2.6a).⁹²

The Keggin anions exhibit an aromaticity.⁹³ Nonbonding d-orbitals (d_{xy} -orbitals) on the M atoms of the MO₆ octahedrals interact with each other leading to electron delocalization. Thus the charges of the Keggin anions are delocalized.⁹³ As the M atoms are separated by M-O-M bridges, their aromaticity is weaker compared to the aromaticity of adjacent atoms such as in organic components (*e.g.* benzene).⁹³

Due to their strong acidity, thermal stability and electronic versatility 94,95 , POMs find many application *e.g.* as catalyst for selective oxidation¹⁶ or in sustainable energy conversion and storage^{17,96}. Even in medicine they could be useful due to their antiviral and antitumoral properties.⁹⁷

Regarding their catalytic properties, the stability (thermal⁹⁸ and ph-depending⁹⁹) of Keggin type POM is important. In most cases the Keggin anion is not the catalytic active structure but the slightly decomposed lacunary structure.¹⁰⁰ The thermal and pH-depending stability depends on the used central atom and on the addendum atom.^{95,98}

UV-vis and IR measurement showed that $\text{SiW}_{12}\text{O}_{40}^{4-}$ (used in this thesis) is stable from pH values of 1 to 7.⁹⁹ At higher pH values, it hydrolyzed into the lacunary structure $\text{SiW}_{11}\text{O}_{39}^{8-}$. Above a pH value of 8.5, it completely decomposed into SiO_{4}^{2-} and WO_{4}^{2-} .⁹⁹ In aqueous solutions POMs with a low charge density like $\text{SiW}_{12}\text{O}_{40}^{4-}$ adsorb at hydrated polar interfaces due to their choatropic nature: Upon their adsorption, water from the hydration shell of the interface is released increasing the overall entropy.¹⁰¹ These interfaces may be surfactant loaded air / liquid interfaces or surfactant micelles. Due to their adsorption, POMs dehydrate interfaces and may induce electrostatic charge to non-charged systems.¹⁹
Chapter 3

Experimental section

3.1 Materials and sample preparation

Surfactants

The cationic surfactant tetradecyltrimethylammonium bromide (C_{14} TAB, CAS: 1119-97-7, Fig. 3.1a) was purchased from Sigma-Aldrich (Steinheim, Germany) and purified (3-fold recrystallization in EtOH and acetone) prior to the experiments. It was chosen because it is the shortest member of the C_n TAB series that form stable foam films on its own.¹⁰²

Chain-deuterated d₂₉-C₁₄TAB (d-C₁₄TAB) was purchased from CDN Isotopes (Quebec, Canada) and used as received. The used C₁₄TAB concentration ($c_{C_{14}TAB} = 10^{-4}$ M) lies below the cmc for all used salt concentrations.¹⁰³

The commercial non-ionic surfactant BrijO10 (CAS: 9004-98-2) was purchased from Sigma Aldrich (Steinheim, Germany) and used as received. BrijO10 is a polydisperse S with $C_{18:1}E_{10}$ as main fraction (Fig. 3.1b). The used BrijO10 concentration ($c_{BrijO10} = 0.5 \text{ mM}$) lies above the cmc of 0.04 mM, thus micelles are expected to be in the solutions, foam films, and foams.¹⁰⁴



FIGURE 3.1: Chemical structure of a) $C_{14}TAB$ and b) BrijO10.

Polyelectrolytes

Monosulfonated polyphenylene sulfone (sPSO₂-220, $M_W = 100$ kDa with Li⁺ as counterion, Fig. 3.2a) was synthesized by the group of Klaus-Dieter Kreuer (Max Planck Institute for Solid State Research, Stuttgart, Germany) and further purified as follows: A suspension of sPSO₂-220 in ultrapure water was centrifuged (4000 rpm, 60 min) and the resulting solution was filtered through a cellulose acetate filter (pore diameter of 0.2 µm). The resulting solution was collected and separated *via* centrifugation (7500 rpm, 3 min × 15 min) against centrifugal filters (Amicon Ultra 10K, Merck Millipore, Darmstadt, Germany). The supernatant sPSO₂-220 was freeze-dried and redissolved for the experiments.

sPSO₂-220 exhibit a dissociation degree of $54 - 61 \%^{105,106}$ and a $l_{\rm P}$ of $(20 \pm 2) \,\rm nm^{83}$. Thus it is a rather stiff P. In chapter 4, the interfacial structures formed of sPSO₂-220 / C₁₄TAB mixtures are studied while focusing on the impact of P flexibility. As comparison, mixtures containing sodium poly(styrenesulfonate) (PSS) are used. PSS and sPSO₂-220 have a similar chemical structure (Fig. 3.2) but with an $l_{\rm P}$ of $1 \,\rm nm^{107}$, PSS is a more flexible P.

PSS (CAS: 25704-18-1, $M_W = 70 \text{ kDa}$, Fig. 3.2b) was purchased from Sigma Aldrich and used as received. The polyelectrolyte concentrations in this thesis are varied between 10^{-5} monoM and 3×10^{-3} monoM, which denotes the molar concentration of the respective monomer.



FIGURE 3.2: Chemical structure of one monomer of a) sPSO₂-220 and b) PSS.

Salts

LiBr (99.995%, CAS: 7550-35-8) and NaCl ($p \ge 99.5\%$, CAS: 7647-14-5) were purchased from Sigma-Aldrich. NaBr (Suprapur[®], 99.995%, CAS 7647-15-6) was purchased from Merck (Darmstadt, Germany). All salts were cleaned from organic impurities by heating to 500 °C overnight before use. The polyoxometalate tungstosilicic acid (HSiW, CAS: 12027-43-9, $H_4SiW_{12}O_{40} \cdot x H_2O$, $p \ge 99.9\%$, Fig 3.3), with x = 14 from thermogravimetric analysis, was purchased from Sigma Aldrich and used as received. HSiW exhibiti the Keggin structure.



FIGURE 3.3: Chemical structure of SiW⁴⁻ anion.

Sample preparation

All solutions were prepared using ultrapure water (Milli-Q-system, Merck Millipore, Darmstadt, Germany, total organic content ≤ 4 ppb; resistivity = $18 \text{ M}\Omega \text{ cm}$).

For the experiments including P/S mixtures, the mixing procedure was the following: the S solution $(V_S = \frac{1}{2}V_{\text{final}})$ was slowly poured into the P solution $(V_P = \frac{1}{2}V_{\text{final}})$ to avoid a locally high S concentration in the P solution.^{63,108} Afterwards the solution was gently rotated to avoid crossing a phase boundary and precipitation of P/S complexes.¹⁰⁹ Both S and P solutions contained the desired salt concentration and twice the desired S or P concentration, respectively. The final mixture volumes (2 mL $\geq V_{\text{final}} \leq 50 \text{ mL}$) depended on the measurements. All freshly mixed samples were clear to the naked eye with no precipitation for a couple of days (maximal time scale of the different measurement techniques). Furthermore, turbidity measurements showed no formation of larger P/S aggregates (sec. A.3).

3.2 Methods

3.2.1 Thin Film Pressure Balance

The Thin Film Pressure Balance (TFPB) is a common method to study foam films. The technique was developed by Scheludko and Exerowa²³ in 1959 and since then it



FIGURE 3.4: Schematic setup of a Thin Film Pressure Balance.

has been continuously improved $^{24-26,28,29}$. With a TFPB, horizontal, free standing foam films can be investigated. Disjoining pressure isotherms are obtained while at the same time the foam films are monitored *via* a CCD camera.

Basic principle and setup Fig. 3.4 shows the basic setup of a TFPB. The foam film is formed across a hole (diameter 1 mm) inside a porous glass disk (porosity P4, pore size $10 - 15 \,\mu\text{m}$). The glass disk is connected to a glass capillary tube containing the sample solution. The glass tube is situated in a stainless steel cell so that the glass disk is inside the cell but the top of the capillary tube is outside the cell. A reservoir of sample solution is placed inside the measuring cell to provide a saturated vapor atmosphere. Using a reflected-light microscope (Nikon, Düsseldorf, Germany), cold filtered white light illuminates the foam film through a window above the porous glass disk. The light reflected at the foam film is spitted into two beams: the first one reaches a camera (JAI Go-2400C-USB camera, Stemmer Imaging, Germany) and allows monitoring the foam film. The second beam passes a filter ($\lambda = 632 \,\mathrm{nm}$) and is amplified by a photomultiplier. The recorded intensity is transmitted to a computer. The pressure inside the cell is measured using two differential pressure transducers (MKS Instruments, Germany, one up to 10 mbar - the other one up to 100 mbar). A piston pump is used to adjust the pressure inside the cell. The piston pump and the pressure transducers are controlled and read out by a computer.

Data evaluation: disjoining pressure Π and thickness h At equilibrium, the disjoining pressure Π balances the capillary pressure P_{Ca} and equals the difference

between pressure in the film P_{film} and the pressure of the bulk liquid P_{l} .

$$\Pi = P_{\rm Ca} = P_{\rm film} - P_{\rm l} \tag{3.1}$$

Since the foam film can be considered as a flat film, P_{film} equals the gas pressure in the measuring cell P_{g} and eq. 3.1 can be rewritten:

$$\Pi = P_{\rm g} - P_{\rm l} \tag{3.2}$$

The pressure of the bulk liquid $P_{\rm l}$ is composed of three parts: 1) the atmospheric reference pressure $P_{\rm r}$, 2) the capillary pressure $\frac{2\gamma}{r}$, where γ is the surface tension of the sample solution and r is the radius of the glass capillary tube, and 3) the hydrostatic pressure $\Delta \rho g h_c$, where $\Delta \rho$ is the density difference between the gas phase and the sample solution and $h_{\rm c}$ is the height of the sample solution inside the glass capillary tube with respect to the height of the foam film. So, eq. 3.2 can be rewritten:

$$\Pi = P_{\rm g} - P_{\rm r} + \frac{2\gamma}{r} - \Delta\rho g h_{\rm c}$$
(3.3)

The differential pressure transducers measure the difference $P_{\rm g} - P_{\rm r}$ as ΔP . Eq. 3.3 can be simplified to:

$$\Pi = \Delta P + \frac{2\gamma}{r} - \Delta \rho g h_c \tag{3.4}$$

and the disjoining pressure Π can be calculated from the recorded pressure difference ΔP . The maximal accessible Π depends on different parameter of the setup such as the pore width of the porous glass disk, the pistil pump, and the length of the glass tube. For the used setup, the maximal accessible Π lies around 10 600 Pa.

The equilibrium thickness h is determined interferometrically. The white light is reflected at the upper and the lower air / liquid interface of the foam film. The two waves interfere with a phase shift difference, which can be correlated to the film thickness h. This interferometrically methods scales the intensity of the reflected light with the intensity minimum I_{\min} and the intensity maximum h_{\max} .¹¹⁰ Thus, hcan be calculated as follows:

$$h = \frac{\lambda}{2\pi n_{\rm s}} \arcsin \sqrt{\frac{\Delta}{1 + (4R(1-\Delta)/(1-R)^2)}}$$
(3.5)

with
$$\Delta = \frac{I - I_{\min}}{I_{\max} - I_{\min}}$$
 and $R = \frac{(n_{\rm s} - 1)^2}{(n_{\rm s} + 1)^2}$ (3.6)

where λ is the wavelength of the used photomultiplier ($\lambda = 632 \text{ nm}$), n_s is the refractive index of the solution ($n_s = 1.33$), and I is the current light intensity. I_{max} and I_{min} are measured during film formation and after film rupture, respectively. At the maximum, the foam film is around 118 nm thick. With decreasing thickness the destructive interference between the two reflected waves increases and the foam film becomes darker.

Measurement procedure All glassware (expect the glass tube with the porous glass disk) were cleaned with the alkaline detergent mixture Q9 (3-5%, Bernd Kraft GmbH) overnight and rinsed generously with ultrapure water before use. The film holder (capillary glass tube + porous glass disk) was cleaned by flushing with EtOH (Uvasol[®], Merck, Germany) and ultrapure water for several times and subsequently boiling in ultrapure water for at least 4 hours. Afterwards, it was dried in a N₂ steam, rinsed 5 times with the sample solution and placed over night in the sample solution for fully wetting. The glass disk was pulled out the sample solution 30 min before an experiment for equilibration of the surfaces.

The foam film stability is judged by the maximal disjoining pressure (Π_{max}), which can be applied before the foam film ruptures. If larger fluctuation of the foam film stability occurred (sec. A.1), only reproducible Π_{max} are used in this thesis. The disjoining pressure isotherms shown in the thesis are averaged over at least three individual measurements, if not stated otherwise. The foam film thickness is determined after the reflected intensity was constant for 15 min to ensure an equilibrated foam film. All measurement are preformed at 25 °C.

Calculation of disjoining pressure isotherms For the P/S mixtures, the measured disjoining pressure isotherms were fitted using a first order exponential decay function to obtain the experimental Debye length κ_{exp}^{-1} .¹¹¹ This κ_{exp}^{-1} was used as a starting point for the model calculation of the non-linear PB eq. (section 2.1.2). For the BrijO10 + HSiW samples, the theoretical Debye length κ_{theo}^{-1} -- taking into account the corresponding concentrations and valences of HSiW -- was used as stating point for the model calculations.

The calculations were compared to the measured disjoining pressure isotherms to determine the *apparent* surface potential Ψ_{app} . The model calculations were done

with an algorithm by Chan¹¹² under constant potential. The numerically algorithm considers two identically charged plates which are separated by a distance z. Two boundary conditions are needed: First, at the median plane the potential vanishes and second, electroneutrality is fulfilled. During the performed evaluation, the potential Ψ and κ^{-1} are successively adjusted until the calculated curves coincides with the experimental data. Only the value of Ψ and not the sign is obtained out of the calculation. The PB calculations were only done for rather stable foam films ($\Pi_{\text{max}} >$ 500 Pa) due to the otherwise low number of data points and higher vulnerability of the low part of the disjoining pressure isotherm. Due to the experimental error of the TFPB an average error of $\pm 10\%$ can be assumed.

For the BrijO10 + HSiW samples a an der Waals component of the disjoining pressure $\Pi_{\rm vdW}$ was additionally calculated according to eq. 2.15 with a Hamaker constant A of 3.7×10^{-20} J (air/water/air system)³⁰. This was done in order to verify the adaptability of the DLVO theory to these samples. The *apparent* surface potential $\Psi_{\rm app}$ was later converted into an *apparent* surface charge density q_0 using the Graham equation. Here, not the form for symmetric electrolytes (eq. 2.9) was used but an adapted form to account for the asymmetric nano-ion (1:4)³⁰:

$$q_0 = \sqrt{2\epsilon\epsilon_0 c \cdot \left(4\exp\left(\frac{-e\Psi_{\rm app}}{kT}\right) + \exp\left(\frac{4e\Psi_{\rm app}}{kT}\right) - 5\right)} \tag{3.7}$$

3.2.2 Specular Neutron Reflectometry

Basic principles¹ Specular neutron reflectometry (NR) is a versatile technique that is used routinely to resolve the composition and structure of layers at fluid interfaces in soft matter systems.¹¹³⁻¹¹⁶ NR probes material contained within the first few hundreds of nanometers of the reflecting surface and is powerful for two reasons in particular. First, the interaction of neutrons with atoms varies according to the isotopic composition of the sample, so samples with chemically-equivalent composition can be measured in different states, which allows a greater level of information to be resolved. Second, the neutrons themselves have wavelengths on the nanometer scale, which is comparable with the interfacial thickness of many self-assembled soft matter systems, so the presence of interference fringes in the data, called Kiessig fringes¹¹⁷, pinpoints the length scales to which the materials extend.

¹Parts of this paragraph are published in "Polymers and surfactants at fluid interfaces studied with specular neutron reflectometry" L. Braun, M. Uhlig, R.A. Campbell, R. v. Klitzing, *Adv. Colloid Interface Sci.*, **2017**, 247, 130-148. Reprinted with permission. Copyright 2017 Elsevier.⁷⁰

In specular NR, the incident and reflection angles of the neutrons with respect to the surface are equal (θ in Fig. 3.5), and this approach is sensitive to the density profile of atoms in the z-direction normal to the reflecting surface.¹¹⁸ The reflectivity, R, is defined as the ratio of the intensity of neutrons in the specular reflection with respect to that incident on the sample. R is measured with respect to the incident angle, θ (in monochromatic mode) or the neutron's wavelength λ (in time-of-flight mode) to generate plots of R with respect to the momentum transfer, Q_z , given by

$$Q_z = \frac{4\pi}{\lambda}\sin\theta \tag{3.8}$$

When neutrons reflect off a material with a higher scattering length density (SLD) (e.g. from air to D_2O), there is total reflection below a critical angle and therefore below a critical value of Q_z . Above this value the Fresnel reflectivity falls as a function of Q_z^4 and the fall-off depends on the structure of the material near the interface. The reflectivity plots ($R \ vs. Q_z$) are fitted to extract information such as the density, thickness and roughness of individual layers.¹¹⁹



FIGURE 3.5: Schematic drawing of specular neutron reflectometry at the air / water interface with adsorbed S molecules.

As stated above, the value of specular NR in the study of soft matter systems is enhanced by hydrogen/deuterium substitution. This method is particular exploitable because the two isotopes of hydrogen have very different scattering lengths, $b_{\rm H} = -3.74 \times 10^{-5}$ Å for ¹H and 6.67×10^{-5} Å for ²H. A particularly common example of this is water, as a mixture of 8.9 wt% D₂O in H₂O has a SLD of zero, which is the same as that of air. This mixture is called air contrast matched water (ACMW) and is used in the experiments at the air / liquid interface to highlight the scattering from the interfacial layer.

The surface excess (in mol/area) of a species x, Γ_x , in a single uniform layer is given by:

$$\Gamma_x = \frac{\mathrm{SLD}_x \cdot d}{b_x \cdot N_A} \tag{3.9}$$

where d is the thickness of the layer.

At very low values of Q_z and in the thin film limit of just a few nanometers, the product SLD $\cdot d$ in the applied structural model of an interfacial layer on ACMW becomes virtually independent of specific details of the structural model applied within reasonable bounds. In this case, the product can be considered simply as a scattering excess, which is related proportionately to the surface excess for a single-component system. This condition is true even if the interfacial layer contains air or solvent as they are both effectively invisible to the neutrons. Hence the measurement of a deuterated compound at the surface of ACMW at low Q_z values using specular NR is a direct way to quantify its surface excess. For more complex systems, such as those comprising of different components or more extended interfacial layers, the surface composition and structure are usually determined by varying the isotopic contrast of components at the interface and the subphase in order to simultaneously fit data recorded in multiple isotopic contrasts to a common structural model.^{76,120,121}

Experimental details² Specular NR experiments were performed on the Fluid Interfaces Grazing Angles ReflectOmeter (FIGARO)¹²³ at the Institut Laue-Langevin (Grenoble, France). The FIGARO is a time-of-flight instrument. Here, the continuous neutron beam gets converted into neutron pulses by the use of choppers. Afterwards, the neutron pulse spread out as the neutrons with a lower wavelength are faster than those with a higher wavelength. The detector measures the intensity of neurons with time, which correspond to a wavelength resolution. Data of successive pulses are combined to increase the signal-to-noise ratio. For the experiments the wavelength resolution was $d\lambda/\lambda = 7\%$ in the used wavelength range $2\text{ Å} \leq \lambda \leq 30$ Å. Two different sets of experiments were done, one to obtain the surface excess of P and S separately (low Q_z analysis) and one to resolve the formed structures at the interface (full Q_z analysis).

low Q_z analysis In the first set of experiments, data were recorded at $\theta = 0.62^{\circ}$ at reduced low $Q_z < 0.03 \text{\AA}^{-1}$. Samples with two different contrasts were measured: (Ia) P / cm-C₁₄TAB / ACMW and (Ib) P / d-C₁₄TAB / ACMW, where P refers to

²Parts of this and the following sections are published in "Insights into extended structures and their driving force: Influence of salt on polyelectrolyte / surfactant mixtures at the air / water interface" L. Braun, M. Uhlig, O. Löhmann, R.A. Campbell, E. Schneck, R. v. Klitzing, *ACS Applied Materials & Interfaces*, **2022**, 14, 27347-27359. Reprinted with permission. Copyright 2022 American Chemical Society.¹²²

either sPSO₂-220 or PSS and cm-C₁₄TAB is a contrast matched C₁₄TAB (4.4 wt% d-C₁₄TAB in h-C₁₄TAB) with a SLD of zero. Fig. 3.6 shows sketches of the deuteration schemes. In case (Ia) only P contributes to the intensity of the specular reflection; in case (Ib) the deuterated C₁₄TAB (d-C₁₄TAB) dominates the specular reflection. The data were not background corrected, and the background was determined as 2.72 x 10^{-5} from several measurements of pure ACMW.



FIGURE 3.6: Schematic drawing of deuteration schemes of the low Q_z analysis: (Ia) P / cm-C₁₄TAB / ACMW and (Ib) P / d-C₁₄TAB / ACMW. Greyish colored components are contrast matched to have a SLD of zero.

full Q_z analysis In the second set of experiments, data were recorded at two incident angles: $\theta = 0.63^{\circ}$ and $\theta = 3.8^{\circ}$ covering the full accessible Q_z -range (truncated in the reduction at $Q_z = 0.27 \text{\AA}^{-1}$). Here, the reflectivity is sensitive to the interfacial composition and the internal structure; it depends on the SLD profiles along the direction perpendicular to the interface, z. Samples with three different contrasts were measured over the full Q_z -range: (IIa) P / d-C₁₄TAB / ACMW, (IIb) P / d-C₁₄TAB / D₂O and (IIc) P / h-C₁₄TAB / D₂O. Fig. 3.7 shows sketches of the deuturation schemes. The data were background corrected using the area detector. For the analysis, data recorded over the low Q_z -range in the contrast (IId) P / cm-C₁₄TAB / ACMW were added to ensure the right amount of P. Since this particular data set contains fewer data points, the errors were weighted higher by the calculation of χ^2 .



FIGURE 3.7: Schematic drawing of deuteration schemes of the full Q_z analysis: (IIa) P / d-C₁₄TAB / ACMW, (IIb) P / d-C₁₄TAB / D₂O and (IIc) P / h-C₁₄TAB / D₂O.

Data evaluation: surface excess Γ and interfacial structure

low Q_z analysis The data analysis for the first set of experiments was done with the Motofit software¹²⁴ using a one-layer model. The roughness of the layer was fixed to 3.5 Å. In the low Q_z regime, the product of SLD and thickness d (SLD $\cdot d$) is related to the surface excess of a component Γ_i with respect to its scattering properties while being insensitive to the actual interfacial structure.^{70,125} Thus, using arbitrary SLD values (2 × 10⁻⁶ Å⁻² and 4 × 10⁻⁶ Å⁻² for case (Ia) and case (Ib), respectively), the thickness of a single layer was fitted for each measurement to solve the following equations simultaneously^{70,85}:

(Ia)
$$(\text{SLD} \cdot d) = N_{\text{A}}(b_{\text{P}} \cdot \Gamma_{\text{P}})$$
 (3.10)

(Ib)
$$(\text{SLD} \cdot d) = N_{\text{A}}(b_{\text{P}} \cdot \Gamma_{\text{P}} + b_{\text{d-C}_{14}\text{TAB}} \cdot \Gamma_{\text{d-C}_{14}\text{TAB}}).$$
 (3.11)

That way the surface excess of P ($\Gamma_{\rm P}$) and of C₁₄TAB ($\Gamma_{\rm C_{14}TAB}$) are obtained.

full Q_z analysis To analyze the data of the second set of experiments a model based on the volume fractions of all components was used. The procedure was implemented in a self-written fitting program based on the IDL software package (www.harrisgeospatial.com) similar as described in Ref. 126. The SLD profile (SLD(z)) follows from the volume fraction profiles of all components $\Phi_i(z)$:

$$SLD(z) = \sum_{i} \Phi_{i}(z) \cdot SLD_{i}$$
(3.12)

where SLD_i is the scattering length density for each component which is related to its scattering length b_i divided by the molecular volume $V_{\text{m,i}}$. The surfactant volume fraction was divided into head groups and chains because they exhibit different SLD values, especially when changing between h-C₁₄TAB and d-C₁₄TAB. The volume fraction profiles of each single component (chain (ch), head group (hg) and polyelectrolyte (P)) were modeled as homogeneous slabs with adjustable thicknesses (d_{ch} , d_{hg} and d_{P}) and SLD values (SLD_{ch}, SLD_{hg}, SLD_P). The center position of the upper layer of chains is fixed at the air / liquid interface. To consider the interfacial roughness induced by capillary waves¹²⁷, each volume fraction profile is gradually truncated to the adjacent layer by an error function with an adjustable roughness parameter $\sigma_{i,j}$.

Component	SLD (x 10^{-6} Å^{-2})	b (x 10^{-5} Å)
d-chain ^a	7.16	286
h-chain ^a	-0.39	-15.40
head group ^{a}	0.18	2.12
$cm-C_{14}TAB$	0	0
$d-C_{14}TAB^a$	5.14	288
PSS^{b}	1.85	50.80
$sPSO_2-220^c$	3.05 - 3.50	62

TABLE 3.1: SLDs and scattering lengths b used.

^{*a*} taken from $^{85 \ b}$ taken from $^{77 \ c}$ fit parameter, details described in the text

The adsorbed amount of component i is obtained by integration:

$$D_{\rm i} = \int_{-\infty}^{\infty} \Phi_{\rm i}(z) dz.$$
(3.13)

 $D_{\rm i}$ corresponds to the thickness of an "equivalent layer" composed of 100% of component i and can be converted into the surface excess $\Gamma_{\rm i}$ according to

$$\Gamma_{\rm i} = \frac{{\rm SLD}_{\rm i}}{b_{\rm i} N_{\rm A}} D_{\rm i}. \tag{3.14}$$

To ensure equal numbers of chains and head groups, their amounts were coupled considering the respective molecular volumes. The SLD values were fixed to values from literature and are listed in Tab. 3.1. For sPSO₂-220, the SLD was calculated with the SLD calculator of the Motofit software: using a mass density of 1.75 g cm^{-3 106}, resulting in an SLD of $3.05 \times 10^{-6} \text{ Å}^{-2}$. For calculating the SLD the smaller solvent-excluded volume is more relevant, thus a SLD range between 3.05×10^{-6} and $3.5 \times 10^{-6} \text{ Å}^{-2}$ was allowed for the SLD of sPSO₂-220 in the fitting procedure.

Error consideration for the surface excess For the surface excess, two different kinds of errors have to be considered: the statistical error from the fitting procedure of the reflectivity data and systematic errors from the sample preparation. According to Bevington and Robinson¹²⁸, the statistical error associated with a 95.4% (two-sigma) confidence interval coincides with an increase by 4 of the χ^2 deviation between fit and experimental data. For the surface excess that equals the fitted layer thickness *d* (see eq. 3.10 and 3.11), the dependence of (reduced) χ^2 on *d* is shown exemplarily in Fig. 3.8 for the sample "c_{sPSO2-220} = 8 × 10⁻⁵ monoM, c_{LiBr} = 10⁻² mol, contrast cm-C₁₄TAB / ACMW". In this case, a statistical error in $\Gamma_{\rm sPSO_2-220}$ of $0.05\times10^{-6}\,\rm mol\,m^{-2}$ is obtained.



FIGURE 3.8: Reduced χ^2 in dependence of the fit parameter. The two vertical arrows indicate the error of the fit parameter. $\Gamma_{\rm sPSO_2-220}$ is calculated using eq. 3.11.

The same procedure was preformed to obtain the error of the thickness of the second contrast (Ib). Since $\Gamma_{C_{14}TAB}$ depend on the fit results of both contrasts (d-C₁₄TAB in ACMW and cm-C₁₄TAB in ACMW, eq. 3.11), an error propagation for calculating the error of $\Gamma_{C_{14}TAB}$ from the two fitted thicknesses was additional preformed. The statistical error bars obtained in this way are shown in Fig. 3.9 for three sPSO₂-220 concentration (3 × 10⁻⁵, 8 × 10⁻⁵ and 4 × 10⁻⁴ monoM) as black error bars.



FIGURE 3.9: Surface excess of sPSO₂-220 (blue triangle) and C₁₄TAB (red diamond) in dependence of sPSO₂-220 concentration with $c_{\text{LiBr}} = 10^{-2}$ M. The vertical dotted line marks the bulk stoichiometric mixing point BSMP. The black error bars correspond to the statistical error. The colorful errors correspond the systematically error.

The systematic error introduced during sample preparation can only be crudely estimated. The samples were prepared using different batches of ACMW, each having a certain uncertainty of SLD due to preparation. The same applies to the cm- C_{14} TAB. The systematically error of sample preparation was estimated to be 7%. Fig. 3.9 shows the corresponding error bars (colorful error bars). For most of the samples, the systematic errors largely dominate the uncertainty of the surface excess. Thus, the systematic errors are shown in the thesis.

3.2.3 Tensiometry

Surface tension measurements were performed to obtain an overview on the surface activity of S solutions and P/S mixtures. The surface tension of a pure liquid results from an energetic difference between molecules situated at the surface and those inside the bulk liquid.¹²⁹ Molecules at the surface are only partly surrounded by neighboring molecules, thus having less attractive interactions compared with those in bulk. Hence, increasing the surface - bringing more molecules to the surface - requires a work w proportional to the increase in area A^{129} :

$$w = \int_0^A \gamma dA = \gamma A \tag{3.15}$$

The proportional constant γ is the surface tension of the liquid. In this thesis, surface tension measurements were preformed with a K11 Tensiometer (KRÜSS GmbH[®], Hamburg, Germany) using the Du Noüy ring technique¹³⁰. A thin Pt wire ring is raised through the liquid. A liquid meniscus is pulled out by the ring after it passes the surface. Thereby the force is measured by a force balance. A force maximum occurs just before the ring detaches from the liquid surface. This maximum correlates with the surface tension γ^{131} :

$$\gamma = \frac{F_{\max}}{4\pi R \cos \Theta} \tag{3.16}$$

where R is the radius of the ring and Θ the contact angle. A Pt wire is used because of its good wetting behavior, resulting in a contact angle of zero (cos (0) = 1). The detachment method and correction factors according to Huh & Mason¹³² were used. The S and P solutions were prepared 1 day beforehand. Solutions were mixed in a Teflon vessel (diameter 5 cm) 2 hours before the measurement. The surface tension was measured until it leveled at a constant value for 20 min. All measurements were carried out at (25.0 ± 0.1) °C.

3.2.4 Additional techniques

Several experimental techniques were used to further characterize the interfacial and bulk properties of the samples. They are summarized in the following.

Ellipsometry Ellipsometry is a non-destructive optical technique to measure different properties (the refractive index n and the thickness d) of thin films at solid and liquid interfaces. To this end, the change in the state of polarization caused by reflection at the interfacial layers is detected and analyzed.¹³³ The change in polarization is quantified by the change of the polarizer angle Ψ and the analyzer angle Δ . tan Ψ describes the ratio of the p and s reflectivities amplitudes³⁸:

$$\tan \Psi = \frac{|r_{\rm p}|}{|r_{\rm s}|} \tag{3.17}$$

and Δ is the phase change between the p and s polarized reflected light³⁸:

$$\Delta = \delta_{\rm p} - \delta_{\rm s}.\tag{3.18}$$

Measurements of the ellipsometric angles Δ and Ψ were conducted with an Optrel Multiskop ellipsometer (Sinzing, Germany) working with a wavelength of $\lambda = 632.9$ nm and an angle of 58°. Experiments were performed with solutions in a Petri dish 2 hours after mixing and pouring the P/S samples into the dish. The dishes were covered during this time to reduce evaporation.

Brewster angle microscopy Brewster angle microscopy (BAM) is a non-invasive optical microscopy technique that allows visualization of air / liquid interfaces.¹³⁴ A laser beam impinges on an air / liquid interface at the Brewster angle. At the Brewster angle of a pure liquid no parallel polarized light is reflected, but adsorbed material changes the refractive index resulting in light reflections. A camera detects these light reflections allowing real-time images of the air / liquid interface.¹³⁵

Experiments were performed with an Ultrabam system by Accurion (Göttingen, Germany) with a laser wavelength of $\lambda = 658$ nm. The image data were processed using the software Accurrion Image to correct for the Scheimpflug effect. The Ultrabam setup was equiped with the highly sensitive CCD camera with 1360 pixels x 1024 pixels. The lateral resolution was 2 µm. The images were recorded at the angle of incidence ~53.3° (experimentally determined Brewster angle prior to the

experiment) with analyzer and polarizer set to 0° . BrijO10 + HSiW samples were poured into a small Teflon trough and monitored up to 90 min to ensure successful and complete adsorption.

Electrophoresis and dynamic light scattering The mean electrophoretic mobility u_{ζ} is an indicator for the charge of a particle. u_{ζ} is correlated to the velocity \vec{v} of the particle in an electric field \vec{E}^{136} :

$$\vec{v} = u_{\zeta} \cdot \vec{E} \tag{3.19}$$

The used Malvern Zetasizer NanoZ (Malvern Instruments, Germany) performs laser doppler electrophoreses¹³⁷ to measure u_{ζ} . P/S mixtures were measured 5 min after mixing. The same instrument was used to measure the mean hydrodynamic diameter $d_{\rm h}$ of the complexes performing dynamic light scattering. Here, the sample is illuminated with a laser (wavelength $\lambda = 633 \,\mathrm{nm}$) and the intensity fluctuations of the scattered light are analyzed to obtain the size of the complexes. To reduce multi-scattering and the effect of dust, backward scattering with an angle of 173° was used. Due to low concentration and too polydisperse samples, $d_{\rm h}$ could only be determined for two samples: $c_{\rm sPSO_2-220} = 6 \times 10^{-4} \,\mathrm{monoM}$ and $10^{-3} \,\mathrm{monoM}$ both with $c_{\rm LiBr} = 10^{-2} \,\mathrm{M}$.

UV-vis spectroscopy The turbidity of P / S mixtures was measured with a Varian Cary 50 UV-vis spectrometer. The optical density (OD) of the samples was determined from the absorbance A at 400 nm:

$$OD_{400} = A_{400} \cdot \ln 10 \tag{3.20}$$

Measurements were carried out 5 min after mixing. Since neither the P nor S have an adsorption band above 350 nm, increased values of OD_{400} indicate the presence of larger P/S aggregates.

Chapter 4

Effect of salt on interfacial structures of P / S mixtures

Similar content is published in "Insights into extended structures and their driving force: Influence of salt on polyelectrolyte/surfactant mixtures at the air/water interface" L. Braun, M. Uhlig, O. Löhmann, R. A. Campbell, E. Schneck, R. v. Klitzing, *ACS Applied Materials & Interfaces*, **2022**, 14, 27347-27359. Reprinted with permission. Copyright 2022 American Chemical Society.¹²²



4.1 Abstract

This chapter addresses the effect of P stiffness on the interfacial structure of P/S mixtures. As foam films consist of two facing air / liquid interfaces, structures formed at these interfaces are expected to affect the foam films.

Two different anionic Ps with different intrinsic persistence length $l_{\rm P}$ are studied while

varying the salt concentration (0 - 10^{-2} M). Either sPSO₂-220 ($l_P \sim 20$ nm) or PSS ($l_P \sim 1$ nm) is mixed with C₁₄TAB well below its cmc and studied with tensiometry and NR experiments. The S concentration (10^{-4} M) is kept constant, while the P concentration ($10^{-5} - 10^{-3}$ monoM) is varied. P and S adsorb at the air/liquid interface for all studied mixtures. Around the BSMP, PSS/C₁₄TAB mixtures lose their surface activity, whereas sPSO₂-220/C₁₄TAB mixtures form extended structures perpendicular to the surface (meaning a layer of S with attached P and underneath additional layers of P and S instead of only a monolayer of S with P). Considering the different P monomer structures as well as the impact of salt, the driving force for the formation of these extended structures is identified: compensation of all interfacial charges (P/S ratio ~ 1) to maximize the gain of entropy. By increasing the flexibility of P, the interfacial structures can be tuned from extended structures to monolayers.

4.2 Introduction

P/S complexes are highly surface-active and alter the surface tension of the mixtures compared to the single components.^{67,79,80,83}

Besides the surface tension, knowledge of the interfacial structures of the P/S layer is of great technological relevance for foaming and foam film stability.^{85,138,139} Using the advantages of NR⁷⁰ different layer structures have been identified, ranging from a simple monolayer up to several layers. Li and coworkers reviewed the formation of interfacial multilayers in detail.¹⁴⁰ These multilayers formed by a dispersion of P/S aggregates at high S concentration result from many repeat units of P and S at the interface. They have been interpreted both in terms of self-assembly of these repeat units¹⁴¹ and of liquid crystalline aggregates at the interface.¹⁴² In PSS/dodecyltrimethylammonium bromide (C₁₂TAB) films spread from concentrated aggregate dispersions, extended structures can be found depending on the charge and structures of the aggregates.¹⁴³ These extended structures result from intact aggregates embedded in the spread film and are not stable with time.

Recently, the appearance of interfacial extended structures for P/S mixtures at low S concentration (solution of complexes) was reported.⁸⁵ These structures rationalize the non-monotonous foam film stability of sPSO₂-220 / C_{14} TAB mixtures without added salt. Thus, interfacial structures seem to be relevant for understanding foam films. Before the effect of salt on foam films is examined (chapter 5), one smaller scale is studied: the single air / liquid interface.

In the present chapter, the extended structures will be examined in more detail with the focus on why these structures form and how the formation can be controlled. Tensiometry is used to study the surface adsorption as well as NR to resolve both the interfacial composition and the interfacial structures.

To identify the reasons for self-assembly into an extended structure, we first vary the ionic strength by different amount of added salt. Second, we compare two P/S mixtures: $sPSO_2-220/C_{14}TAB$ and $PSS/C_{14}TAB$. The former shows extended structures but the later not. The two Ps have a chemically similar monomer (sulfate group as the charged part and a benzene ring as the hydrophobic part), but differ in flexibility⁸³ and structure (Fig. 3.2). Third, we consider isotopic effects. For the sake of completeness, a few reflectivity data, which were already published⁸⁵ are included and re-interpreted. With these results, we gain insights into the effect of salt of the interfacial behavior of P/S mixtures. Moreover, the results help to elucidate the driving force for the formation of extended structure.

4.3 Results

The results section is divided into two parts each addressing one of the mixtures studied (sPSO₂-220 / C_{14} TAB and PSS / C_{14} TAB). For both mixtures, first the surface tension data are presented followed by the results of the low Q_z analysis (surface excess of the polyelectrolyte Γ_P and of the surfactant $\Gamma_{C_{14}TAB}$ obtained by eq. 3.10 and eq. 3.11) and the full Q_z analysis (interfacial structures) of the NR data. We differentiate between three kinds of interfacial structures: a) a compact monolayer structure meaning a S monolayer with a compact P layer bound to the head groups, b) a swollen monolayer structure meaning a S monolayer with a swollen P layer bound to the head groups, and c) an extended structure meaning a S monolayer with P bound to the head groups and additional layers consisting of P and S underneath.

4.3.1 $sPSO_2-220 / C_{14}TAB$ mixtures

Tensiometry

As a first investigation of the surface activity of sPSO₂-220 / C₁₄TAB mixtures, their surface tension was measured. Fig. 4.1 shows the surface tension as function of $c_{\rm sPSO_2-220}$ for different LiBr concentrations ($c_{\rm LiBr} = 0 - 10^{-2}$ M). The dashed



FIGURE 4.1: Surface tension of sPSO₂-220 / C_{14} TAB mixtures as a function of c_{sPSO_2-220} for different salt concentrations ($c_{LiBr} = 0 - 10^{-2}$ M). The dotted vertical line marks the BSMP. The dashed horizontal lines correspond to the surface tension of the pure C_{14} TAB solutions ($c_{C_{14}TAB} = 10^{-4}$ M) at the respective LiBr concentration.

horizontal lines correspond to the surface tension of the respective pure $C_{14}TAB$ solutions ($c_{C_{14}TAB} = 10^{-4}$ M) for the given salt concentrations. The dotted vertical line marks the BSMP at which the concentration of sPSO₂-220 monomers equals that of $C_{14}TAB$ molecules.

Below the BSMP the surface tension is highly reduced compared to the pure $C_{14}TAB$ solutions (40 - 45 mN/m and 70 - 60 mN/m, respectively). This reduction in surface tension denotes the formation of interfacial structures which lowers the surface energy with respect to the bulk activities. Around the BSMP, all mixtures have similar surface tension values around 41 mN/m, which rise sharply above the BSMP (maxima at 60, 58, 50 and 44 mN/m for 0, 10⁻⁴, 10⁻³ and 10⁻² M LiBr, respectively). With further increase of c_{sPSO_2-220} , the surface tension for the low salt concentrations ($c_{LiBr} = 0$ and 10^{-4} M) decreases to a value around 51 mN/m. For the high salt concentrations ($c_{LiBr} = 10^{-3}$ and 10^{-2} M), the surface tension remains at around 50 and 44 mN/m, respectively. The surface tension stays below the values of the corresponding pure $C_{14}TAB$ solutions.

Low Q_z analysis

To obtain the surface excesses Γ of P and S in terms of number of adsorbed molecules / monomers per unit area, NR of two contrasts were measured: one contrast matching



FIGURE 4.2: Surface excess of $C_{14}TAB$ (a) and $sPSO_2-220$ (b) in $sPSO_2-220 / C_{14}TAB$ mixtures as a function of c_{sPSO_2-220} . The data point without LiBr are taken from Ref. 85 with permission from the Royal Society of Chemistry. The solid horizontal line corresponds to the surface excess for a pure $C_{14}TAB$ solution at 10^{-4} M. The dashed horizontal line corresponds to the surface excess for 3.5×10^{-3} M $C_{14}TAB$ solution (cmc). The dotted vertical lines mark the BSMP. For the sake of clarity the surface excess of $sPSO_2-220$ is expressed in mol/m² in terms of monomer units.

the solvent (water) and one contrast matching the solvent and $C_{14}TAB$ (details see chapter 3.2.2; for the reflectivity data see Fig. A.5).

Fig. 4.2 summarizes $\Gamma_{C_{14}TAB}$ (Fig. 4.2a) and Γ_{sPSO_2-220} (Fig. 4.2b) as a function of c_{sPSO_2-220} for the different LiBr concentrations ($c_{LiBr} = 0 - 10^{-2}$ M). The solid lines in Fig. 4.2a correspond to $\Gamma_{C_{14}TAB}$ of the pure $C_{14}TAB$ solutions ($c_{C_{14}TAB} = 10^{-4}$ M, $c_{LiBr} = 0 - 10^{-2}$ M). The dotted vertical line marks the BSMP. Without salt added, $\Gamma_{C_{14}TAB}$ peaks at 6.5×10^{-5} monoM sPSO₂-220. The maximal $\Gamma_{C_{14}TAB}$ exceeds the value of the pure 10^{-4} M $C_{14}TAB$ solution (solid line) and of a $C_{14}TAB$ solution at its cmc ($c_{C_{14}TAB} = 3.5 \times 10^{-3}$ M, dashed horizontal line). This already hints to a more extended interfacial structure than one containing only a monolayer of surfactant. By adding LiBr, the position of the maximal $\Gamma_{C_{14}TAB}$ slightly shifts to higher c_{sPSO_2-220} and the value decreases; at 10^{-2} M LiBr the sharp maximum vanishes.

For sPSO₂-220, a maximum in Γ_{sPSO_2-220} appears *around* the BSMP. Adding LiBr changes this maximum Γ_{sPSO_2-220} rather unsystematically: the position varies *around* the BSMP. *Above* the BSMP, only the addition of 10^{-2} M LiBr slightly increases Γ_{sPSO_2-220} .

Fig. 4.3 shows $\Gamma_{\rm sPSO_2-220}$ and $\Gamma_{\rm C_{14}TAB}$ plotted with the surface tension for comparability. Fig. 4.3a displays the results without salt added, and Fig. 4.3b the results with $c_{\rm LiBr} = 10^{-2} \,\mathrm{M}$ (for $c_{\rm LiBr} = 10^{-4} \,\mathrm{and} \, 10^{-3} \,\mathrm{M}$ see Fig. A.6). Without added salt



FIGURE 4.3: Surface excess of sPSO₂-220 (blue triangles) and C₁₄TAB (red diamonds) and surface tension (taken from Fig. 4.1) for sPSO₂-220 / C₁₄TAB mixtures as a function of $c_{\rm sPSO_2-220}$ without added salt (a) and with $c_{\rm LiBr} = 10^{-2}$ M (b). The solid horizontal lines correspond to the surface excess for a pure C₁₄TAB solution at 10^{-4} M at the respective LiBr concentration. The dashed horizontal lines correspond to the surface tension of pure C₁₄TAB solution at the respective LiBr concentration. The dotted vertical lines mark the BSMP. For the sake of clarity the surface excess of sPSO₂-220 is expressed in mol/m² in terms of monomer units. Samples marked by an arrow are used for the full Q_z analysis.

and below the BSMP (Fig. 4.3a), the surface tension only slightly decreases with increasing $c_{\rm sPSO_2-220}$ ($\Delta \gamma \sim 5 \,\mathrm{mN/m}$) while $\Gamma_{\rm sPSO_2-220}$ and $\Gamma_{\rm C_{14}TAB}$ strongly increases ($\Delta \Gamma \sim 3 \times 10^{-6} \,\mathrm{mol}\,\mathrm{m}^{-2}$). From a $c_{\rm sPSO_2-220}$ of $2 \times 10^{-4} \,\mathrm{monoM}$ on, the surface tension strongly decreases ($\Delta \gamma \sim 10 \,\mathrm{mN/m}$), but $\Gamma_{\rm sPSO_2-220}$ and $\Gamma_{\rm C_{14}TAB}$ remain nearly constant ($\Delta \Gamma \sim 0.5 \times 10^{-6} \,\mathrm{mol}\,\mathrm{m}^{-2}$). For the mixtures with $10^{-2} \,\mathrm{M}$ LiBr (Fig. 4.3b), the surface tension stays nearly constant while $\Gamma_{\rm sPSO_2-220}$ and $\Gamma_{\rm C_{14}TAB}$ increases *around* the BSMP.

Fig. 4.4 shows the interfacial P/S ratio in dependence of $c_{\rm sPSO_2-220}$ for the used $c_{\rm LiBr}$ obtained from the measured $\Gamma_{\rm sPSO_2-220}$ and $\Gamma_{\rm C_{14}TAB}$. Below the BSMP the ratio is below 1, thus uncompensated S charges are present. By increasing the $c_{\rm sPSO_2-220}$, the ratio reaches a value of 1 around the BSMP and more or less maintains this value.

Full Q_z analysis

In order to better understand the influences of the $sPSO_2$ -220 and LiBr concentration on the interfacial structure, NR over the full Q_z -range were measured in three different contrasts. Both the solvent (D₂O or ACMW) and the kind of C₁₄TAB (deuterated or protonated C₁₄TAB) were varied in order to highlight particular components and



FIGURE 4.4: Ratio of the adsorbed sPSO₂-220 monomers to adsorbed C₁₄TAB molecules as function of $c_{\rm sPSO_2-220}$ for different LiBr concentration $(c_{\rm LiBr} = 0 - 10^{-2} \,\mathrm{M})$. The dotted vertical line marks the BSMP. The solid horizontal line marks a ratio of 1.

one low Q_z contrast is included. By simultaneously fitting one structural model to these data, distinct volume fraction profiles are obtain. Thus, the interfacial structure of the P / S mixtures can be resolved (details see chapter 3.2.2). Three bulk sPSO₂-220 concentrations were measured: *below* the BSMP ($c_{sPSO_2-220} = 10^{-5} \text{ monoM}$), *around* the BSMP ($c_{sPSO_2-220} = 8 \times 10^{-5} \text{ monoM}$), and *above* the BSMP ($c_{sPSO_2-220} = 3 \times 10^{-3} \text{ monoM}$). The three samples are marked in Fig. 4.3.

(a) below the BSMP The upper panel of Fig. 4.5a shows the reflectivity data measured for the 4 contrasts in separate experiments without LiBr. The reflectivity data exhibit no distinct features like a Kiessig fringe indicating a thin adsorption layer. The lines correspond to the modeled reflectivity resulting from optimized parameters in the common structural model for all contrasts. Fig. 4.5b shows the corresponding volume fraction profiles as solid lines. The C₁₄TAB chains (solid orange line) are located between air (solid gray line) and water (solid light blue line) at $z_c \sim 4$ Å (z_c : center position of the layer, z = 0Å marks the top of the first layer in absence of roughness). The chain layer is loosely packed with a maximal volume fraction of 0.5 at its center and has a thickness of ~ 7 Å (FWHM). The head groups (solid yellow line) are located below the chains ($z_c \sim 8$ Å) as defined by the fitting procedure (see chapter 3.2.2). Their layer partly overlaps with the chains due to capillary wave roughness giving an expected distribution of the C₁₄TAB molecules at the air / liquid interface. The sPSO₂-220 layer (solid turquoise line) is located below the head groups



FIGURE 4.5: Below the BSMP: a) reflectivity data of sPSO₂-220 / C_{14} TAB mixtures with no LiBr added (top, data points taken from Ref. 85 with permission from the Royal Society of Chemistry) and with 10^{-2} M LiBr (down). Solid lines correspond to the model fits. b) Volume fraction profiles of sPSO₂-220 / C_{14} TAB mixtures with no LiBr added (solid lines) and with 10^{-2} M LiBr (dashed lines). For the color code see sketch on the top.

 $(z_{\rm c} \sim 12$ Å). The layer of sPSO₂-220 and of the head groups highly overlap indicating a strong interaction between the two components. Contrary to the chain layer, both sPSO₂-220 and head group layer are hydrated indicated by the increasing volume fraction of water below the chain layer (z > 10 Å). The good agreement of the experimental and simulated reflectivity data verify this common structural model (average χ^2 value of 3.5). The volume fraction profile agrees with the structural model used in a previous work.⁸⁵ The lower panel of Fig. 4.5a shows the reflectivity data of the 4 contrasts with 10^{-2} M LiBr added. As without LiBr, the data exhibit no minima indicating a thin adsorption layer. The common structural model of a compact monolayer fits all 4 contrasts simultaneously (solid lines in the lower panel of Fig. 4.5a). Fig. 4.5b shows the corresponding volume fraction profile as dashed lines. Fig. A.7 shows the data and resulting volume fraction profiles for 10^{-4} M and 10^{-3} M, which are as well described with the compact monolayer structural model. The addition of LiBr slightly and systematically modifies the maximal volume fraction of the chains (between 0.5 and 0.6) and the head groups (between 0.2 and 0.3).

(b) around the BSMP Fig. 4.6a shows the reflectivity data without LiBr added around the BSMP. The data of d-C₁₄TAB / ACMW (dark green) and of d-C₁₄TAB / D₂O (purple) both exhibit a distinct minimum (Kiessig fringe) around $Q_z = 0.08 \text{ Å}^{-1}$ and $Q_z = 0.16 \text{ Å}^{-1}$, respectively. The Kiessig fringe in the ACMW contrast suggests

an extended structure with a length scale of around 80 Å (Bragg's law).⁸⁵ This Kiessig fringe is characteristic for an interfacial structure of a monolayer and a bilayer of surfactant even if the bilayer does not completely cover the whole surface.¹⁴⁰ For such an incomplete bilayer the position of the Kiessig fringe not only depends on the dimension of the bilayer but also on its degree of coverage.¹⁴⁰ Fitting all 4 contrasts equally well with one structural model was not possible, which is further discussed below. The contrasts were paired according to the used water (ACMW or D_2O). Fig. 4.6a shows the obtained model structure fits: upper panel for ACMW and lower panel for D_2O . The structural model found for the ACMW contrasts is the following: beneath a monolayer of $C_{14}TAB$ (Fig. 4.6b: orange lines for the chain and yellow lines for the head groups) lies a layer of $sPSO_2-220$ (turquoise line) and underneath the sPSO₂-220 layer an extended layer of material forms. The data do not resolve this extended layer in detail, although the Kiessig fringes in the reflectivity data can only be described by the presence of additional S underneath the primary S monolayer and bound P, which indeed accounts for the additional S present at the interface implied by the surface excess as shown in Fig. 4.2. Therefore, the volume fraction profiles of chain, head groups, and sPSO₂-220 were allowed to completely overlap. The maximal volume fraction of this third layer is around 0.2 for both chains (solid orange line) and $sPSO_2-220$ (solid turquoise line) indicating that this layer is neither dense nor fully covered and rather swollen with water. Even though this model fits the full Q_z -range data (d-C₁₄TAB in ACMW) quite well, a slightly higher amount of adsorbed material needs to be taken into account than suggested by the low Q_z analysis ($\Gamma_{C_{14}TAB}$: $5.57 \times 10^{-6} \text{ mol m}^{-2} \text{ vs. } 5.09 \times 10^{-6} \text{ mol m}^{-2} \text{ and}$ $\Gamma_{\rm sPSO_2-220}$: 4.11 × 10⁻⁶ mol m⁻² vs. 4.05 × 10⁻⁶ mol m⁻²), which indicates a reduction in the accuracy of the full Q_z analysis regarding the surface excess.

The samples in D₂O show less distinct features that necessitated a bimodal distribution of S in the volume fraction profile (Fig. 4.6b, lower panel) suggesting a less dense extended structure. Hence, for fitting these data, we attempted to keep the first layer of C₁₄TAB and sPSO₂-220 the same and just adjusted the extended layer. As expected the extended layer contains less C₁₄TAB according to the obtained fit results (overall low volume fraction of chains and head groups, dashed orange and yellow line in Fig. 4.6b). Furthermore, the layers of the chains and of the head groups appear less distinct and more as a smeared out part of the first S layer. Maybe due to this smeared out S layer the position of the first P layer shifts towards the bulk compared to the ACMW samples. $\Gamma_{C_{14}TAB}$ is lower than suggested by the low Q_z analysis ($\Gamma_{C_{14}TAB}$: 4.46 × 10⁻⁶ mol m⁻² vs. 5.09 × 10⁻⁶ mol m⁻²).



FIGURE 4.6: Around the BSMP, no salt added: a) reflectivity data of sPSO₂-220 / C_{14} TAB mixtures. Data points are taken from Ref. 85 with permission from the Royal Society of Chemistry. Fits are optimized for ACMW contrasts (top) and the D₂O contrasts (down), respectively. Solid lines correspond to the model fits. b) Volume fraction profiles of sPSO₂-220 / C_{14} TAB mixtures, solid lines correspond to the fits for the ACMW contrasts and dashed lines to the fit of the D₂O contrasts. For the color code see sketch on the top.

For sake of completeness, the contrasts were also paired *via* the used kinds of $C_{14}TAB$ (d- $C_{14}TAB$ and protonated $C_{14}TAB$ (h- $C_{14}TAB$)) to match the approach used when this phenomenon was found in previous work.⁸⁵ The obtained structure models (Fig. A.8) are similar to the ones above. Pairing the kinds of water instead of the kinds of $C_{14}TAB$ reduced the average χ^2 values for the simulated fits by a factor of 1.3 and 1.4, respectively.

Using the same approach (fitting the contrasts with the same kind of water individually) the data of the samples containing 10^{-4} M LiBr were analyzed (Fig. A.9). The volume fraction profiles resemble the ones without added salt. Pairing the contrasts with the same kind of C₁₄TAB resulted in similar volume fraction profiles, but neither improved or worsened the χ^2 values (Fig. A.10). Besides small differences of the sPSO₂-220 distribution in the extend layer, the interfacial structures are the same for both salt concentrations ($c_{\text{LiBr}} = 0$ and 10^{-4} M). The reflectivity data of the two high salt concentrations ($c_{\text{LiBr}} = 10^{-3}$ M and 10^{-2} M) do not show any pronounced features that would suggest an extended structure (Fig. A.11). The data for both LiBr concentrations could be fitted with a common structural model. For 10^{-3} M LiBr a swollen sPSO₂-220 layer (FWHM ~ 18 Å) is formed under the S (swollen monolayer structure). For 10^{-2} M LiBr the volume fraction profiles resemble those *below* the



FIGURE 4.7: Above the BSMP: a) reflectivity data of $sPSO_2-220 / C_{14}TAB$ mixtures with 0 M LiBr (top, data points taken from Ref. 85 with permission from the Royal Society of Chemistry) and 10^{-2} M LiBr (down). Solid lines correspond to the model fits. b) Volume fraction profiles of $sPSO_2-220 / C_{14}TAB$ mixtures with 0 M LiBr (solid lines) and 10^{-2} M LiBr (dashed lines). For the color code see sketch on the top.

BSMP (compact monolayer structure), hence it can be concluded that the addition of salt in this case extinguishes the extended structure.

(c) above the BSMP The reflectivity data of the samples above the BSMP (Fig. 4.7a for 0 M and 10^{-2} M LiBr and Fig. A.13a for 10^{-4} and 10^{-3} M LiBr added) exhibit no distinctive Kiessig fringes as the data around the BSMP. For all salt concentrations the compact monolayer structural model simultaneously fits the 4 contrasts (solid lines in Fig. 4.7a and Fig. A.13a). The addition of salt only slightly influences the interfacial structures in terms of maximal volume fraction of sPSO₂-220 (turquoise lines in Fig. 4.7b). For the data without added salt a structural model containing an extended highly swollen sPSO₂-220 layer was found within a layer-based analysis used before.⁸⁵ For sake of comparison, a similar volume fraction profile was modeled (Fig. A.12). The average χ^2 value was reduced by a factor of 3 when using the compact monolayer ($\chi^2 = 4.8$) instead of a swollen monolayer ($\chi^2 = 15.9$). However, a very swollen and extended sPSO₂-220 layer only slightly changes the SLD profile. Thus, such details are not fully resolved by the data.

To summarize, the interfacial structures of $sPSO_2-220 / C_{14}TAB$ mixtures change with $sPSO_2-220$ and LiBr concentration: at intermediate $sPSO_2-220$ concentration (*around* the BSMP) extended structures form at the interface, and LiBr ($c_{\text{LiBr}} \ge 10^{-3}$ M) suppresses the formation of these extended structures.



FIGURE 4.8: Surface tension of PSS / C_{14} TAB mixtures as a function of c_{PSS} for different salt concentrations ($c_{NaBr} = 0 - 10^{-2}$ M). The dotted vertical line marks the BSMP. The dashed horizontal lines correspond to the surface tension of pure C_{14} TAB solutions ($c_{C_{14}TAB} = 10^{-4}$ M) at the different NaBr concentrations.

4.3.2 $PSS / C_{14}TAB$ mixtures

Tensiometry

Fig. 4.8 shows the surface tension of PSS / C_{14} TAB mixtures as a function of c_{PSS} for different NaBr concentrations added. Addition of low concentrations of PSS to the C_{14} TAB solution (*below* the BSMP mark as dotted vertical line) reduces the surface tension compared with that of the respective pure C_{14} TAB solution (dashed horizontal lines). The BSMP is a threshold concentration above which the surface tension sharply jumps to values close to those of the pure C_{14} TAB solution. Thus, it can be inferred that *above* the BSMP the interfacial structure may have changed. Compared to the solution without salt added, the lowest concentration of NaBr ($c_{NaBr} = 10^{-4}$ M) has no effect on the progression of the surface tension. Higher concentrations ($c_{NaBr} \ge 10^{-3}$ M) lead to a lowering of the surface tension (*below* and *above* the BSMP) and to a more gradual jump.

Low Q_z analysis

Fig. 4.9 shows the results of the low Q_z analysis of the NR data (for the reflectivity data see Fig. A.14) as function of c_{PSS} . Fig. 4.9a depicts the results without added



FIGURE 4.9: Surface excess of PSS (blue triangles) and $C_{14}TAB$ (red diamonds) and surface tension (taken from Fig. 4.8) for PSS / $C_{14}TAB$ mixtures as a function of c_{PSS} : a) without added salt and b) with 10^{-2} M NaBr. The solid horizontal lines correspond to the surface excess for the pure $C_{14}TAB$ solutions, and the dashed horizontal lines correspond to the surface tension of pure $C_{14}TAB$ solution ($c_{C_{14}TAB} = 10^{-4}$ M), each at the respective NaBr concentrations. The vertical dotted line marks the BSMP. For the sake of clarity the surface excess of PSS is expressed in mol/m² in terms of monomer units. Note, that the almost vanishing $\Gamma_{C_{14}TAB}$ at $c_{PSS} = 3 \times 10^{-4}$ monoM is not interpreted as it can not be excluded that it is an artifact. Samples marked by an arrow are used for the full Q_z analysis.

salt and Fig. 4.9b the results with 10^{-2} M NaBr added. The solid horizontal lines in both panels correspond to $\Gamma_{C_{14}TAB}$ of a pure $C_{14}TAB$ solution ($c_{C_{14}TAB} = 10^{-4}$ M). The surface tension γ is plotted for comparison. PSS and $C_{14}TAB$ adsorb at the interface *below* the BSMP and are sharply depleted from the interface *above* the BSMP. The salt added increases $\Gamma_{C_{14}TAB}$ and Γ_{PSS} . Both, PSS and $C_{14}TAB$, deplete more gradual from the interface when changing c_{PSS} than without added NaBr. For both salt concentrations, the depletion correlates with the jump in surface tension and slightly more PSS than $C_{14}TAB$ adsorb at the interface *above* the BSMP indicating loops of PSS at the interface.

Full Q_z analysis

The dependence of surface tension (Fig. 4.8) and surface excess (Fig. 4.9) suggest different conditions for the molecular ordering at the interface *below* and *above* the BSMP. Thus, NR of these two regimes – *below* and *above* the BSMP – were measured over the full Q_z -range (samples are marked with an arrow in Fig. 4.9 and noted in Tab. A.1).

(a) *below* the BSMP Fig. 4.10a shows the reflectivity data measured for 4 contrasts below the BSMP. The reflectivity data without added salt (upper panel) exhibit no minima thus indicating a rather thin adsorption layer. Indeed the compact monolayer structural model describes the 4 data sets. Fig. 4.10b shows the corresponding volume fraction profiles (solid lines). The chain layer is dense with a maximal volume fraction of 0.9 at its center and has a thickness of ~ 7 Å (FWHM). The PSS layer (solid turquoise line) is ~ 11.6 Å thick - similar to the diameter of a PSS chain of ~ 12 Å¹⁴⁴. The lower panel of Fig. 4.10a shows the reflectivity data with 10^{-2} M NaBr added. The data sets for the two contrasts with D_2O as solvent each exhibit a distinct minimum at intermediate Q_z ($Q_z \approx 0.08 \text{ Å}^{-1}$ for d-C₁₄TAB / D₂O (purple) and $Q_z \approx$ 0.15 Å^{-1} for h-C₁₄TAB / D₂O (red)), indicating the formation of a thicker adsorption layer compared with the system in the absence of added NaBr. A common structural model simultaneously fitting the reflectivity data in all different contrasts was not found, implying slightly different structures in each contrast. However, each full Q_z data set could be fitted well with a monolayer structural model (solid lines in the lower panel of Fig. 4.10a correspond to the best fit for each contrast). They all consist of a monolayer of $C_{14}TAB$ and PSS (e.g. Fig. 4.10b, dashed lines for d- $C_{14}TAB$ /ACMW) where a swollen PSS layer results in the Kiessig fringe observed in the data. Only the model parameter for the PSS layer (position, thickness and adsorbed amount) differ between the contrasts (for details see Tab. A.2 and Fig. A.15). For the d- $C_{14}TAB$ / D_2O contrast, a compact PSS layer is found instead of a swollen PSS layer. To further study theses differences between the deuteration schemes, ellipsometry measurements were preformed (Tab. A.5). The results validate the different adsorbed amounts found by the full Q_z fits.

(b) *above* the BSMP Fig. 4.11a shows the reflectivity data measured for the samples *above* the BSMP. Without NaBr added (upper panel) the reflectivity data of the 4 different contrasts exhibit no pronounced features, and the two contrasts recorded in D₂O are practically indistinguishable, indicating only very little adsorption at the air / liquid interface. The compact monolayer structural model turns out to be well suited also *above* the BSMP. It simultaneously fits all 4 reflectivity data (solid lines). Fig. 4.11b shows the corresponding volume fraction profiles as solid lines. Indeed, the maximal volume fraction of each component are rather small (~0.3, <0.1, and ~0.2 for the chains, the head groups and PSS, respectively) compared to the situation *below* the BSMP (Fig. 4.10b). The layers of the chains, head groups and PSS are all close to the surface (up to $z \sim 10$ Å) corresponding to a highly compact



FIGURE 4.10: Below the BSMP: a) reflectivity data of PSS / C_{14} TAB mixtures with 0 M NaBr (top) and with 10^{-2} M NaBr (bottom). Solid lines correspond the model fits. For the data with 10^{-2} M NaBr, the solid lines correspond to the fit optimized for each full Q_z contrast individually. b) Volume fraction profiles of PSS / C_{14} TAB mixtures with 0 M NaBr (solid lines) and 10^{-2} M NaBr (dashed lines, optimized for the d- C_{14} TAB / ACMW contrast). For the color code see sketch on the top.

adsorption layer. The low adsorbed amounts obtained by this compact monolayer structural model are in line with the depletion of material *above* the BSMP (Fig. 4.9a).

The lower panel of Fig. 4.11a shows the reflectivity data for the 4 contrasts with 10^{-2} M NaBr. All 4 data sets could be fitted simultaneously with the compact monolayer structural model (solid lines in the lower panel of Fig. 4.11a, corresponding volume fraction profile in Fig. 4.11b, dashed lines). The layer of PSS and the head groups highly overlap. In line with the results of the low Q_z analysis, the adsorbed amount of PSS and C_{14} TAB are higher compared to the case without added salt (Tab. A.3).

For the sake of completeness it should be mentioned that for the PSS / C_{14} TAB mixtures no extended structures were found *around* the BSMP (Fig. A.16). To summarize, contrary to the sPSO₂-220 / C_{14} TAB mixtures all interfacial structures of the PSS / C_{14} TAB mixtures are best described by a monolayer of C_{14} TAB and an attached layer of PSS. Although the details differ, neither changes in the PSS concentration nor in the NaBr concentrations qualitatively modify the types of interfacial structures.



FIGURE 4.11: Above the BSMP: a) reflectivity data of PSS / C_{14} TAB mixtures with 0 M NaBr (top) and with 10^{-2} M NaBr (bottom). Solid lines correspond to the model fits. b) Volume fraction profiles of PSS / C_{14} TAB mixtures with 0 M NaBr (solid lines) and 10^{-2} M NaBr (dashed lines).

TABLE 4.1: Characteristic of sPSO₂-220 and PSS as well as their mixtures with C_{14} TAB.

	$sPSO_2-220$	\mathbf{PSS}
location of the benzene ring	backbone	side chain
flexibility	low	high
extended interfacial structures	yes	no

4.4 Discussion

In the following part, the interfacial structures and how they change with the P's stiffness and concentration are discussed. Table 4.1 summarizes the main characteristics of the studied sPSO₂-220 and PSS as well as of the interfacial structure of their respective mixtures with $C_{14}TAB$. Extended interfacial structures only form in presence of sPSO₂-220 *around* the BSMP with $C_{14}TAB$. By comparing mixtures containing one or the other type of polyelectrolyte, the reasons for the formation of extended structures will be identified.

4.4.1 $sPSO_2-220 / C_{14}TAB$ mixtures

The most striking characteristic of the $sPSO_2-220 / C_{14}TAB$ mixtures is the selfassembly into extended structures *around* the BSMP. Fig. 4.12 illustrates the c_{P} dependency of these extended structures. In the following we want to elucidate the reasons of this behavior. We consider the P/S ratio at the interface. Below the BSMP, the P/S ratio is below 1 (Fig. 4.4), meaning uncompensated S charges are present. Probably, the mixtures contain too little $sPSO_2$ -220 to compensate the S charges. By increasing the c_{sPSO_2-220} , the ratio reaches a value of 1 around the BSMP. This value depicts the most favorable ratio because all counterions are released and the highest gain in entropy is accomplished. However, considering only the first layer of S and P of the extended structure, one obtains a P/S ratio around 0.4. Therefore, only by adsorbing the additional P and S, the system obtains the favorable ratio of 1. sPSO₂-220 is a rather stiff P with an intrinsic persistence length $l_{\rm P}$ of 20 nm.⁸³ Even with a low P/S ratio, not every charge of the P might be compensated by S considering geometric constraints of stiff P such as the distance between charges of the P compared to the distance of S head groups and the required orientation of all P sulfate groups towards the S monolayer. Potential uncompensated charges at the lower part of the P layer drag additional S and P to the interface allowing the system to reach a P/S ratio of 1. The stiffness and flat adsorption⁸³ of $sPSO_2$ -220 facilitate the self-assembly in extended structures and even require these extended structures.

The extended structures *around* the BSMP are probably formed by distinct micelles or hemimicelles which do not cover the whole interface. Isotopic discrepancies were found for these structures. These discrepancies can be resolved by taking into account either the used kind of water or the used kind of C_{14} TAB. The first one implies hydrogen bonds as additional driving force for the extended structures as the strength of hydrogen bonds differ for protonated and deuterated substances.^{145,146} The second one suggests an impact of the S hydrophobicity on the extended structures as the hydrophobicity depends on the isotope.^{147,148} As the data do not allow to definitely exclude one of the mentioned possibilities, we cannot claim which isotopic effect is dominant in these mixture. Therefore, a more detailed discussion on the isotopic effect is shifted to section A.4. However, we can conclude: isotopic effects affect the amount of extended structures formed.

Increasing the ionic strength leads to a more flexible $sPSO_2-220$ (reduced l_P). Now, the need to self-assemble in extended structures is lower due to less sterical hindrance for charge compensation. And indeed, increasing both c_P and c_{salt} suppresses the extended structures while maintaining a P/S ratio of 1 at the interface (Fig. 4.4). Coiling of $sPSO_2-220$ explains the swollen $sPSO_2-220$ layer for 10^{-3} M LiBr *around* the BSMP.



FIGURE 4.12: Sketch of the interfacial structures of $sPSO_2-220 / C_{14}TAB$ mixtures. The change with increasing ionic strength I via c_P and c_{salt} concentration is illustrated.

4.4.2 PSS / C_{14} TAB mixtures

Contrary to sPSO₂-220 / C₁₄TAB mixtures, PSS / C₁₄TAB mixtures do not form extended structures at the interface (Fig. 4.13). Instead, only monolayers were observed for all c_{PSS} and c_{NaBr} and a depletion of material *around* the BSMP. As discussed above, the main driving force for the extended structures is to accomplish a P/S ratio of 1 at the interface, *i.e.* charge compensation. For the PSS/ C_{14} TAB mixtures the ratio at the interface lies around 1 irrespective of c_{PSS} or c_{NaBr} (Fig. A.17). Due to a higher flexibility of the PSS chain, charge compensation is facilitated and there is no need for an extended structure. Looking at the molecular structures of PSS and $sPSO_2-220$ (Fig. 3.2), one notices that the sulfate groups are located at the end of the side chains for PSS, but directly at the backbone for $sPSO_2$ -220. The charged groups of PSS stick more out and have a higher degree of rotational freedom. Its high flexibility $(l_{\rm P} \sim 1 \, {\rm nm}^{107})$ allows PSS to rearrange at the surface in order to compensate the S charges even *below* the BSMP. Considering the amount of PSS and S, a depletion (loss of surface activity) is found *around* the BSMP (Fig. 4.9). The surface excess of PSS (~ $2.6 \times 10^{-6} \,\mathrm{mol}\,\mathrm{m}^{-2}$ and ~ $0.5 \times 10^{-6} \,\mathrm{mol}\,\mathrm{m}^{-2}$) corresponds to an average area per monomer of $\sim 63 \text{ Å}^2$ and $\sim 291 \text{ Å}^2$ below and above the BSMP. respectively. Adsorbing PSS onto dioctadecyldimethyl ammoinum bromide (DODA) monolayers resulted in similar areas per monomer.¹⁴⁹ The change in area per monomer is attributed to a change from a condensed lipid phase to a fluid lipid phase upon changing the lateral surface pressure.¹⁴⁹

57

The abrupt loss in surface activity for PSS / C_nTAB mixtures was explained in terms of a changed hydrophobicity of the P / S complex due to hydrophobic interaction of S chains and hydrophobic parts of PSS (backbone and benzene ring).^{138,150,151} This interaction leads to more hydrophilic complexes, which represent an alternative possibility of self-assembled structures. In order to rearrange and allow a new self-assembly, a certain exchange dynamic of P and S is necessary, which is comparable to polyelectrolyte multilayers where salt is needed to ensure the mobility of P^{152} . At low ionic strengths, the exchange dynamics is suppressed. The interfacial self-assembly in this case (low ionic strength) might be strongly influenced by the hydrophobic / hydrophilic balance of the formed bulk complexes. Increasing $c_{\rm P}$ at fixed $c_{\rm S}$ reduces the S available for each P chain and the surface activity of the complex. Although we cannot comment on bulk complexes based on the data, they might explain the loss of surface activity around the BSMP. Keeping in mind the increased ionic strength when increasing $c_{\rm P}$ (higher amount of counterions), P bind less tightly to the S monolayer. Both effects (increased ionic strength and hydrophobicity of bulk complexes) affect the interfacial self-assembled structure.

Looking at the influence of salt, one notices that the depletion is less pronounced. Salt screens the charges and thus promotes the S and P adsorption at the surface. Furthermore, potential repulsive image charges, which weaken P adsorption^{153,154}, are screened as well. *Below* the BSMP, a swollen monolayer is found. We have an excess of S compared to P monomers in the sample. Due to the added salt, the P will be more coiled. The high Γ_{PSS} results in a low surface area for each coiled PSS chain, thus there is a rather swollen PSS layer *below* the BSMP. The observed isotopic discrepancies (by NR and ellipsometry) may be a hint for hydrogen bonds, *e.g.* between the oxygen atoms of sulfate groups and the water, as additional driving force for the formation of the swollen P layer. The strengths of hydrogen bonds are slightly isotopic-sensitive in strength.¹⁴⁶ Above the BSMP, less PSS is adsorbed (reduced Γ_{PSS} , Fig. 4.9), thus each PSS chain can occupy a higher surface area. The coiled PSS chains decoil at the interface and form the compact monolayer.

4.4.3 Comparison of polyelectrolytes

Comparing the two Ps and the interfacial structure of their mixtures with $C_{14}TAB$ allows us to deduce conditions for an interfacial self-assembly of P / S mixtures in extended structures. First, there is a link between uncompensated charges of P, thus



FIGURE 4.13: Sketch of the interfacial structures of PSS / C_{14} TAB mixtures. The change with increasing ionic strength *I via* $c_{\rm P}$ and $c_{\rm salt}$ concentration is illustrated. (The structure *around* the BSMP with salt added is shown faded because the fitting results are not so unambiguous as for the other samples. However no hints for an extended structure are found, Fig. A.16)

the potential to bind a second S layer, and the formation of extended structures. The tendency for forming extended structures is to accomplish an interfacial P / S ratio around 1. This driving force will be reinforced at low ionic strength due to the higher gain of entropy compared with high ionic strength. Second, a rather flat adsorption of the P promotes the extended structure as it facilitates the self-assembly in a layered geometry and provides the uncompensated charges. Additional driving forces may play a role as pointed out by the isotopic effect. Any potential hydrophobic interaction between P and S should be excluded in order to obtain extended structures. Keeping these requirements in mind, it becomes clear why the addition of salt suppresses these structures: Via increasing the ionic strength, the driving force for the binding of S and P will be decreased. The P will be more coiled, thus the conformational ability to drag a second S layer will be decreased. By influencing the ability of P to bind with an interfacial ratio of 1 (low flexibility / low ionic strength), we can control the formation of extended structures at low S concentration (solution of complexes). In this context, experiments with an even less flexible and natural P (e.q. DNA) might help to further confirm these findings. In-depth studies of the isotopic effects and information about the lateral distribution of the extended structures would be helpful to entirely understand these structures.
4.5 Conclusions

The surface of two aqueous P / S mixtures were studied: $sPSO_2-220 / C_{14}TAB$ and $PSS / C_{14}TAB$ in the absence and presence of salt by tensiometry and neutron reflectometry. A constant low S concentration (well below the cmc) is used to ensure the absence of large bulk aggregates. $sPSO_2-220 / C_{14}TAB$ mixtures form extended structures *around* the BSMP, which are suppressed with increased ionic strength. Contrary, $PSS / C_{14}TAB$ mixtures form only monolayers. By comparing the two mixtures, we obtained insights into the formation of the extended structures: the main driving force is to compensate all interfacial charges (P/S ratio ~ 1). Increasing the flexibility of the P (via increasing the ionic strength or using the more flexible PSS) enables the P to compensate all S charges in a monolayer structure. Hence, the formation of these extended structures is suppressed. Considering that many applications of P/S mixtures are based on adsorption onto fluid interfaces, these fundamental findings on interfacial extended structures may help to improve applications. The effect of chain stiffness on interfacial structures of polymer / amphilile complexes is of high relevance for natural polymers like proteins, polysaccharides and DNA. Usually natural polymers are stiffer than simple synthetic ones and show a large variety in bulk and interfacial structures.^{155,156}

In the next chapter, these findings on the structures formed at a single air / liquid interface will be used to obtain insights on the foam film properties of $sPSO_2-220 / C_{14}TAB$ mixtures.

Chapter 5

Effect of salt on foam films of $sPSO_2-220 / C_{14}TAB$ mixtures

Similar content is in "When bulk matters: Disentanglement of the role of polyelectrolyte/surfactant complexes at surfaces and in bulk of foam films" L. Braun, R. v. Klitzing, submitted to *Langmuir*



5.1 Abstract

This chapter addresses the impact of added LiBr on foam films of sPSO₂-220 / C_{14} TAB mixtures. Using a TFPB allow studies of surface forces. Regarding surface forces, we attempt to disentangle the effect of the foam film surfaces and the foam film bulk. Adding a small amount of salt (up to 10^{-3} M) decreases the foam film stability due to a reduced electrostatic repulsion. In contrast, a high amount of salt (10^{-2} M) unexpectedly increases the foam film stability. Disjoining pressure isotherms reveal that the reason of the increased stability is an additional steric stabilization, which is attributed to sPSO₂-220 / C_{14} TAB complexes in the film bulk. These bulk complexes also contribute to the measured *apparent* surface potential between the two air / liquid

interfaces. For the first time, the formation of NBFs for mixtures of anionic Ps and cationic Ss is found.

5.2 Introduction

P/S mixtures are able to stabilize foam films (see chapter 2.2.3). They exhibit a non-monotonous foam film stability in dependence of $c_P^{82--84,138}$: around the BSMP they lack of stability thus no stable foam film can be formed. For understanding the foam film stability different parameter were considered: surface tension, surface elasticity or surface excess of P and S, but did not fully succeed. Furthermore, the effect of salt on foam films stabilized by P/S mixtures is barely studied. An increased stability with salt is commonly attributed to denser packed surface layer.⁹⁰ However, chapter 4 showed that there is no simple increase of the surface excess of P/S mixtures with added salt. For sPSO₂-220/C₁₄TAB mixtures the surface excess of both, S and P, either stays constant or even decreases with added LiBr, depending on the sPSO₂-220 concentration.

Thus, there is a necessity to systematically study the effect of salt on foam films of P/S mixtures. This chapter focuses on $sPSO_2-220/C_{14}TAB$ mixtures, which form CBF in absence of added salt.⁸³ The question arises how salt (LiBr) affect the thickness and stability of foam films. In chapter 2.1.2 the different forces appearing in foam films are presented. Another question addresses the disentanglement of film surfaces' and film bulks' contribution to the overall interaction across foam films. To answer these questions we take into account not only the knowledge about one air / liquid interface obtained in chapter 4 but also consider contributions of bulk P/S complexes.

5.3 Results and discussion

5.3.1 Foam film stability and type of foam film



FIGURE 5.1: Foam film stability Π_{max} of sPSO₂-220 / C₁₄TAB mixtures in dependence of c_{sPSO_2-220} with different LiBr concentrations ($c_{\text{LiBr}} = 0 - 10^{-2}$ M). Solid horizontal lines correspond to the foam film stability of the pure C₁₄TAB solutions ($c_{\text{C14}TAB} = 10^{-4}$ M) at the respective LiBr concentration. The lines for $c_{\text{LiBr}} = 10^{-3}$ M and 10^{-2} M overlap around 160 Pa. The dotted vertical line marks the BSMP. Data without LiBr are taken from Ref. 83 with permission from the Royal Society of Chemistry. Shaded areas represent the regimes of CBF -- NBF transitions before the foam films rupture. The smaller NBF regime is valid for $c_{\text{LiBr}} = 10^{-4}$ M and the broader one for $c_{\text{LiBr}} = 10^{-3}$ and 10^{-2} M.

Fig. 5.1 shows the foam film stability Π_{max} of sPSO₂-220 / C₁₄TAB mixtures in dependence of c_{sPSO₂-220} for different LiBr concentrations ($c_{\text{LiBr}} = 0 - 10^{-2}$ M). The solid horizontal lines correspond to the foam film stability of the pure C₁₄TAB solutions ($c_{\text{C}_{14}\text{TAB}} = 10^{-4}$ M) at the respective LiBr concentration. The dotted vertical line marks the BSMP. *Below* the BSMP, the foam films are less stable than the ones of the pure C₁₄TAB solutions. LiBr barely influences the foam film stability. At 6.5×10^{-5} monoM sPSO₂-220 no foam films with a lifetime longer than a few seconds can be formed -- irrespective of the added LiBr.

For this c_{sPSO_2-220} regime (*below* and *around* the BSMP, shaded areas in Fig. 5.1) the appearance of the foam films changed due to the addition of LiBr: the CBF transforms into a NBF just before rupturing (Fig. 5.2). The transition appears *via* a "fingerlike"

pattern as seen for foam films of C_{14} TAB mixed with sodium dodecanoate.⁵⁴ The NBF grows from a single black dot until either the whole foam film is covered or ruptures (Fig. A.18 - Fig. A.20). The NBF itself is thinner than the surrounding CBF and the excess liquid (including sPSO₂-220 / C_{14} TAB complexes) accumulates in the rim around the NBF. During the growth of the NBF, the rim splits into single droplets. The colorful appearance¹⁵⁷ of the rim indicates that its thickness is significantly larger than the surrounding NBF, CBF and the diameter of the rim itself. Due to its high aspect ratio the rim can be considered as cylindrical surface.⁵⁴ Such pearling and break-up phenomenons of cylindrical surfaces are described by Rayleigh-Plateau instabilities.¹⁵⁸ The mechanism originally used for liquid jets¹⁵⁹ is not restricted to them, but also reported for tubular vesicles¹⁵⁸ and the formation of white spots around thinner foam film domains^{28,160}. Differences in the aspect ratios of the rim¹⁶¹ or expansion dynamics²⁸ may be responsible for the different appearance of the Rayleigh-Plateau instabilities in foam films (colorful droplets inside the NBF as in Fig 5.2 vs. white spots around the NBF¹⁶²).

The formed NBFs are rather unstable and rupture within a few seconds. For stable NBFs close-packed adsorption layers are necessary.¹⁶³ Around the BSMP the surface excess of C_{14} TAB exceeds the one of the pure C_{14} TAB solutions (Fig. 4.4). However, no information about the lateral distribution of P and S was obtained by the NR measurements. Presumably the adsorbed layer is too inhomogeneous to result in stable NBFs. The existence of a CBF -- NBF transition hints to a low repulsion between the two facing film interfaces. To our knowledge, these are the first NBFs observed for mixtures of anionic P and cationic S. So far, NBFs were only observed for P/S mixtures containing positively charged P and non-ionic S.^{86,151} This point will be discussed later.

Above the BSMP, the foam film stability significantly increases with increasing sPSO₂-220 concentration (Fig. 5.1). All foam films are CBFs, and no NBFs were observed. LiBr destabilizes the foam films (*e.g.* $c_{\rm sPSO_2-220} = 2 \times 10^{-4}$ monoM in Fig. 5.1) up to a concentration of $c_{\rm LiBr} = 10^{-3}$ M, but with $c_{\rm LiBr} = 10^{-2}$ M added, the foam films become more stable again.

The first destabilization up to $c_{\text{LiBr}} = 10^{-3} \text{ M}$ may be due to screening of the electrostatic repulsion between the two film interfaces. The increased foam film stability with higher c_{LiBr} , however, is not in line with this mechanism.

In the following, we try to elucidate the underlining mechanism for this unexpected stabilization at a high LiBr concentration. First, the individual disjoining pressure



FIGURE 5.2: Images of foam films of sPSO₂-220 / C₁₄TAB mixtures $(c_{\rm sPSO_2-220} = 10^{-4} \text{ monoM}, c_{\rm C_{14}TAB} = 10^{-4} \text{ M})$ with different LiBr concentrations: a) $c_{\rm LiBr} = 10^{-4} \text{ M}$ and b) $c_{\rm LiBr} = 10^{-3} \text{ M}$. Images are taken during the formations of NBFs seconds before the foam films ruptured. Images of the whole transition processes are shown in Fig. A.18 - Fig. A.20.

isotherms will be analyzed for a selective c_{sPSO_2-220} as well as the influence of LiBr on them. Afterwards, the results of the PB calculations as well as bulk complexes will be included into the considerations.

5.3.2 Disjoining pressure isotherms

As the foam film *below* the BSMP are rather unstable, only single measurements without any calculation or analysis are shown in Fig. A.21. The disjoining pressure isotherms for all $sPSO_2-220 / C_{14}TAB$ mixtures (including PB calculations) around and above the BSMP can be found in Fig. A.22 - Fig. A.24. Here, the disjoining pressure isotherms for $c_{\rm sPSO_2-220} = 6 \times 10^{-4} \,\rm{monoM}$ (above the BSMP) are discussed exemplarily. Fig. 5.3 shows the disjoining pressure isotherms of $sPSO_2-220 / C_{14}TAB$ mixtures ($c_{\text{sPSO}_2-220} = 6 \times 10^{-4} \text{ monoM}, c_{\text{C}_{14}\text{TAB}} = 10^{-4} \text{ M}$) with different LiBr concentrations ($c_{\text{LiBr}} = 10^{-4} - 10^{-2} \text{ M}$). The main findings are the same for all studied mixtures. Compared to the data without added LiBr⁸³, 10⁻⁴ M LiBr barely influences the disjoining pressure isotherms and only reduces Π_{max} (Fig. A.23). At the lowest LiBr concentration studied ($c_{\text{LiBr}} = 10^{-4} \text{ M}$, (a) in Fig. 5.3), the foam film thins with increasing disjoining pressure. Adding more LiBr results in thinner foam films; the two air / liquid interfaces get closer to each other before the disjoining pressure becomes operative. The PB calculations (solid lines in Fig. 5.3) show decreasing potentials Ψ with increasing c_{LiBr} . All of these findings are in line with a reduced electrostatic repulsion due to the addition of LiBr. From the slopes of the disjoining pressure isotherms the experimental Debye lengths κ_{exp}^{-1} were extracted. Tab. 5.1 compares



FIGURE 5.3: Disjoining pressure isotherms of $sPSO_2-220 / C_{14}TAB$ mixtures $(c_{sPSO_2-220} = 6 \times 10^{-4} \text{ monoM}, c_{C_{14}TAB} = 10^{-4} \text{ M})$ with different LiBr concentrations: a) $c_{\text{LiBr}} = 10^{-4} \text{ M}$, b) $c_{\text{LiBr}} = 10^{-3} \text{ M}$ and c) $c_{\text{LiBr}} = 10^{-2} \text{ M}$. Solid lines correspond to PB calculations at constant potential Ψ . Later in the text Ψ will be called Ψ_{app} (apparent surface potential).

TABLE 5.1: Experimental Debye lengths κ_{exp}^{-1} extracted from the disjoining pressure isotherms of sPSO₂-220 / C₁₄TAB mixtures $(c_{sPSO_2-220} = 6 \times 10^{-4} \text{ monoM}, c_{C_{14}TAB} = 10^{-4} \text{ M})$ and calculated κ_{calc}^{-1} (complete dissociation of sPSO₂-220 and sPSO₂-220 / C₁₄TAB complex formation in a 1:1 ratio). The obtained surface potentials Ψ from the PB calculations are shown as well. Later in the text Ψ will be called Ψ_{app} (apparent surface potential).

$c_{\rm LiBr}$ / M	$\kappa_{\rm exp}^{-1}$ / nm	$\kappa_{\rm calc}^{-1}$ / nm	$\Psi (= \Psi_{\rm app}) \ / \ {\rm mV}$
10-4	19.4	14.4	100
10^{-3}	9.1	8.3	75
10^{-2}	3.4	3.0	45

 $\kappa_{\rm exp}^{-1}$ with $\kappa_{\rm calc}^{-1}$, which is the calculated Debye length for the samples assuming 1:1 binding between sPSO₂-220 and C₁₄TAB and complete dissociation of the excess component (P⁻ or S⁺). If $\kappa_{\rm exp}^{-1}$ is higher then $\kappa_{\rm calc}^{-1}$, less electrolytes than expected are in the foam film, thus no full dissociation of sPSO₂-220 occurs. In contrast, if $\kappa_{\rm exp}^{-1}$ is lower then $\kappa_{\rm calc}^{-1}$, more electrolytes than expected are in the foam film, thus no 1:1 binding occurs. For all $c_{\rm LiBr} \kappa_{\rm exp}^{-1}$ is higher than $\kappa_{\rm calc}^{-1}$, meaning that sPSO₂-220 is not fully dissociated. The same holds true for the other $c_{\rm sPSO_2-220}$ (Tab. A.6).

In the PB theory the obtained potential Ψ corresponds to a constant surface potential $\Psi_{\rm s}$ of two identical charged planes separated by a distance z.¹¹² This assumption



FIGURE 5.4: Electrophoretic mobility $|u_{\zeta}|$ of sPSO₂-220 / C₁₄TAB complexes in dependence of $c_{\rm sPSO_2-220}$ for different LiBr concentrations: $c_{\rm LiBr} = 10^{-4}$ M (triangles), $c_{\rm LiBr} = 10^{-3}$ M (diamonds) and $c_{\rm LiBr} = 10^{-2}$ M (squares). The dotted vertical line marks the BSMP. The solid horizontal line denotes an electrophoretic mobility of zero. Open symbols correspond to the *apparent* surface potential $\Psi_{\rm app}$ obtained from PB calculations at the respective LiBr and sPSO₂-220 concentration.

describes the experimental disjoining pressure isotherm for most thicknesses and LiBr concentration. For pure S solutions the obtained Ψ values and the resulting surface charge density q_0 correlates with the adsorbed amount of surfactant^{43,51}. For the P/S mixtures the obtained surface potential is quite high although the interfacial P/S ratio is close to 1 (Fig. 4.4) indicating a low surface charge and low surface potential. With increasing LiBr concentration the P/S ratio increases slight from 1 to 1.1 (Fig. 4.4) while the obtained surface potential decreases by more than a factor of 2 (Tab. 5.1). Recently the application of the PB framework to P/S mixtures was questioned by Uhlig et al.⁸⁵ Furthermore, current DLVO calculation, like the one used here, assume an unrealistically thin adsorption layer, which is however a crucial parameter for calculating Π as reported by Peng et al.¹⁶⁴ Thus, it seems that the use of the PB eq. in the present case is not valid. The foam films do not fulfill the preconditions of the PB eq. However, an electrostatic repulsion between the foam films is measured and there must be a reason for the obtained apparent surface potentials Ψ_{app} . (From now on the potentials will be referred only as apparent surface potentials because the PB eq. is not valid.) A possible origin may lay in the $sPSO_2-220 / C_{14}TAB$ complexes in the foam film bulk.

Fig. 5.4 shows the electrophoretic mobility $|u_{\zeta}|$ of the sPSO₂-220 / C₁₄TAB complexes

in dependence of $c_{\rm sPSO_2-220}$ for different LiBr concentrations (for sake of clarity the absolute values are plotted, u_{ζ} is negative for all samples). $|u_{\zeta}|$ correlates to the charge of the sPSO₂-220 / C₁₄TAB complexes. Starting from rather uncharged complexes at $c_{\rm sPSO_2-220} = 10^{-5}$ monoM ($|u_{\zeta}| \approx 0 \,\mu{\rm m}\,{\rm cm}/{\rm Vs}$), the charge of the complexes slightly increases with increasing concentration of sPSO₂-220. Up to the BSMP (dotted vertical line), the complexes are slightly charged ($|u_{\zeta}| < 1.2 \,\mu{\rm m}\,{\rm cm}/{\rm Vs}$) irrespective of $c_{\rm LiBr}$. Above the BSMP, $|u_{\zeta}|$ differs depending on $c_{\rm LiBr}$: with 10^{-4} M LiBr the charge of the complexes continues to increase with increasing $c_{\rm sPSO_2-220}$. LiBr reduces the charge of the complexes and for 10^{-2} M LiBr $|u_{\zeta}|$ remain rather constant ($|u_{\zeta}| \approx$ $1.7 \,\mu{\rm m}\,{\rm cm}/{\rm Vs}$).

Fig. 5.4 also shows the *apparent* surface potential values Ψ_{app} as open symbols. (From the PB calculation only the absolute values can be obtained.) The formation of NBFs *around* the BSMP hints to rather low potentials for these foam films. Ψ_{app} increases with c_{sPSO_2-220} , but decreases with c_{LiBr} . For 10^{-2} M LiBr, Ψ_{app} stays at 45 mV irrespective of c_{sPSO_2-220} . These rough trends are well correlated with the electrophoretic mobility of the bulk complexes. Therefore, a major role of the bulk sPSO₂-220 / C₁₄TAB complexes for the *apparent* surface potentials Ψ_{app} can be concluded. Another argument supporting the role of the bulk complexes is that the P / S ratio and the adsorbed amounts at the air / liquid interface remains almost contestant *above* the BSMP, but the foam film stability increases with increasing sPSO₂-220 concentration.

It seems that a minimum charge (u_{ζ}) of the complexes is necessary to obtain stable foam films because *below* the BSMP the foam films are rather unstable, independent of the amount of LiBr added. *Below* the BSMP, the NR measurements show P/S ratios between 0.5 and 0.75 (Fig. 4.4), thus more $C_{14}TAB$ molecules than sPSO₂-220 monomers are adsorbed at the air/liquid interface and the interface is properly positively charged. At first glance, one might question the low foam film stability for positively charged interfaces. But note first the low absolute surface excess values of both $C_{14}TAB$ and sPSO₂-220 (Fig.4.2) - thus the interfaces are only slightly charged - and second the above-mentioned relative low negative charge of the bulk complexes (Fig. 5.4). There are slightly positively charged interfaces and slightly negatively charged bulk complexes. This condition is in line with the proposed conditions⁸⁶ for a NBF formation: oppositely charges of the interfaces and bulk components without a complexation of both. Other possible mechanisms for the NBF formation may either be $sPSO_2$ -220 chains bridging the two facing air / liquid interfaces or an attractive depletion force due to the exclusion of bulk complexes from the NBF.

Neither the values of the *apparent* surface potential Ψ_{app} nor of the charge of the complexes u_{ζ} explain the increased foam film stability for high c_{sPSO_2-220} and high c_{LiBr} . The foam film stability of sPSO₂-220 / C₁₄TAB mixtures without added LiBr was previously rationalized with the structures formed at a single air / liquid interface: an extended mixed layer of $sPSO_2$ -220 and $C_{14}TAB$ normal to the interface results in an unstable foam film *around* the BSMP, whereas an extended, swollen $sPSO_2-220$ layer leads to a stable foam film *above* the BSMP.⁸⁵ In chapter 4, the vanishing of the extended structures with increasing LiBr concentration was found that resulted in similar monolayer structures irrespective of $c_{\rm sPSO_2-220}$. Thus, the interfacial structures alone cannot explain the increased foam film stability and there must be another explanation for it. A closer look at the disjoining pressure isotherms reveals a small but systematic deviation for the highest LiBr concentration ($c_{\text{LiBr}} = 10^{-2} \text{ M}$, Fig. 5.3c)) from the PB calculation: with increasing Π , the foam film thickness stays constant at a value around 17 nm. This phenomenon is even more pronounced for the highest $c_{\rm sPSO_2-220}$ studied (Fig. A.24). A constant thickness with increasing disjoining pressure is characteristic for sterically stabilized foam films.¹⁰ In the present case, the steric repulsion cannot base solely on the adsorbed $sPSO_2-220 / C_{14}TAB$ layers at the two air / liquid interfaces as the thickness of each one lays around 2 nm and no hints for coiling of the sPSO₂-220 layer with increasing c_{LiBr} was found above the BSMP. 122 The origin of this steric stabilization may be the $\rm sPSO_2\text{-}220\,/\,C_{14}TAB$ complexes inside the foam film. The hydrodynamic diameter of the complexes for this sample is (25.7 ± 1.1) nm as light scattering measurements of the bulk solution showed. Slightly compressed complexes are reasonable to explain the steric stabilization. Albeit parameters such as surface elasticity 5^{2} affect the stability of foam films, in the present case the increase in foam film stability at high LiBr and high $sPSO_2$ -220 concentrations (Fig. 5.1) can be ascribed to the steric repulsion between the P/S complexes in the foam film bulk and the interfacial P / S layers.

Fig. 5.5 summarizes the effect of LiBr on foam films of $sPSO_2-220 / C_{14}TAB$ mixtures above the BSMP. The shaded areas correspond to the extent of thickness and disjoining pressure that the foam films cover for the respective LiBr concentration. With a low amount of LiBr ($c_{\text{LiBr}} = 10^{-4} \text{ M}$), the foam film thickness depends not only on the disjoining pressure, but as well on the $sPSO_2-220$ concentration. The thickness spectrum ranges from $h \approx 100 \text{ nm}$ to $h \approx 30 \text{ nm}$. With increasing LiBr concentration



FIGURE 5.5: Overview of foam films of $sPSO_2-220 / C_{14}TAB$ mixtures and the influence of LiBr on them. Shaded areas correspond to the thickness and disjoining pressure regimes of the foam films for each LiBr concentration.

the effect of $c_{\rm sPSO_2-220}$ diminishes. For 10^{-2} M LiBr, the disjoining pressure isotherms overlap resulting in constant $\kappa_{\rm exp}^{-1}$ and $\Psi_{\rm app}$ values (Tab. A.6 and Fig. 5.4). The concentration, which dictate the foam film properties, changes from $c_{\rm sPSO_2-220}$ to $c_{\rm LiBr}$ once $c_{\rm LiBr}$ is higher than $c_{\rm sPSO_2-220}$.

This work directly proofs a contribution of P/S bulk complexes to the foam film properties. On the one hand, the *apparent* surface potentials Ψ_{app} and the foam film stability Π_{max} cannot be explained by the ratio of adsorbed sPSO₂-220 monomers to C_{14} TAB molecules. On the other hand, a qualitative correlation is found between the *apparent* surface potentials and the charges of the bulk complexes. A minimum u_{ζ} seems to be necessary for stable foam films. Moreover, once LiBr thins the foam film down to the size of the complexes, they sterically stabilize the foam films. This study verifies that not only the two facing air / liquid interfaces are relevant for foam films but in fact the film bulk between them matters.

5.4 Conclusions

The influence of LiBr on foam films formed by $sPSO_2-220 / C_{14}TAB$ mixtures was studied with varying $sPSO_2-220$ content. LiBr was found to lower the electrostatic repulsion between the two facing air / liquid interfaces leading to thinner foam films. The stability of foam films depend on both the $sPSO_2-220$ and LiBr concentration. Below the BSMP, unstable foam films are formed irrespective of c_{LiBr} . Above the BSMP, stable foam films form. A low amount of added LiBr destabilizes the foam films, whereas a high amount of added LiBr stabilizes the foam films. This stabilizing effect is attributed to a steric contribution of the bulk sPSO₂-220 / C₁₄TAB complexes. The *apparent* surface potential Ψ_{app} seems to be more affected by the bulk complexes than by the single air / liquid interfaces and represent a projection of all charged components inside the foam film.

We learn that fully covered interfaces not necessarily lead to stable foam films: around the BSMP the addition of LiBr result in the formation of unstable NBFs -- for the first time seen for the used combination of anionic P and cationic S. This is explained by opposite charges of the film surface and the film bulk complexes. Finally, we found that for the formation of stable foam films, a minimum charge of the P/S complexes is necessary. These finding can be extended to other P/S mixtures and might play a role in a better understanding of the rheology of foams in technical applications or the interaction between natural P and lipid membranes.

Chapter 6

Effect of time on sPSO₂-220 / C₁₄TAB mixtures



6.1 Abstract

P/S mixtures are known to exhibit non-equilibrium behavior. Their bulk phase behavior may change with time. In the following chapter, the effect of time on sPSO₂-220 / C₁₄TAB mixtures containing 10⁻³ M LiBr is investigated. Therefore, the freshly mixed samples from chapter 5 are compared to aged ones. After 1 month storage time, the mixtures are studied with bulk characterization methods (UV-vis spectroscopy, electrophoresis) as well as with tensiometry. Furthermore, the foam films of the aged mixtures are investigated. The mixtures have phase separated resulting in a higher optical density compared to the freshly mixed ones. Below the BSMP, the surface tension increases to values similar to those of the pure C₁₄TAB solution. A charge reversal hints to the formation of larger sPSO₂-220 / C₁₄TAB aggregates. Above the BSMP, aggregation is less distinct. The formation of aggregates increases the foam film stability. These findings reveal the importance of taking time effects into account, in particular when considering the wide range of application of P / S mixtures.

6.2 Introduction¹

Not only the concentration of P, S and salt affects the phase behavior of P/S mixtures: aging effects as well may play a role.^{67,108} Interfacial properties of P/S mixtures cannot always be considered separately from bulk properties as the two are able to influence each other.¹⁶⁵ Especially, the surface tension is affected by the bulk phase behavior.

The impact of a sufficient time to equilibrate as well as non-equilibration effects (e.g.mixing procedure) are not only important for applications, but are also in the focus of more fundamental questions. Two prominent systems have attracted the attention of the research community: PSS / C₁₂TAB and poly(diallyldimethylammonium chloride) (PDADMAC) / SDS with 0.1 M NaCl due to their - seemingly contradictory - surface tension isotherms. Surface tension isotherms of PDADMAC / SDS show always a peak close to the two phase regime independent of the age of the solution. $PSS / C_{12}TAB$ mixtures may show this peak only in certain measurements.⁷ Different approaches were used to understand this phenomenon and to answer the question which surface tension isotherm represents the equilibrium state of these mixtures. Thomas and Penfold 78 suggest that no peak appears in the equilibrium surface tension isotherm for $PSS / C_{12}TAB$ mixtures. Their argumentation is based on differences in the binding nature of the two systems: PDADMAC and SDS bind strongly cooperative whereas the binding of PSS and C_{12} TAB is highly non-cooperative. The former leads to a loss in surface activity at a certain S content and to the surface tension peak. The later leads to complexes with diverse stoichiometries and thus no peak should appear at a certain S concentration.⁷⁸ In contrast, Campbell and Varga find the same general behavior for both systems: a depletion of material from the air / liquid interface results in the surface tension peak at the two phase regime.⁷⁹ The only difference is the time scale of this depletion. For PDADMAC / SDS the depletion happens over couple of days, whereas for PSS / C_{12} TAB it takes about 1 month. Studies on PSS / C_{12} TAB mixtures at the oil / water interface support this idea of a long equilibrium time for the depletion of material.¹⁶⁶

Aging effects are especially important around the two-phase regime. The margins of the two-phase regime can be determined e.g. by tracking the optical density (OD) of

¹Parts of this section are published in "Stability of aqueous foam films and foams containing polymers: Discrepancies between different length scales" L. Braun, M. Kühnhammer, R. v. Klitzing *Current Opinion in Colloid and Interface Science*, **2020**, 50, 101379. Reprinted with permission. Copyright 2020 Elsevier.⁷

P/S mixtures with time. Complexes with sufficient electrostatic colloidal stability show a constant turbidity and constant *OD* values. But insufficiently stabilized complexes aggregate, precipitate or even sediment with time, leading to a change in *OD*.^{53,81}

The following chapter focuses on the effect of aging on $sPSO_2-220 / C_{14}TAB$ mixtures containing 10^{-3} M LiBr. Freshly mixed and aged samples are compared regarding their sample appearance, their surface activity, and their ability to stabilize foam films.

6.3 Results

Sample appearance Freshly prepared $sPSO_2-220 / C_{14}TAB$ mixtures appear clear to the naked eye and exhibit a low optical density (sec. A.3). The mixtures containing 10^{-3} M LiBr were stored quiescently for around 1 month. After this time, the appearance of the samples changed: they became slightly turbid. When shaking the samples, white flakes were visible which afterwards precipitated. Fig. 6.1 shows an image of the aged samples containing 3×10^{-5} monoM sPSO₂-220, where the flakes and streaks are visible at the bottom of the glass bottle. This precipitation was more pronounced for the samples *below* the BSMP than *above* the BSMP.



FIGURE 6.1: Images of a sPSO₂-220 / C_{14} TAB mixtures 1 month after mixing containing 10^{-3} M LiBr and 3×10^{-5} monoM sPSO₂-220 (a). b) shows a close up of a). Additional images of different samples can be found in Fig. A.26.

Bulk properties Fig. 6.2 shows the optical density (OD_{400}) of the aged samples (filled symbols) compared to the freshly mixed samples (open symbols). Due to the aging, OD_{400} increased by one order of magnitude for all sPSO₂-220 / C₁₄TAB mixtures. This increase hints to the formation of larger sPSO₂-220 / C₁₄TAB aggregates.



FIGURE 6.2: Optical density OD_{400} of sPSO₂-220 / C₁₄TAB complexes in dependence of $c_{\rm sPSO_2-220}$ containing 10^{-3} M LiBr. The dotted vertical line marks the BSMP. Open symbols correspond to the values of freshly mixed samples (5 min after mixing), whereas filled symbols correspond to the aged samples (1 month after mixing, but slightly shaken before the measurement). The errors of the OD_{400} values are within the size of the symbols.



FIGURE 6.3: Electrophoretic mobility u_{ζ} of sPSO₂-220 / C₁₄TAB complexes in dependence of $c_{\rm sPSO_2-220}$ containing 10^{-3} M LiBr. The dotted vertical line marks the BSMP. The solid horizontal line denotes an electrophoretic mobility of zero. Open symbols correspond to the values of freshly mixed samples (5 min after mixing), whereas filled symbols correspond to the aged samples (1 month after mixing).



FIGURE 6.4: Surface tension of sPSO₂-220 / C_{14} TAB complexes in dependence of c_{sPSO_2-220} containing 10^{-3} M LiBr. The dotted vertical line marks the BSMP. The dashed horizontal line corresponds to the surface tension of the pure C_{14} TAB solution ($c_{C_{14}TAB} = 10^{-4}$ M) at the respective LiBr concentration. Open symbols correspond to the values of freshly mixed samples (2 h after mixing), whereas filled symbols correspond to the aged samples (1 month after mixing).

The electrophoretic mobility changed as well after 1 month (Fig. 6.3). The values for the aged samples (filled symbols) are less negative compared to the values of the freshly mixed samples (open symbols). *Below* the BSMP (dotted line), a charge reversal occurs from negative to positive charge.

Tensiometry The aged samples were left to precipitate (if necessary or possible) and the supernatant was carefully separated. Fig. 6.4 shows the surface tension of the supernatant (filled symbols) compared to the surface tension of the freshly mixed samples (open symbols). *Below* the BSMP, γ increased from values of 42 mN/m to values around 65 mN/m due to aging. For the aged samples, γ lies around the value of the pure C₁₄TAB solution ($c_{C_{14}TAB} = 10^{-4}$ M, $c_{LiBr} = 10^{-3}$ M, dashed horizontal line in Fig. 6.4). *Above* the BSMP, γ of the freshly mixed and aged samples lies around 50 mN/m. Aging seems to play only a minor role for the surface tension *above* the BSMP.

Foam films The changes observed due to aging might as well influence the foam films of the P/S mixtures. Thus, disjoining pressure isotherms were recorded for one aged sample *below* the BSMP ($c_{sPSO_2-220} = 3 \times 10^{-5} \text{ monoM}$) and for one aged



FIGURE 6.5: Disjoining pressure isotherms of sPSO₂-220 / C_{14} TAB mixtures (*below* the BSMP, $c_{sPSO_2-220} = 3 \times 10^{-5}$ monoM, c_{C14} TAB = 10^{-4} M) containing 10^{-3} M LiBr. Open symbols correspond to three individual measurements of the fresh mixture (2 - 3 days after mixing) and filled symbols to three individual measurements of the aged mixtures (1 month after mixing).

sample *above* the BSMP ($c_{sPSO_2-220} = 10^{-3} \text{ monoM}$). In the following, the disjoining isotherms of the two aged samples are compared to the ones of the freshly mixed samples (discussed in chapter 5).

Fig. 6.5 shows three individually recorded disjoining pressure isotherms of foam films of the freshly mixed sample (open symbols) and the aged sample (filled symbols) below the BSMP. The foam films of the freshly mixed sample are rather unstable with a $\Pi_{\rm max}$ of 130 Pa. At maximum only 4 data points could be recorded. The foam film thickness for a fixed Π value differs by 10 to 30 nm for the individual measurements. This huge thickness range reflects the low sensitivity of the disjoining pressure isotherm in the low Π regime (chapter 3.2.1). The foam films of the aged sample are slightly more stable ($\Pi_{\rm max} \sim 190 \,{\rm Pa}$). The foam film thickness has similar values to those of the fresh mixture; if any effect is recognizable, the foam films are a bit thicker. Fig. 6.6 shows images of two foam films: one of the freshly mixed sample (Fig. 6.6a) and one of the aged sample (Fig. 6.6b). Both images have the same scale, but were taken at different stages of the measurements, so the foam films differ in size. The foam films of the freshly mixed sample contain small inhomogeneities (especially in the lower part of the image). Brighter areas are visible. They appear as little spots or as larger defined areas. The brighter color hints to a slightly increased thickness of these parts of the foam film. In this $c_{\rm sPSO_2-220}$ -regime NBFs form before film rupture



FIGURE 6.6: Images of foam films of $sPSO_2-220 / C_{14}TAB$ mixtures (*below* the BSMP, $c_{sPSO_2-220} = 3 \times 10^{-5}$ monoM, $c_{C_{14}TAB} = 10^{-4}$ M) containing 10^{-3} M LiBr. Foam film are formed by a freshly mixed sample (2 - 3 days after mixing, a)) or by the aged sample (1 month after mixing, b)). Images were digitally post-processed to increase the contrast.



FIGURE 6.7: Disjoining pressure isotherms of $sPSO_2-220 / C_{14}TAB$ mixtures (*above* the BSMP, $c_{sPSO_2-220} = 10^{-3}$ monoM, $c_{C_{14}TAB} = 10^{-4}$ M) containing 10^{-3} M LiBr. Open symbols correspond to the freshly mixture (3 - 4 days after mixing) and filled symbols to the aged mixture (1 month after mixing). The solid line corresponds to PB calculations at constant *apparent* surface potential Ψ_{app} .

(Fig. 5.1). The thicker parts of the foam film slow down the spreading of the NBF. Thus, they deform the otherwise circular NBF (Fig. A.27). The foam films of the aged sample (Fig. 6.6b) appear a bit brighter. As for the foam films of the freshly mixed sample, streaky areas are visible. Beside these, the foam film is homogeneous and shows no signs of incorporated aggregates. NBFs formed before the film rupture for the aged sample, too.

Fig 6.7 shows the disjoining pressure isotherms of the freshly mixed sample



FIGURE 6.8: Images of foam films of $sPSO_2-220 / C_{14}TAB$ mixtures (*above* the BSMP, $c_{sPSO_2-220} = 10^{-3}$ monoM, $c_{C_{14}TAB} = 10^{-4}$ M) containing 10^{-3} M LiBr. Foam film are formed by a freshly mixed sample (3 - 4 days after mixing, a)) or by the aged sample (1 month after mixing, a)). Images were digitally post-processed to increase the contrast.

(open symbols) and the aged sample (filled symbols) *above* the BSMP. The foam films of the aged sample increased in stability by a factor of two from $\Pi_{\text{max, fresh}}$ = 400 Pa to $\Pi_{\text{max, aged}}$ = 900 Pa. The thicknesses mostly overlap for both samples. The foam films of the aged sample are stable enough to successfully calculate the disjoining pressure isotherm (solid line in Fig 6.7). An *apparent* surface potential Ψ_{app} of 80 mV is obtained. Referring to Fig. 5.4 and the respective discussion, the value matches quite well to the rough trends between the *apparent* surface potential Ψ_{app} and the electrophoretic mobility u_{ζ} of the bulk complexes. However, as the sPSO₂-220 / C₁₄TAB mixtures aged with time, it seems wrong to include this value into Fig. 5.4. Fig. 6.8 shows images of foam films of the freshly mixed (Fig. 6.8a) and the aged (Fig. 6.8b) samples *above* the BSMP. Both appear mostly homogeneous, even when little white spots occur. These spots are properly small droplets of excess liquid as they both appear and disappear close to the white rim surrounding the foam film (Fig. A.28).

6.4 Discussion

The results for the aged samples (precipitation / turbidity) suggest the formation of larger $sPSO_2-220 / C_{14}TAB$ aggregates after 1 month. Close to charge neutrality, the complexes lack of colloidal stability and start to agglomerate and even to precipitate.⁸¹ Above the BSMP, the complexes still are charged enough to have a higher colloidal stability after 1 month and the precipitation is less pronounced. The supernatant of the samples was roughly separated from the precipitated material a prior to the

tensiometry and foam film measurements. Hence, less P and S are in the separated samples than in the freshly mixed ones. This obvious depletion of material explains the higher γ values *below* the BSMP: a more distinct precipitation should lead to a higher depletion due the separation of samples. However, it is important to keep in mind that γ and the surface excess of sPSO₂-220 and C₁₄TAB are not directly correlated as shown in chapter 4. Nevertheless, a depletion of material from the interface is in line with the formation of larger P/S aggregates *below* the BSMP.

Depending on the initial bulk P/S ratio and salt content, phase separation can occur either as associative phase separation or as segregative phase separation.¹⁶⁷ Association occurs at intermediate P/S ratios or in salt-free systems, one phase is enriched in both P and S, whereas the other one is diluted of both. Segregation is described for a high salt content (~ 1 M) and certain P/S ratios. The mixture separates in one P enriched and one S enriched phase.¹⁶⁷ In the present case with a moderate LiBr concentration of 10^{-3} M and P/S ratios from 1:10 to 10:1, the associative phase separation is more likely. But, no details of the actual P/S ratios in the supernatant and the precipitation are available.

The foam films *above* the BSMP showed no incorporated P/S aggregates (no inhomogeneities), thus either the separated samples are completely free of aggregates (rather unlikely as traces of precipitation were visible after the aged samples were studied over a couple of days) or the aggregates do not enter into the foam film. Surprisingly, the stability of the foam films *above* the BSMP increased more than the one of the foam films *below* the BSMP. *Above* the BSMP, the actual P/S ratios may changed more drastically than one aspects due to the associative phase separation, leading to the increase in stability. However, the similar u_{ζ} values of the complexes as well as the overlapping disjoining pressure isotherm, hint to quite similar samples - independent of the sample age.

The fundamental question arises what actually determines the stability of foam films. In chapter 5 a steric contribution by the bulk complexes was found for a high salt concentration. This situation is not given for the foam films discussed in this chapter as the foam films are thicker (40 nm vs. 17 nm) and the disjoining pressure isotherms suggest mainly an electrostatic stabilization. The charge of the bulk complexes did not change significantly after 1 month, suggesting a rather equal foam film stability. But, no information about the amount or size of bulk complexes is obtained, which may play a huge role for the electrostatic stabilization. More, but smaller complexes could have formed due to the phase separation, which leads to higher osmotic pressures and thus, to higher foam film stabilities. The amount of complexes in the bulk and in the foam film bulk might not necessarily be identical as the larger aggregates of the bulk solution do not enter the foam films (no inhomogeneities).

Another parameter known to affect the foam films stability is the surface elasticity.⁵² The brighter areas found on the film's interface *below* the BSMP, might be thicker parts, however a change of refractive index due to a more dense and rigid lateral interfacial structure is as well a possible reason for the brighter color. Interfacial domain formation is known for non-ionic surfactants¹⁶⁸ and higher alkanes¹⁶⁹. Rigid areas will surely affect the elasticity of the film's interfaces. For the foam films *above* the BSMP no rigid areas occurred (Fig. 6.8). Furthermore, the appearance of the foam films have not detestably changed and a rather mobile interface is seen irrespective of the age of the sample. These findings hints a prior to an unchanged film interface. The flow condition inside the foam film is another point which may come into play.^{170,171} All these aspects and parameters interact and affect the foam film stability, complicating the question of its origin.

Clearly, not only the single interfaces (e.g. γ) or the bulk (e.g. u_{ζ} of the bulk complexes) are relevant, but as well their interplay. The effect of aging depicts the necessity to distinguish between bulk and foam film bulk: their properties may differ. The above findings show that freshly mixed P/S mixtures not always equilibrate on short time scales. The question what the equilibrium state of P/S mixtures is and how it can be influenced (ratio of P to S, addition of salt, mixing procedure) is highly debated in fundamental research.^{58,79} Considering the wide range of applications of P/S mixtures, the aging effect is not only of academic interest. For the use as hair conditioner or in a large scale facility of froth flotation, knowledge about changes in the performance of P/S mixtures with time is crucial.

6.5 Conclusion

The effect of time on $sPSO_2-220 / C_{14}TAB$ mixtures containing 10^{-3} M LiBr was studied. The mixtures were stored for 1 month and afterwards bulk properties (turbidity, electrophoretic mobility), their surface tension, and their foam films were compared to freshly mixed samples. A distinct flocculation *below* the BSMP due to reversal of the complex' charge was found. *Above* the BSMP, the complexes still have an sufficient (negative) charge to maintain in a stable solution and flocculation is less pronounced. Consequently, the effect of aging is less pronounced *above* the BSMP than *below* the BSMP (increased surface tension *below* the BSMP). These findings highly suggest the formation of $sPSO_2-220 / C_{14}TAB$ aggregates *below* the BSMP. The foam film stability increased *above* the BSMP but the thickness and the disjoining pressure isotherm remained similar to the ones of the freshly mixed sample. These results show that additional to the ratio of P to S and the way of mixing, the age of P/S mixtures has to be considered when talking about the properties of these mixtures. The effect of time is not only interesting for fundamental research, but as well relevant for plenty of industrial applications of P/S mixtures, where a constant performance of the P/S mixtures is preferred.

Chapter 7

Effect of HSiW on BrijO10 foam films and foams

Similar content will be published in "Insights into the non-ionic foam stabilization mechanism by chaotropic nano-ions" L. Braun, M. Hohenschutz, O. Diat, P. Bauduin, R. v. Klitzing. This study was performed in collaboration with Max Hohenschutz. He performed the measurements on the macroscopic foams (foam scan and SANS measurements).



7.1 Abstract

The Keggin polyoxometalate $\mathrm{SiW}_{12}\mathrm{O}_{40}^{4-}$ (SiW) was recently shown to adsorb onto non-ionic soft matter interfaces owing to a water-mediated driving force called the superchaotropic effect. At the interfaces of non-ionic surfactant foams the chaotropic adsorption of SiW leads to a strong stabilization of the foam. In order to elucidate the stabilizing mechanism of SiW on all length scales, both macroscopic foams and single foam films are investigated. Imaging, conductimetry and small angle neutron scattering (SANS) on macroscopic foams enable the monitoring of the foam collapse under free drainage and the evolution of film thickness. TFPB measurements on single foam films enable to determine their resistance to external pressure and the identification of intra--film forces. The combined results reveal that SiW adsorbs onto BrijO10 covered foam interfaces and thus induces electrostatic repulsion between bubbles interfaces. Beyond a concentration corresponding to an adsorption saturation, excess of SiW screens the electrostatic repulsion that thins the foam films. Regardless, the foams remain very stable, which is assigned to the presence of micelles inside the foam films providing a steric stabilization and a reservoir of surfactants in the subinterfacial region. This reservoir is assumed to promote self-healing of the interface upon disturbances leading to more resistant foam films and finally to a longer foam lifetime.

7.2 Introduction

Depending on the liquid volume fraction ϕ_1 of the foam, one distinguishes: a bubbly liquid ($\phi_1 > 30\%$) where the spherical bubbles do not touch, a wet foam ($5\% \leq \phi_1 < 30\%$) where the bubbles touch and start to deform, and a dry foam ($\phi_1 \leq 5\%$) where the bubbles are polyhedral and the foam films and Plateau borders are thin.⁵ Foaming in general is a highly dynamic process and foam decay is an interplay of three different mechanisms: i) drainage, the downwards flow of liquid due to gravity, ii) coarsening, the gas transfer between bubbles of different size, and iii) coalescence, the rupture of individual foam films.⁵ Upon drainage, foam films become thinner until adjacent bubble interfaces start to interact and surface forces result in the disjoining pressure Π . The various components of Π are presented in chapter 2.1.2.

The present chapter deals with the foam stabilization mechanism of the Keggin POM $SiW_{12}O_{40}^{4-}$ (SiW). POMs associate with non-ionic surfactant self-assemblies^{101,172}, polymers^{173,174} and zwitterionic lipid membranes¹⁷⁵. Upon association, both the interface and the chaotropic ion release hydration water into the bulk resulting in negative Gibbs free energies, comprised of an enthalpic gain accompanied by an entropic penalty, providing the chaotropic thermochemical signature.^{176,177}

A recent work showed that SiW stabilizes foams of the non-ionic surfactant BrijO10 at millimolar SiW concentrations similar to ionic surfactants and proposed that the increased foam stability is linked to electrostatic repulsion inside the foam films.¹⁹ This chapter uses a multi-scale approach from macroscopic foams to single foam films to elucidate in detail this stabilizing effect of SiW on non-ionic BrijO10 foams. The decay and the film thickness of macroscopic foams are studied with a foam scan and SANS. Single foam films are studied with a TFPB in order to identify stabilizing surface forces and to follow the foam film resistance against external pressures.

7.3 Results and discussion

a) b) 250 mM BrijO10 0.5 mM BrijO10 + 0.5 mM HSiW 250 + 0.5 mM HSiW 20 mM NaCl 0.5 mM HSiW + 20 mM NaCl + 0.5 mM HSiW + 2.5 mM HSiW + 20 mM NaCl 20 2.5 mM HSiW Foam volume / ml 20 Έ 20 mM NaCl Foam volume 150 100 100 50 50 0 100 50 100 150 200 50 150 200 Time / min Time - t_c / min

7.3.1 Macroscopic foams¹

FIGURE 7.1: Foam volume vs. time for foams of $0.5 \,\mathrm{mM}$ BrijO10 in the presence of 20 mM NaCl, $0.5 \,\mathrm{mM}$ HSiW, $2.5 \,\mathrm{mM}$ HSiW and $0.5 \,\mathrm{mM}$ HSiW + 20 mM NaCl. The behavior of BrijO10 + 20 mM NaCl corresponds to the behavior of the bare BrijO10 foam, see text. In b) the foam collapse is normalized by the critical drainage time defined as $t_{\rm c}$ in a). The light areas below each curve represent standard deviations determined from three independent measurements.

Foam stability Foam stability is determined by monitoring the foam volume over time.⁷ The foam volume was determined *via* conductimetry measurements within a glass column. Further details on the foam generation and measurement procedure can be found in Ref. 19. Fig. 7.1a) shows the foam volume as function of the time of BrijO10 stabilized foam with and without HSiW added. The foams passes through three stages: I) the foam generation, indicated by a steep increase of foam volume up to four minutes. II), a drainage stage, where the liquid passes trough the Plateau borders and the foam films due to gravity up to a critical drainage time t_c . III) the

 $^{^{1}}$ The measurements and analysis of macroscopic foams were preformed by Max Hohenschutz and are shortly summarized in this section.

foam collapse, characterized by a strong decrease in foam volume. To compare the collapse rates of the foams, the curves were offset by the respective t_c (Fig 7.1b)). The foam of 0.5 mM BrijO10 with 20 mM NaCl collapse rather quickly (green squares). As bare BrijO10 foam exhibit a too low conductance the used device could not determine its volume. Comparative image analysis showed no effect of NaCl on the foam of bare BrijO10.¹⁹ Thus, the values for 0.5 mM BrijO10 + 20 mM NaCl are used as reference for the bare BrijO10 foam. Once HSiW is added, the foams show an increased stability (light blue circles: 0.5 mM BrijO10 + 0.5 mM HSiW and dark blue triangles: 0.5 mM BrijO10 + 2.5 mM HSiW). However, the foam of 0.5 mM BrijO10 + 0.5 mM HSiW and 20 mM rapidly collapses (gray triangles).



FIGURE 7.2: a) SANS curves of 0.5 mM BrijO10 with increasing concentrations of HSiW in an IQ^4 vs. Q plot. The curves were offset with arbitrary multipliers for clarity. b) Acquired foam film thicknesses from reflectivity fitting of the SANS curves

Small-angle neutron scattering SANS can be used to study the internal structures of macroscopic foam.⁷ In wet foams, the scattering is dominated by dispersed structures such as S micelles or protein aggregates.¹⁷⁸ In dry foams, however, the thin foam films are the mainly scattering objects¹⁷⁹ and their thickness can be extracted by mimicking the features of a SANS curve¹⁷⁸. In the following SANS curves of BrijO10 stabilized foams with different HSiW concentrations are presented. The foams were formed with D₂O as solvent to increase to scattering contrast between air and the liquid. The liquid volume fractions were below 5% (dry foam). Details on the measuring procedure and analysis can be found in Ref. 19 Fig. 7.2 shows an IQ^4 vs. Q plot of the SANS data to focus on oscillations arising from the neutron reflection on the foam films. The bare BrijO10 foam shows barely visible oscillations, however with addition of HSiW they become more distinct and change their period. The oscillation period ΔQ correlates with the film thickness d as $d = \frac{2\pi}{\Delta Q}$. The apparent film thicknesses were extracted by fitting a reflectivity model of a D₂O layer in between two air phases (Ref.¹⁹ and Fig 7.2b). For the bare BrijO10 foam, a film thickness of (25 ± 5) nm is obtained. With increasing HSiW content, the films thickens to (35 ± 1) nm with 0.5 mM HSiW and afterwards thins down to (22 ± 2) nm with 2.5 mM HSiW.

7.3.2 Foam films



FIGURE 7.3: Disjoining pressure isotherms of 0.5 mM BrijO10 with variable HSiW concentration. The solid lines correspond to calculations according to the DLVO theory from which the *apparent* surface charge densities q_0 are obtained. The horizontal marks on the y-axis indicate the maximal disjoining pressure Π_{max} .

Disjoining pressure isotherms Fig. 7.3 shows the disjoining pressure isotherms of 0.5 mM BrijO10 without and with 0.05, 0.5, and 2.5 mM HSiW, respectively. Solid lines correspond to calculated disjoining pressure isotherms according to DLVO theory (details see chapter 3.2.1). For pure BrijO10 (green squares in Fig. 7.3), the disjoining pressure isotherm shows a jump to a considerably thinner foam film (from $h \sim 80$ nm to $h \sim 10$ nm) below 100 Pa. Microscopy images show the transition of a CBF to a NBF via black spots formation (Fig. 7.4). The CBF at low Π results from weak electrostatic repulsion due to the electric charge of bare air / liquid interfaces.^{43,51} Above 100 Pa,

the disjoining pressure isotherm is almost vertical, which is characteristic for sterically stabilized NBFs. Indeed the film thickness corresponds to approximately two extended BrijO10-molecules ($l \approx 6 \text{ nm}$ when extended; computed with Avogadro¹⁸⁰). Above the cmc, the electrostatic barrier for the CBF -- NBF transition is low and overcome easily for non-ionic surfactants.¹⁸¹



FIGURE 7.4: Images of a CBF -- NBF transition *via* black spot formation of 0.5 mM BrijO10. The indicated times are relative to the first image. Images were digitally post-processed.

Adding 0.05 mM HSiW thickens the foam film (light blue diamonds in Fig. 7.3). Starting with a thickness of around 110 nm at 90 Pa, the disjoining pressure increases steadily with compression of the film. The thickness range and high compressibility indicates an electrostatically stabilized CBF. At high thicknesses, the disjoining pressure isotherm coincides with the calculated one according to DLVO theory (light blue solid line in Fig. 7.3). The experimental screening length κ_{exp}^{-1} is 13.6 nm and the apparent surface charge density is $q_0 = -3.5 \,\mathrm{mC}\,\mathrm{m}^{-2}$. From the calculation only the value of q_0 is obtained and the negative sign is assumed from the charge of SiW. SiW adsorbs at the interfaces and increases the energetic barrier of the NBF -- CBF transition. Increasing the HSiW content to 0.5 mM leads to thinner foam films below 1000 Pa (blue circles in Fig. 7.3). The disjoining pressure isotherm is steeper indicating a shorter screening length ($\kappa_{exp}^{-1} = 6.5 \,\mathrm{nm}$). For a foam film thicker than around 40 nm the disjoining pressure isotherm coincides with the calculated one, thus electrostatic repulsion determines the thickness. The apparent surface charge density increases to $q_0 = -7.4 \,\mathrm{mC}\,\mathrm{m}^{-2}$. This increased apparent surface charge density indicates that more SiW has adsorbed on the foam film interfaces at 0.5 mM HSiW compared to 0.05 mM HSiW. For 0.5 mM HSiW, we assume a saturation of adsorbed SiW (deduced from adsorption measurements as inferred from flotation experiments on the BrijO10 / HSiW system¹⁰¹).

Further increased HSiW content to $2.5 \,\mathrm{mM}$ (dark blue triangles in Fig. 7.3) again leads to a thinner foam film at low Π values. Meanwhile, the slope of the disjoining pressure isotherm is much steeper in comparison to the foam films at lower HSiW concentrations and hence, the screening length ($\kappa_{exp}^{-1} = 4.3 \,\mathrm{nm}$) is further decreased. The lower part of the disjoining pressure isotherm agrees with the calculated one, resulting in an apparent surface charge density $q_0 = -6.9 \,\mathrm{mC} \,\mathrm{m}^{-2}$ similar to the value at $0.5 \,\mathrm{mM}$ HSiW ($q_0 = -7.4 \,\mathrm{mC} \,\mathrm{m}^{-2}$). This is in line with a saturation of SiW at the film interfaces. Current DLVO calculation, like the one used here, assume an unrealistically thin adsorption layer, which is however a crucial parameter for calculating Π as reported recently by Peng and co-workers¹⁶⁴. SiW has been shown to intercalate between the head groups of non-ionic surfactant micelles.¹⁰¹ Accordingly, we expect that the interfacial charges are located between the surfactant head groups inside the foam films. The actual depth of the charge plane cannot be directly determined and the resulting *apparent* surface charge densities should therefore be taken only as a qualitative result. If no more SiW adsorbs at the interfaces, when increasing the HSiW content from 0.5 to 2.5 mM, the additional amount is present in the bulk liquid. The bulk HSiW leads to a screening of the electrostatic double layer repulsion *i.e.* decreased screening length, and thus to the thinning of the foam film. The surface tension of the samples is unaffected by the add of HSiW.¹⁹ Furthermore, the samples are above the cmc of BrijO10 ($cmc_{BrijO10} = 0.04 \, mM^{104}$) Hence, no information about changes of the adsorbed amount of BrijO10 or SiW can be obtained from the analysis of surface tension isotherms.

For the three disjoining pressure isotherms with HSiW added, deviation from the calculated disjoining pressure isotherms for thinner foam films occurs below ~ 20 nm, ~ 40 nm, and ~ 30 nm, for 0.05 mM, 0.5 mM, and 2.5 mM HSiW, respectively, where the foam films are thicker than predicted by DLVO. This observation implies that an additional repulsive non-DLVO force is present. Especially for the disjoining pressure isotherm of 0.05 mM HSiW a kink occurs at ~ 20 nm that suggests a distinct change in stabilization. Disjoining pressure isotherms with similar shape are often observed for polymeric surfactants.¹⁸² A steric interaction of the polymeric non-ionic head groups stabilizes the foam film (at high disjoining pressures). The "soft", coiled head groups provide the foam film with compressibility at short distances in contrast to a typically incompressible NBF.¹⁸² A similar stabilization mechanism can explain the kink in the disjoining pressure isotherm at 0.05 mM HSiW. The loosely packed BrijO10 forms a bilayer-like compressible region near the interface as seen for other surfactants above the cmc⁴⁷. However, because a BrijO10 concentration far above the cmc is

used, micelles may be trapped in between the two interfaces and would thus cause an additional steric repulsive force. For higher HSiW content $(0.5 \,\mathrm{mM})$ and $2.5 \,\mathrm{mM}$, the transition is less distinct (no kink) as the disjoining pressure isotherms are already quite steep at low Π . The almost parallel disjoining pressure isotherms of $0.05 \,\mathrm{mM}$ and 0.5 mM HSiW above $\sim 4000 \text{ Pa}$ indicates a similar stabilization. Further increase of the HSiW content to 10 mM leads to a fully incompressible foam film (Fig. A.30) similar to a NBF - supporting the above assumption of a steric stabilization. The minimal thickness of the foam film at high disjoining pressure depends on the HSiW content. Higher amounts of adsorbed SiW will dehydrate the BrijO10 interfaces more and lead to more rigid and less compressible interfaces and micelles. Furthermore, the addition of POMs affects the shape and size of micelles formed by non-ionic surfactants: e.g. for a micellar $C_{12}E_8$ solution the adsorption of SiW shortens the former cylindrical elongated $C_{12}E_8$ micelles (maximal length ~ 180 nm and a crosssection radius of $2.1 \,\mathrm{nm}$) down to spheres (with a radius of $2.4 \,\mathrm{nm}$).¹⁷² Although we assume the presence of micelles trapped inside the foam films, no indication of structural forces was detected, which is often the case for surfactant foam films at concentrations above the cmc. Compression of such micellar foam films causes a stepwise thinning of the foam films (stratification) due to a layer wise expulsion of micelles out of the foam film^{160,183,184}. This exciting observation of absence of stratification will be discussed later.

HSiW increases the foam film stability. The maximal disjoining pressure before film rupture, Π_{max} , is marked on the y-axis in Fig. 7.3. Π_{max} increases from ~ 6300 Pa without HSiW to values around 9000 - 10 000 Pa with HSiW. For the highest HSiW concentration of 2.5 mM shown in Fig. 7.3, the foam films did not rupture during the measurement as Π_{max} exceeded the accessible instrumental pressure range.

Due to their nanometric size, POMs like SiW might be considered as colloidal particle. Therefore, the question if they act as a simple ion or as a colloidal particle is commonly debated ^{185,186} and ionic or colloidal behavior may arise depending on the type of investigation ¹⁸⁵⁻⁻¹⁸⁷. A striking difference between classical ions and charged colloidal particles is their contribution to the ionic strength and the screening length κ^{-1} of the medium. According to the jellium model, a charged colloidal particle in water does not contribute to κ^{-1} and the ionic strength arises solely from the counterions of the colloidal particle.^{49,188--190} In contrast, in electrolytes of low molecular weight ions, anions and cations equally contribute to the ionic strength and their distribution follows a Boltzmann distribution. For these two limiting cases, the values of κ^{-1}

$c_{\rm HSiW}$ / mM	$\kappa_{\rm exp}^{-1}$ / nm	$\kappa_{\rm colloidal \ particle}^{-1}$ / nm	$\kappa_{\rm ion}^{-1}$ / nm
0.05	13.6	30.4	13.6
0.5	6.5	9.6	4.3
2.5	4.3	4.3	1.9

TABLE 7.1: Experimental Debye length κ_{exp}^{-1} and calculated Debye lengths for the "colloidal particle case" or the "ion case".

for the BrijO10 solutions that contain HSiW are calculated. This leads to the two values $\kappa_{\rm ion}^{-1}$ and $\kappa_{\rm colloidal \ particle}^{-1}$. The former takes both SiW⁴⁻ and H⁺ into account for the screening, and the later considers only H⁺ as screening ions. These values are compared to the experimental Debye length $\kappa_{\rm exp}^{-1}$ obtained from the DLVO calculations in Fig. 7.3 (Tab. 7.1). At 0.05 mM HSiW, $\kappa_{\rm exp}^{-1}$ is well reproduced by $\kappa_{\rm ion}^{-1}$. At 0.5 mM HSiW, $\kappa_{\rm exp}^{-1}$ is in between the ion and the colloidal particle case, while at 2.5 mM HSiW $\kappa_{\rm exp}^{-1}$ is identical to $\kappa_{\rm colloidal \ particle}^{-1}$. These results indicate that the behavior of the nano-ion HSiW (like an ion or like a colloidal particle) depends on its concentration and can be described as a classical ion at low concentrations and transitions to a colloidal particle at high concentrations.

Analogous to the SANS measurements, the effect of NaCl-addition on foam films containing 0.5 mM BrijO10 + 0.5 mM HSiW is studied (Fig. 7.5). Already the addition of 8 mM NaCl leads to a distinct change in foam film behavior: The foam film is significantly less stable compared to the ones without NaCl. Fig. 7.5 shows the disjoining pressure isotherm of 0.5 mM and 2.5 mM HSiW added as reference. Furthermore, a NBF forms around 130 Pa.



FIGURE 7.5: Disjoining pressure isotherms of 0.5 mM BrijO10 + 0.5 mM HSiW with 2 mM HSiW, 4 mM NaCl and 8 mM NaCl. The horizontal marks on the y-axis indicate the maximal disjoining pressure Π_{max} . The inset shows the formed NBF with 8 mM NaCl added. The scale bar is 40 µm.

The added salt turned the sample turbid and lead to precipitation, which occurs as bright inhomogeneities (precipitated flakes and excess liquid surrounding them) inside the NBF (image in Fig. 7.5). The inhomogeneities reflects more light than the surrounding NBF, thus the measured total light intensity is higher as without precipitate. The size of the inhomogeneities is in the order of 10 to $40 \,\mu\text{m}$, and the averaged area analyzed by the photomultiplier is $20 \times 20 \,\mu\text{m}^2$. According to eq. 3.5, the higher intensity leads to an apparent higher film thickness $(h \sim 20 \,\mathrm{nm})$ as expected for the NBF ($h \sim 10 \,\mathrm{nm}$ as for the bare BrijO10). In contrast to the foam film of $0.5 \,\mathrm{mM}$ BrijO10 + 10 mM HSiW ($h \sim 20 \,\mathrm{nm}$, Fig. A.30), which is probably sterically stabilized by trapped micelles, the foam film with 8 mM NaCl resembles more closely a classical NBF (sterically stabilized by the BrijO10 loaded interfaces). We distinguish these two cases here by the presence or absence of Newton rings around the foam film: for NBFs the Newton rings are merged due to the high contact angle between the foam film and the surrounding bulk liquid and thus not observed.¹⁹¹ This absence of Newton rings is only the case for the black films with 8 mM NaCl and not with 10 mM HSiW (Fig. 7.6). Thus, 8 mM NaCl is above the critical salt concentration for the CBF -- NBF transition³⁹ in this system. Furthermore, the NBF hints to the absence of micelles inside the foam film before rupture.


FIGURE 7.6: Images of foam films formed by 0.5 mM BrijO10 + 0.5 mM HSiW + 8 mM NaCl (a) + b)) and BrijO10 + 10 mM HSiW (c) + d)).
b) and d) show enlargements of the marked areas on a) and c). A NBF -- CBF transition is shown in a). Precipitation is visible in the liquid around the foam film (especially in upper right part). On b) the absence of Newton rings for the NBF and their presence for the CBF are noticeable.

In contrast, adding 4 mM NaCl leads to a clear solution and a stable foam film (light gray circles in Fig. 7.5). The disjoining pressure isotherm resemble the one of 0.5 mM BrijO10 + 2.5 mM HSiW in thickness and slope. This overlap underlines the above finding on the behavoir as collodial partical: 4 mM NaCl results in the same screening length as 2 mM HSiW, if only the H⁺ contribute to the screening. The foam film stability Π_{max} decreases with NaCl: $\Pi_{\text{max}, 4 \text{ mM} \text{ NaCl}} = 8167 \text{ Pa}$ compared to $\Pi_{\text{max}, 0.5 \text{ mM} \text{ SiW}} = 9081 \text{ Pa}$ and $\Pi_{\text{max}, 2.5 \text{ mM} \text{ SiW}} = 10.647 \text{ Pa}$. The existence of a critical salt concentration above which a CBF transforms into a NBF is a characteristic of foam films stabilized by ionic surfactants.⁴³ The above results confirm the charging of interfaces *via* adsorption of SiW as NaCl is able to screen the electrostatic repulsion and leads to a NBF.



FIGURE 7.7: Images of foam films of 0.5 mM BrijO10 in the presence of 0.5 mM HSiW at 388 Pa (a) and in the present of 2.5 mM HSiW at 373 Pa (b). Images were digitally post-processed. BAM image of 0.5 mM BrijO10 + 0.5 mM HSiW (c). The times refer to purring the solution into the Teflon trough. The scale bar is 100 µm.

Foam film appearance In contrast to the foam films of bare BrijO10 (Fig. 7.4), the foam films of BrijO10 with HSiW or NaCl added appear not completely homogeneous. They show seaweed-like surface structures (Fig. 7.7a and b with HSiW and Fig. A.29 with 100 mM NaCl). Unlike the precipitation occurring with 8 mM NaCl added, these surface structures form only within the foam film and are not visible in the bulk liquid surrounding the foam film (Fig. 7.6). The slight brightness difference results in a certain uncertainty of the thickness determination (Fig. A.31 shows images without digital post-processing). An image analysis revealed an approximate thickness difference of $\sim 1 - 2$ nm between the formed structure and the surrounding foam film. These values lie within the uncertainty of averaging over individual measurements. Another explanation might be a local variation in refractive index.

To investigate the structures further, BAM measurements were performed and flowerlike brighter domains were found to form and grow with time (Fig. 7.7c and Fig. A.32). Since these domains have a different refractive index than the surrounding liquid and do not compress under contact, they are probably a more rigid liquid condensed phase of BrijO10. The adsorbed BrijO10 self-assemblies at the interface and forms these closer packed flower-like domains. Adding HSiW or NaCl promotes this selfordering. Such self-ordering, phase separation and domain formations of non-ionic surfactants¹⁶⁸ and higher alkanes¹⁶⁹ were formerly reported. BrijO10 is a polydisperse non-ionic surfactant and contains several $C_{18-1}E_n$ fractions, which might account for the observed self-ordering or phase separation at the interface. Simple foam extraction reduces the domain formation at the interface. The process may be similar to flotation as the fractions of BrijO10 are separated by their surface activity. It should be noted that these domains form at equilibrated (foam film) interface on a time scale of tens of minutes. Thus, they not necessarily form in macroscopic foams with their highly dynamic interfaces.

7.3.3 Combining SANS and TFPB results with a stabilization mechanism

Before the effect of HSiW on foam and foam films of BrijO10 are discussed, differences between the used measurement techniques are addressed. TFPB and SANS exhibit the same trends in the film thickness with HSiW concentration, but the determined thickness values differ for the two methods. Apparently, no NBF $(h \sim 10 \text{ nm})$ forms in the macroscopic foam of bare BrijO10, which is probably because of the different conditions of the films within a foam and single foam films. The macroscopic foam and its films are out of equilibrium and therefore constantly evolve, while the single foam films are measured in thermodynamic equilibrium under well-defined conditions (constant applied pressure). Further, the contrast of the film within TFPB and SANS measurements is different and thus leads to different film thicknesses. In TFPB experiments, a uniform refractive index is assumed within the foam film to calculate h. This thickness includes the adsorbed layer of BrjiO10 (especially the aliphatic chains in the air phase). In SANS experiments, the film thickness arises from the contrast of D_2O and air (difference in SLD). Thus, solely the thickness of the water layer is considered, while the length of the surfactant chains dangling in air is neglected (Fig. 7.8a)). To correct this experimental difference, twice the length of the aliphatic chains of BrjiO10 was subtracted from $h \ (l_{\text{chain}} \approx 2.4 \,\text{nm}, \text{ calculated})$ with Tanford's formula¹⁹², 2 x $l_{\text{chain}} \approx 5 \text{ nm}$). Note that a similar reduction results from correction according to the three-layer-model including the refractive indices of the chain and head group of BrijO10^{111,193}. For the equimolar sample (same concentration of BrijO10 and HSiW; $c_{\text{BrijO10 / HSiW}} = 0.5 \text{ mM}$), a modified disjoining pressure isotherm reaches h_{SANS} of 35 nm (Fig. 7.2) around 1000 Pa (Fig. 7.8b). To estimate an average pressure with the foam, the capillary pressure Π_{Ca} is estimated from the surface tension γ , the bubble diameter d and the liquid fraction $\phi_{\rm l}$ of the $foam^5$:

$$\Pi_{\rm Ca} \approx \frac{\gamma}{d \cdot \sqrt{\phi_{\rm l}}} \tag{7.1}$$

The equilibrium surface tension of the equimolar sample lies around 33 mN/m^{19} . After drainage, the foam is very dry ($\phi_{l} \sim 0.5 - 2$ % can be assumed). The bubble size is not constant as foam collapses and forms during the experiment and bubble



FIGURE 7.8: a) Sketch of foam film thicknesses detected by different methods. Left: by TFPB assuming an uniform refractive index over the whole foam film, and right: by SANS being sensitive for the SLD difference between D₂O (SLD = $6.34 \times 10^{-6} \text{ Å}^{-2}$) and air (SLD = $0 \times 10^{-6} \text{ Å}^{-2}$). For SANS, the low volume fraction of BrijO10 (0.035% v/v) and the low SLD value (SLD $\approx 0.27 \times 10^{-6} \text{ Å}^{-2}$) results in a low contrast between air and the dangling chains. b) Disjoining pressure isotherm of 0.5 mM BrijO10 + 0.5 mM HSiW as well as a modified isotherm. h_{SANS} correspond to the thickness determined for the macroscopic foam of the sample.

growth / collapse is a stochastic process. However, an average bubble radius of (0.4 ± 0.2) mm was determined¹⁹. Taking these values into account, a $\Pi_{\rm Ca}$ in the order of 1000 Pa is plausible. Hence, by considering the difference of the methods, the obtained values of the film thicknesses in single foam films and in the foams coincide.

The measurements on macroscopic foam, foam films and single foam films give a consistent picture of the impact of HSiW on BrijO10 foams. Without HSiW, BrijO10 adsorbed at the air / liquid interfaces leads to foam films mostly stabilized by steric forces (NBF). The addition of HSiW then results in mixed SiW / BrijO10-interfaces, where SiW adsorbs between the ethoxylated surfactant head groups due to the chaotropic effect¹⁹. The adsorption of SiW generates charged interfaces, thus electrostatic double layer forces stabilize the foam film (CBF). The electrostatic repulsion



FIGURE 7.9: Foam half-life time $t_{1/2}$ as a function of the maximal disjoining pressure Π_{max} of a single foam film. The foam half-life times were calculated from the decay of the foam volume (Fig. 7.1).

results in thicker foam films as observed in both TFPB and SANS experiments. Further added HSiW (> 0.5 mM) thins the foam films presumably due to a self-screening effect: Once the BrijO10-interface is saturated with SiW (at ~ 0.5 mM HSiW), additional HSiW is forced into solution and screens the electrostatic double layer repulsion between the two interfaces – comparable with added NaCl. Furthermore, a steric stabilizing force probably due to attached micelles is dominant at high Π . Hence, the character of foam film stabilization of BrijO10 changes upon HSiW addition: from sterically stabilized by the BrijO10 loaded interfaces over electrostatically stabilized by the charged interfaces to sterically stabilized by trapped micelles.

To quantify the foam lifetime, the commonly used foam half-life time $t_{1/2}$, denoting the time after which the foam decays to half its initial volume^{7,194}, was calculated from the foam decay (Fig. 7.1). Fig. 7.9 shows the obtained $t_{1/2}$ as function of the single foam film stability (Π_{max}). The foam stability of 0.5 mM BrijO10 + 0.5 mM HSiW + 20 mM NaCl is correlated with the single foam film stability of the sample with only 4 mM NaCl added, since a higher amount of salt resulted in an (unstable) NBF (Fig. 7.5). As the values do not correspond to the samples of the same composition, they are bracketed. Nevertheless, $t_{1/2}$ overall correlates well with the maximal disjoining pressure Π_{max} inside a single foam film.

The data raise the question why the stability of foam films increases with added HSiW even when the electrostatics are screened. The present study of single foam films revealed an additional steric stabilization, presumably due to trapped micelles in the foam films. These micelles can act as a reservoir of surfactant close to the interfaces. Hence, there is a high accessibility of surfactants in the subinterfacial region enabling a fast exchange of surfactant between interface and the foam film bulk resulting in fast self-mending of the surfactant covered interface. Furthermore, the excess of surfactants compared to a single air / liquid interface easily stabilizes new interfacial areas due to dampened spatial fluctuations.¹⁹⁵ Such deformations create surface tension gradients inducing foam film rupture. For surface-active alcohols, a fast diffusion of molecules from the subinterfacial region to the interface imposes a buffering effect on surface tension gradients created by interfacial expansion.¹⁹⁶ The presence of micelles as well increases the resistance of the foam films against mechanical disturbances or local depletion zones due to monolayer density fluctuations.¹⁹⁵ During foam collapse, bubbles continuously reorganize, which can lead to film rupture when newly created films areas are not sufficiently covered by surfactants.¹⁹⁷ The availability of surfactants in the subinterfacial region enables a self-healing mechanism preventing the foam films from rupture. Furthermore, the gas permeability (including diffusion and solubility) of the foam films might be affected by the high surfactant concentration due to the trapped micelles, which hinders coarsening and hence further stabilizes the macroscopic foam.

Despite the suggested presence of micelles in the single foam films, no stratifications are observed. Instead, their presence results in long-range steric repulsion. The micelles are not pushed out of the single foam film upon compression, but rather stick to the interfaces and bridge between them. A possible explanation for these trapped micelles may be the H⁺ counterions of SiW. Hydrated H⁺ (H₃O⁺ or H₅O₂⁺) were recently shown to act as promoters for the co-assembly of POMs and a non-ionic glycol ether by SAXS measurements.¹⁹⁸ One might speculate that in a similar way hydrated H^+ and SiW act as molecular glue between micelles and the interfaces. Hence, the micelles remain in the confined films and no stratification occurs. The observed NBF with 8 mM NaCl added suggest that the trapping of micelles at the interface can be suppressed with higher NaCl content, where micelles agglomerate and precipitate, reducing the number of micelles in the liquid. An interesting question arises: how does the counterion of SiW affect this stabilization effect, if hydrated protons promotes the trapping of micelles? The observed destabilization with added NaCl hints to unstable foam films. Without the reservoir of surfactants, we expect a dramatic change as well in macroscopic foam lifetime, when using e.q. NaSiW instead of HSiW.

The present work revealed the astonishing foam stabilization mechanism of chaotropic nano-ions. For many studied systems (P/S mixtures, proteins or mircogels) usually discrepancies are found between the macroscopic foam stability and the stability of single foam films because the different length scales are studied individually.⁷ In contrast, the present study shows a direct correlation between the dynamic foam stability on the one hand and the static foam film stability on the other hand. Thus the present work underpin not only the necessity of multi-scale approaches but also the importance of coordinating the systems and measurements to elucidate foams at all length scales in order to understand their properties and tailor their performance.

7.4 Conclusion

A multi-scale approach is used to study the impact of the nano-ion HSiW on foams and foam films of the non-ionic surfactant BrijO10. Macroscopic foams were investigated by SANS and foam scans, and single foam films by TFPB technique. Consistent results were obtained: because of its superchaotropic nature, SiW adsorbs on BrijO10 and thereby charges the interfaces. This charging mechanism is directly proved by the transition from a sterically stabilized NBF to a CBF stabilized by electrostatic double layer forces. Above the adsorption saturation, HSiW is forced into the bulk and auto screens the repulsion between charged interfaces and thus leads to thinner foam films. Furthermore, micelles trapped inside the foam film lead to an additional long-range steric stabilization. These micelles act as a reservoir of excess surfactant in the subinterfacial region making the foam films more resistant to disturbances and thus leading to stable macroscopic foams.

Chapter 8

General conclusion and future perspectives

Summary and conclusion The present thesis focuses on foam films of mixtures of charged components ((poly)electrolytes) with surfactants. Two different systems were studied: oppositely charged polyelectrolyte / surfactant (P/S) mixtures and mixtures of a non-ionic S and a Keggin polyoxometalate (POM). Particular attention was given to the structure of a foam film: can it be considered as only two interacting air / liquid interfaces? By finding a significant impact of the foam film bulk on *e.g.* the commonly obtained *apparent* surface potential and stability of foam films for both systems, the answer is no, it can not. For obtaining this answer, the different length scales of foam films were elucidated: from a single air / liquid interface, over bulk solutions and the foam films, to macroscopic foams.

The first part of this thesis looked at the single air / liquid interface of two different P/S mixtures: $sPSO_2-220 / C_{14}TAB$ and $PSS / C_{14}TAB$. Using tensiometry and neutron reflectometry, their surface activity, surface composition, and especially the structures formed at the interface were elucidated. $sPSO_2-220 / C_{14}TAB$ mixtures form extended structures around the bulk stoichiometric mixing point (BSMP), which are suppressed with increasing ionic strength (*i.e.* by a higher P concentration or a higher salt concentration). In contrast, $PSS / C_{14}TAB$ mixtures form only monolayers. By comparing the two mixtures, the main driving force for the formation of extended structures was revealed: a gain in entropy by reaching an interfacial P:S ratio of 1. Increasing the flexibility of the P (*via* increasing the ionic strength or using the more

flexible PSS) enables the P to reach that favored P:S ratio in a monolayer structure. Hence, the formation of the extended structures is suppressed.

The second and third part focused on the foam films of the sPSO₂-220 / C₁₄TAB mixtures. Their stability depends on both the sPSO₂-220 and LiBr concentration. *Below* the BSMP, unstable foam films are formed irrespective of the salt content added. *Above* the BSMP, stable foam films form. A low amount of added LiBr destabilizes the foam films, whereas a high amount of added LiBr leads to a stabilization. This stabilizing effect was attributed to a steric contribution of the bulk sPSO₂-220 / C₁₄TAB complexes. The obtained *apparent* surface potential Ψ_{app} seems to be more affected by the bulk complexes than by the single air / liquid interfaces and represents a projection of all charged components inside the foam film.

It was found that fully covered interfaces do not necessarily lead to stable foam films: *around* the BSMP the addition of LiBr results in the formation of unstable NBFs -for the first time seen for the used combination of cationic S and anionic P.

For mixtures containing 10^{-3} M LiBr the effect of a longer storage time (~ 1 month) was elucidated. The formation of sedimenting larger P / S aggregates was found to affect both the mixtures' surface activity as well the foam film stability.

The formerly used framework for understanding foam film stability, based solely on the two facing air / liquid interfaces and their structures, was updated: the charge of the P / S complexes is now taken into account. For stable foam films a minimum charge of the complexes is necessary.

In the last part, mixtures of the non-ionic S BrijO10 and the Keggin POM HSiW were studied. By combining the results of single foam film measurements and macroscopic foam measurements, the foam stabilizing mechanism of HSiW was elucidated. First, SiW charges the air/liquid interfaces *via* its adsorption. Above the adsorption saturation, HSiW auto screens the charged interfaces and thus leads to thinner foam films. Second, BrijO10 micelles are trapped inside the foam films and sterically stabilize them. The micelles act as reservoir of excess surfactant in the subinterfacial region making the foam films more resistant to disturbances and thus leading to stable macroscopic foams. These findings underline the relevance of the foam film bulk for both the foam films and the macroscopic foams. One has to distinguish between the film bulk and the bulk solution: The presence of micelles probably results from the confinement of the two air/liquid interfaces and may not be seen for a single free air/liquid interface. The measurements demonstrate the importance of multi-scale approaches for the understanding of foams. To summarize, this thesis provides a better understanding of foam films: the popular picture of foam films being the combination of two single air / liquid interfaces does not apply anymore. In contrast, the foam film bulk in between them plays a critical role.

Future perspectives This thesis answered former questions about the relevance of the foam film bulk for the stability of foam films. Furthermore, the questions why P/S mixtures form different structures at the air / liquid interface and how HSiW stabilizes non-ionic S foams were answered. However during the work on the thesis new questions and interesting aspects arose.

The structure of foam film bulk sometimes differs from the one of solution bulk as the confinement of the two facing air / liquid interfaces may impact the structures and properties. Consequently, there is a need for *in-situ* methods studying both the surface structures and the film bulk inside a foam film. A possible instrumental setup could be the combination of neutron scattering and the TFPB instrument. That way *e.g.* NR studies could give information on how the interfacial structures are affected by the second air / liquid interface. By *e.g. in-situ* SANS measurements one could prove the presence of S micelles or P / S complexes inside foam films. However for these ideas some hindrances have to be overcome: starting from a required high flux and/or long measuring time for SANS due to the thin sample (thickness ~100 nm and less) to using the same pathway for the neutrons giving the SANS signal and the light for imaging and thickness determination *via* the TFPB (as the same volume should be probed) following the question of detector positioning.

Another relevant aspect is the surface or film elasticity which represent a measure of the capability to stabilize the foam film after deformation. For simple S solutions, surface elasticity seems to explain variations in foam film stability⁵², but for the more complex P/S mixtures surface elasticity failed to rationalize it⁸⁵. Film elasticity calculations are often based on parameters obtained from adsorption isotherms at a single air/liquid interface. Recent studies already follow an approach to *in-situ* measure the film elasticity by using a deformable frame to deform several connected foam films and found differences to the unconfined geometries of S solutions.¹⁹⁹ Combining such measurements with a TFPB could be a promising step to overcome the shortcuts of connecting surface elasticity with foam film properties. Up to this day, extended structures of P/S mixtures remain in the focus of interest: recently published are insights on the control of the coverage of extended structures due to compression and expansion in a Langmuir trough.²⁰⁰ Keeping in mind their application as hair conditioner or in mineral froth flotation, the question arises if similar structures could as well form at solid / liquid interfaces and if they are stable at these interfaces.

Regarding the study on HSiW and the question of its classification as colloidal particles, CP-AFM measurements would be helpful to further clarify this question. With CP-AFM bare HSiW samples and their screening ability can be investigated. Thus, no adsorption on BrijO10 interfaces could interfere with the measurement. Furthermore, the found self-ordering of BrijO10 upon addition of rather low amount of HSiW or higher amount of NaCl opens a novel and promising field of research. How does the structure of the rigid parts differ from the surrounding liquid on a molecular level? Are SiW⁴⁻, Na⁺, or Cl⁻ acting as nucleation seeds for the ordering at the interface? How can one control the self-ordering? Is this phenomenon restricted to BrijO10 or does it also appear for other polydisperse Ss?

Appendix A

Scientific appendix

A.1 Fluctuations of the foam film stability

It should be mentioned that fluctuations in the foam film stability occur between individual measurements of the same sample (on the time scale of days). Some foam films were more stable than other. A particular affected sample was the mixture containing 6×10^{-4} monoM sPSO₂-220, 10^{-4} M C₁₄TAB and 10^{-3} M LiBr. The stability (Π_{max}) varied from 130 Pa to 2300 Pa. No clear correlation between *e.g.* the age of the sample or number of measurement per day could be found. Also shaking of the sample prior to each measurement did not affect the stability fluctuations. However, there was the slight impression that the foam films would become more stable over couple of days. The thickness and its pressure dependency of the foam films were unaffected by these stability fluctuation, Fig. A.1 shows examples of individual measured disjoining pressure isotherms and the resulted averaged disjoining pressure isotherm for the sample containing 6×10^{-4} monoM sPSO₂-220, 10^{-4} M C₁₄TAB and 10^{-3} M LiBr. Above ~ 300 Pa all measured disjoining pressure isotherms overlap. This thesis shows the averaged disjoining pressure isotherms - if not stated other and the used Π_{max} values are reproducible values.



FIGURE A.1: Disjoining pressure isotherms of foam film formed by $sPSO_2-220 / C_{14}TAB$ mixtures $(c_{sPSO_2-220} = 6 \times 10^{-4} \text{ monoM}, c_{C_{14}TAB} = 10^{-4} \text{ M})$ with $c_{\text{LiBr}} = 10^{-3} \text{ M}$. The open symbols correspond to different individual measurements and the fulled ones to the averaged data points. The horizontal lines on the x-axis indicate the maximal disjoining pressure Π_{max} for each individual measurement.

A.2 Effect of LiBr on foam films formed by C₁₄TAB

Fig A.2 shows the disjoining pressure isotherms of foam film formed by pure $C_{14}TAB$ solutions $(c_{C_{14}TAB} = 10^{-4} \text{ M})$ containing different amounts of LiBr added $(c_{\text{LiBr}} = 0 - 10^{-2} \text{ M})$. The LiBr added thins the foam films and reduces the foam films stability $(\Pi_{\text{max}} \text{ depicted as horizontal lines at the x-axis in Fig A.2})$. Both finding are in line with a reduced electrostatic repulsion between the two air / liquid interfaces because of the screening effect of the salt.



FIGURE A.2: Disjoining pressure isotherms of foam films formed by $C_{14}TAB$ $(c_{C_{14}TAB} = 10^{-4} \text{ M})$ for different LiBr concentration $(c_{\text{LiBr}} = 0 - 10^{-2} \text{ M})$. The horizontal lines on the x-axis indicate the maximal disjoining pressure Π_{max} . Data without added salt are reprinted with permission from Ref 80. Copyright 2009 American Chemical Society.

A.3 Optical density of freshly mixed P/S mixtures



FIGURE A.3: UV-vis spectra of selective s PSO₂-220 / $\rm C_{14}TAB$ mixtures containing $10^{-2}\,\rm M$ LiBr.

Fig. A.3 exemplarily shows the UV-vis spectra of selective $sPSO_2-220 / C_{14}TAB$ mixtures containing 10^{-2} M LiBr 5 min after mixing. The values at $\lambda = 400$ nm are used to calculate the optical density of the mixtures (Fig. A.4).



FIGURE A.4: Optical density of freshly mixed P / S mixtures studied in this thesis containing different salt concentration. The vertical dotted line marks the BSMP.

The overall low OD_{400} values indicate no formation of larger P / S aggregates for the freshly mixed mixtures.

A.4 Appendix for chapter 4

sPSO₂-220 / C₁₄TAB mixtures



FIGURE A.5: Examples of neutron reflectivity data and model fits recorded in the low Q-range for samples with $c_{sPSO_2-220} = 10^{-5}$ monoM (green), 8×10^{-5} monoM (red), and 3×10^{-3} monoM (blue) and $c_{C_{14}TAB} = 10^{-4}$ M cm- $C_{14}TAB$ (dark) or d- $C_{14}TAB$ (light) in ACMW. Right with $c_{LiBr} = 10^{-2}$ M, middle with $c_{LiBr} = 10^{-4}$ M and left with $c_{LiBr} = 10^{-3}$ M.



FIGURE A.6: Surface excess of sPSO₂-220 (blue) and C₁₄TAB (orange) and surface tension for sPSO₂-220 / C₁₄TAB mixtures as a function of the sPSO₂-220 concentration with $c_{LiBr} = 10^{-4}$ M (a) and with $c_{LiBr} = 10^{-3}$ M (b). The horizontal solid line corresponds to the surface excess for a pure C₁₄TAB solution ($c_{C_{14}TAB} = 10^{-4}$ M). The horizontal dashed line corresponds to the surface tension of pure C₁₄TAB solution ($c_{C_{14}TAB} = 10^{-4}$ M). The vertical dotted lines mark the BSMP.

Low Q_z analysis



FIGURE A.7: Below the BSMP: a) reflectivity data of sPSO₂-220 / C_{14} TAB mixtures with a sPSO₂-220 concentration of 10^{-5} monoM with 10^{-4} M LiBr (top) and with 10^{-3} M LiBr (down). Solid lines correspond the model fits. b) Volume fraction profiles of sPSO₂-220 / C_{14} TAB mixtures with a sPSO₂-220 concentration of 10^{-5} monoM with 10^{-4} M LiBr (solid lines) and with 10^{-3} M LiBr (dashed lines). For the color code see sketch on the top.



FIGURE A.8: Around the BSMP: a) Reflectivity data of $sPSO_2-220 / C_{14}TAB$ mixtures with a $sPSO_2-220$ concentration of 8×10^{-3} monoM without LiBr. Solid lines correspond the model fits. Fits are optimized the d-C₁₄TAB contrasts (top) and the h-/cm-C₁₄TAB contrasts (down), respectively. b) Volume fraction profiles of $sPSO_2-220 / C_{14}TAB$ mixtures with a $sPSO_2-220$ concentration of 8×10^{-3} monoM without LiBr added, solid lines correspond to the fits for the d-C₁₄TAB contrasts and dashed lines to the fit of the h-/cm-C₁₄TAB contrasts. For the color code see sketch on the top.

Full $\mathbf{Q}_{\mathbf{z}}$ **analysis** Fig. A.12 shows the reflectivity data measured for 4 contrasts as well as the obtained volume fraction profiles *above* the BSMP without added LiBr. Once the fits are optimized for a compact monolayer structure (upper panel of



FIGURE A.9: Around the BSMP, 10^{-4} M LiBr added: a) reflectivity data of sPSO₂-220 / C₁₄TAB mixtures with a sPSO₂-220 concentration of 8×10^{-3} monoM. Solid lines correspond the model fits. Fits are optimized for the ACMW contrasts (top) and D₂O contrasts (down). b) Volume fraction profiles of sPSO₂-220 / C₁₄TAB mixtures, solid lines correspond to the fits for the ACMW contrasts and dashed lines to the fits of the D₂O contrasts. For the color code see sketch on the top.



FIGURE A.10: Around the BSMP, 10^{-4} M LiBr added: a) reflectivity data of sPSO₂-220 / C₁₄TAB mixtures. Fits are optimized for the d-C₁₄TAB contrasts (top) and the h-/cm-C₁₄TAB contrasts (down), respectively. Solid lines correspond to the model fits. b) Volume fraction profiles of sPSO₂-220 / C₁₄TAB mixtures, solid lines correspond to the fits for the d-C₁₄TAB contrasts and dashed lines to the fit of the h-/cm-C₁₄TAB contrasts. For the color code see sketch on the top.

Fig. A.12a and solid lines in Fig. A.12b) and once optimized for a swollen monolayer structure (lower panel of Fig. A.12a and dashed lines in Fig. A.12b).



FIGURE A.11: Around the BSMP: a) reflectivity data of $sPSO_2-220 / C_{14}TAB$ mixtures with 10^{-3} M LiBr (top) and 10^{-2} M LiBr (down). Solid lines correspond to the model fits. b) Volume fraction profiles of $sPSO_2-220 / C_{14}TAB$ mixtures with 10^{-3} M LiBr (solid lines) and 10^{-2} M LiBr (dashed lines). For the color code see sketch on the top.



FIGURE A.12: Above the BSMP: a) reflectivity data of sPSO₂-220 / C₁₄TAB mixtures with a sPSO₂-220 concentration of 3×10^{-3} monoM without added salt. Top: optimized fit for a compact monolayer structure with a $\chi^2 = 4.8$ and down: optimized fit a swollen monolayer structure with $\chi^2 = 15.9$. b) Volume fraction profiles of sPSO₂-220 / C₁₄TAB mixtures, solid lines correspond to the fits optimized for compact monolayer and dashed lines to the fits optimized for the swollen monolayer. For the color code see sketch on the top.

$PSS / C_{14}TAB$ mixtures

Low Q_z analysis



FIGURE A.13: Above the BSMP: a) reflectivity data of $sPSO_2-220 / C_{14}TAB$ mixtures with a $sPSO_2-220$ concentration of 3×10^{-3} monoM with 10^{-4} M LiBr (top) and with 10^{-3} M LiBr (down). Solid lines correspond the model fits. b) Volume fraction profiles of $sPSO_2-220 / C_{14}TAB$ mixtures with a $sPSO_2-220$ concentration of 3×10^{-3} monoM with 10^{-4} M LiBr (solid lines) and with 10^{-3} M LiBr (dashed lines). For the color code see sketch on the top.



FIGURE A.14: Examples of neutron reflectivity data and model fits recorded in the low Q_z range for samples with $c_{PSS} = 10^{-5}$ monoM (green), 8×10^{-5} monoM (red) and 3×10^{-3} monoM (blue) and $c_{C_{14}TAB} = 10^{-4}$ M cm-C₁₄TAB (dark) or d-C₁₄TAB (light) in ACMW with $c_{NaBr} = 10^{-2}$ M. Star shaped symbols correspond to data without added NaBr. Part of the data without added salt were measured during an earlier beam time (10.5291/ILL-DATA.9-12-381) and are not shown here.

Full Q_z **analysis** Fig. A.15 shows the reflectivity data and volume fraction profiles *below* the BSMP for the PSS / C₁₄TAB mixtures without added salt. The upper panel of Fig A.15a as well the solid lines in Fig. A.15b correspond to the fit

TABLE A.1: Overview of PSS concentrations of the samples measured over the full Q_z range for PSS / C₁₄TAB mixtures, $c_{C_{14}TAB} = 10^{-4} M$

	$< \mathrm{BSMP}$	> BSMP		
$c_{\rm NaBr}=0{\rm M}$	$3 \times 10^{-5} \mathrm{monoM}$	$10^{-3}\mathrm{monoM}$		
$c_{\rm NaBr}=10^{-2}\rm M$	$10^{-5}\mathrm{monoM}$	$3 \times 10^{-3} \mathrm{monoM}$		

TABLE A.2: Characteristics of the PSS layer for the full Q_z analysis of the three different contrasts: central position of the layer $z_{c,PSS}$ in Å, thickness d_{PSS} in Å, and surface excess Γ_{PSS} in $10^{-6} \text{ mol m}^{-2}$; $c_{PSS} = 10^{-5} \text{ monoM}$, $c_{NaBr} = 10^{-2} \text{ mol}$.

	$d-C_{14}TAB / ACMW$	d- $C_{14}TAB / D_2O$	$h-C_{14}TAB / D_2O$
$z_{ m c,PSS}$	25.7	18.0	30.8
$d_{\rm PSS}$	22.7	6.1	43.5
$\Gamma_{\rm PSS}$	4.4	1.3	8.6

TABLE A.3: Γ obtained from low Q_z and full Q_z analysis methods, given in $10^{-6} \text{ mol m}^{-2}$.

		$\Gamma_{C_{14}TAB}$		$\Gamma_{\rm PSS}$	$\Gamma_{\rm PSS}$		
	c_{NaBr}	low $Q_{\rm z}$	full $Q_{\rm z}$	low $Q_{\rm z}$	full $Q_{\rm z}$		
below BSMP	0 M	3.20	3.05	2.65	2.25		
	$10^{-2}\mathrm{M}$	3.24	3.25	4.08	$4.40^{\rm a}$		
$above \ \mathrm{BSMP}$	$0 \mathrm{M}$	0.64	0.62	0.57	0.61		
	$10^{-2}\mathrm{M}$	2.24	2.31	2.85	2.69		
^a Value given for the d C TAR / ACMW contract							

^{ι} Value given for the d-C₁₄TAB / ACMW contrast

optimized for the d- $C_{14}TAB / D_2O$ fit. The lower panel in Fig. A.15a as well the dashed lines in Fig. A.15b correspond to the fit optimized for the h- $C_{14}TAB / D_2O$ fit.

Fig. A.16 shows the reflectivity data and volume fraction profiles *around* the BSMP for the PSS / C_{14} TAB mixtures. Even if the shown fits not fully describe all contracts, the reflectivity data show no hint (pronounced fringe) for a more extent structure than a monolayer of C_{14} TAB and PSS.

Fig. A.17 shows the P/S ratio in dependence of c_{PSS} with and without added NaBr obtained from the measured Γ_{PSS} and $\Gamma_{C_{14}\text{TAB}}$. Due to the low amount of adsorbed S *above* the BSMP without salt, the ratio is very high and not shown in the figure. Although the data scatter, the ratio do not follow a trend (neither with increased c_{PSS} nor c_{NaBr}) and presumably maintain at values around 1.



FIGURE A.15: Below the BSMP: a) reflectivity data of PSS / C_{14} TAB mixtures with 0 M NaBr. Solid lines correspond the model fits optimized for the d- C_{14} TAB / D_2O (top) and the h- C_{14} TAB / D_2O contrast. b) Volume fraction profiles of PSS / C_{14} TAB mixtures with 0 M NaBr. For the color code see sketch on the top.



FIGURE A.16: Around the BSMP: a) reflectivity data of PSS / C_{14} TAB mixtures with 0 M NaBr (top) and with 10^{-2} M NaBr (down). Solid lines correspond the model fits. b) Volume fraction profiles of PSS / C_{14} TAB mixtures with 0 M NaBr (solid lines) and with 10^{-2} M NaBr (dashed lines).

TABLE A.4: Surface tension values given in mN/m of the pure polyelectrolyte solution with the respective salt concentration.

	sPSC	0 ₂ -220	PSS		
$c_{\rm P}/~{\rm monoM}$	10^{-5}	$3x10^{-3}$	10^{-5}	10^{-3}	
no salt	71.5 ± 0.1	72.5 ± 0.2	72.7 ± 0.1	72.1 ± 0.1	
$c_{\rm salt}{=}10^{-2}{\rm M}$	72.8 ± 0.1	72.8 ± 0.1	72.7 ± 0.1	72.9 ± 0.2	

Additional surface tension measurements



FIGURE A.17: Ratio of the adsorbed PSS monomers to adsorbed C_{14} TAB molecules as function of c_{PSS} without and with 10^{-2} M NaBr. The data are calculated from Fig. 4.9.

Ellipsometry measurements Ellipsometry measurements were performed to validate the different adsorbed amount (Γ_{PSS}) raveled by NR for the differed contrasts of the sample PSS / C₁₄TAB *below* the BSMP containing 10⁻² M NaBr. Tab. A.5 shows the changes $\delta \Delta$ and $\delta \Psi$ of the ellipsometric angles with respect to the bare interfaces.

TABLE A.5: Results of the ellipsometry measurements together with Γ_{PSS} , given in $10^{-6} \text{ mol m}^{-2}$, as obtained from the full Q_z fit for three different deuteration schemes.

	d- $C_{14}TAB / ACMW$	d- $C_{14}TAB / D_2O$	h- $C_{14}TAB / D_2O$
$\delta \Delta$	1.29°	1.33°	1.87°
$\delta \Psi$	0.04°	0.008°	0.013°
$\Gamma_{\rm PSS}$	4.4	1.3	8.6

Indeed, the measured values differ between the different deuteration schemes, in particular $\delta \Delta$, which is most sensitive to variations in thicknesses of thin layers. To a first approximation, $\delta \Delta$ is proportional to the surface excess²⁰¹, thus we obtained different surface excesses for different deuteration schemes. Especially, for h-C₁₄TAB / D₂O we find both the highest $\delta \Delta$ and the highest surface excess of PSS according to the full Q_z fit. These results suggest that isotopic effects have indeed influence on the adsorption and structure of P/S mixtures at the air / liquid interface. **Discussion of isotopic effect on extended structures** We find isotopic discrepancies, which can be resolved either by paring the solvent or pairing the used kind of C_{14} TAB (Fig. A.9, A.10 and Fig. 4.6). As ACMW consist in large parts of H₂O for the following consideration it can be treated as H₂O.

Pairing the solvent suggest that hydrogen bonds are involved in the formation of extended structure as the strengths of hydrogen bonds differ in D_2O and H_2O^{146} . Hydrogen bonds to be considered here are between the oxygen atoms of sulfate groups (P) and the solvent. Furthermore, the tendency of surfactant to aggregate is higher in D_2O than H_2O as D_2O is a more structured solvent.²⁰² But, we find a higher amount of extended structure in ACMW (H₂O) than in D_2O , which suggest an other driving force for the extended structure than simple aggregation in order to reduced structured water molecules.

Pairing the kind of $C_{14}TAB$, we find the more distinct extended structure when using d-C₁₄TAB. An explanation may be the different hydrophobicities of the two chains. The higher cmc of d-C₁₄TAB (~ 4.3×10^{-3} M) compared to h-C₁₄TAB (~ 3.5×10^{-3} M) indicate a less hydrophobic alkyl chain¹⁴⁷, similar to reduced hydrophobicity of substances when H is exchanged to D¹⁴⁸. Intuitively, one could interpret the higher hydrophobicity of h-C₁₄TAB as a higher surface activity and expect more h-C₁₄TAB at the interface than d-C₁₄TAB. Thus, one would expect a stronger driving force for the interfacial self-assembly of h-C₁₄TAB. However, one could interpret the lower hydrophobicity of d-C₁₄TAB also as follows: for a surface with fixed spaces more d-C₁₄TAB than h-C₁₄TAB is required to lower the free energy by the same amount. Thus, we find a higher amount when using d-C₁₄TAB.

A.5 Appendix for chapter 5

Formation of NBFs around the BSMP



FIGURE A.18: Formation of a NBF for sPSO₂-220 / C₁₄TAB mixtures with $c_{\rm sPSO_2-220} = 10^{-4}$ monoM and $c_{\rm LiBr} = 10^{-4}$ M. The notation a) - h) denotes the progress of the formation. The time from first appearance of the NBF until it ruptures was 2.2 s.



FIGURE A.19: Formation of a NBF for sPSO₂-220 / C_{14} TAB mixtures with $c_{sPSO_2-220} = 10^{-4}$ monoM and $c_{LiBr} = 10^{-3}$ M. The notation a) - e) denotes the progress of the formation. The time from first appearance of the NBF until it ruptures was 3.1 s.



FIGURE A.20: Formation of a NBF for sPSO₂-220 / C₁₄TAB mixtures with $c_{\rm sPSO_2-220} = 3 \times 10^{-5} \, {\rm monoM}$ and $c_{\rm LiBr} = 10^{-2} \, {\rm M}$. The notation a) - j) denotes the progress of the formation. The time from first appearance of the NBF until it ruptures was 1.1 s.

Disjoining pressure isotherms and extracted Debye lengths



FIGURE A.21: Single disjoining pressure isotherms of sPSO₂-220 / C₁₄TAB mixtures ($c_{\rm sPSO_2-220} = 3 \times 10^{-5}$ monoM, $c_{\rm C_{14}TAB} = 10^{-4}$ M) with different LiBr concentrations ($c_{\rm LiBr} = 10^{-4}$ M - 10^{-2} M). Note that the measuring time for each data point was reduced to ~ 2 min in order to obtain the data. As these foam films are rather unstable and the present data have neither a good reproducible (only the most stable measurements are shown -- other exhibit only one data point) nor a adequate validity, we do not compare the slopes or do PB calculations for the samples *below* the BSMP.



FIGURE A.22: Disjoining pressure isotherms of sPSO₂-220 / C₁₄TAB mixtures $(c_{\rm sPSO_2-220} = 10^{-4} \text{ monoM}, c_{\rm C_{14}TAB} = 10^{-4} \text{ M})$ with different LiBr concentrations: a) $c_{\rm LiBr} = 10^{-4} \text{ M}$, b) $c_{\rm LiBr} = 10^{-3} \text{ M}$ and c) $c_{\rm LiBr} = 10^{-2} \text{ M}$. As all foam films are rather unstable ($\Pi_{\rm max} < 500 \text{ Pa}$) no PB calculation was done for these isotherms.



FIGURE A.23: Disjoining pressure isotherms of sPSO₂-220 / C₁₄TAB mixtures $(c_{\rm sPSO_2-220} = 2 \times 10^{-4} \text{ monoM}, c_{\rm C_{14}TAB} = 10^{-4} \text{ M})$ with different LiBr concentrations added: a) without LiBr as reference, d) $c_{\rm LiBr} = 10^{-4} \text{ M}$, c) $c_{\rm LiBr} = 10^{-3} \text{ M}$ and d) $c_{\rm LiBr} = 10^{-2} \text{ M}$. Data without LiBr added are taken from Ref. 83 with permission from the Royal Society of Chemistry. Solid lines correspond to PB calculations at constant *apparent* surface potential $\Psi_{\rm app}$. Low amounts of LiBr do not influence the thickness of the foam films or the slope of the disjoining pressure isotherm, but reduce $\Pi_{\rm max}$.

TABLE A.6: experimental Debye length κ_{exp}^{-1} extracted from the disjoining pressure isotherm and calculated $\kappa_{complex}^{-1}$ (complete dissociation and sPSO₂-220 / C₁₄TAB complex formation in a 1:1 ratio) given in nm. The *apparent* surface potentials Ψ_{app} obtained from the PB calculations are given in mV.

c_{sPSO_2-220}	$c_{\rm LiBr} = 10^{-4} \mathrm{M}$		$c_{\rm LiBr} = 10^{-3}\mathrm{M}$			$c_{\rm LiBr} = 10^{-2} {\rm M}$			
/ monoM	$\kappa_{\rm exp}^{-1}$	$\kappa_{\rm calc}^{-1}$	$\varPsi_{\rm app}$	$\kappa_{\rm exp}^{-1}$	$\kappa_{\rm complex}^{-1}$	$\varPsi_{\rm app}$	$\kappa_{\rm exp}^{-1}$	$\kappa_{\rm complex}^{-1}$	$\varPsi_{\rm app}$
$2\ge 10^{\text{-}4}$	24.8	19.3	65	12.6	9.0	55	3.4	3.0	45
$6\ge 10^{\text{-}4}$	19.4	14.4	100	9.1	8.3	75	3.4	3.0	45
10^{-3}	$/^{a}$	11.9	/	$/^{b}$	7.7	/	3.4	3.0	45

^{*a*} no κ_{exp}^{-1} extracted due to the occurrence of a stratification (Fig. A.25) ^{*b*} no κ_{exp}^{-1} extracted due to a low foam film stability ($\Pi_{max} < 500 \,\mathrm{Pa}$)



FIGURE A.24: Disjoining pressure isotherms of $sPSO_2-220 / C_{14}TAB$ mixtures $(c_{sPSO_2-220} = 10^{-3} \text{ monoM}, c_{C_{14}TAB} = 10^{-4} \text{ M})$ with different added LiBr concentrations: a) $c_{\text{LiBr}} = 10^{-4} \text{ M}$, b) $c_{\text{LiBr}} = 10^{-3} \text{ M}$ and c) $c_{\text{LiBr}} = 10^{-2} \text{ M}$. The solid line corresponds to PB calculations at constant *apparent* surface potential Ψ_{app} . Derivation from the calculation at high Π result from additional steric stabilization due to bulk complexes $(d_{\text{h}} = (20.8 \pm 2.0) \text{ nm})$. The disjoining pressure isotherm for $c_{\text{LiBr}} = 10^{-4} \text{ M}$ contains a kink similar to the data without added LiBr⁸³. Since for this sample an event of stratification (Fig. A.25) occurred before the measurement, the sPSO₂-220 concentration is above c^* . The appearance of the kink might be connected to rearrangement of the P network inside the foam film. Hence, this sample shall not be compared with the data below c^* .

Stratification



FIGURE A.25: Stratification event taking place for sPSO₂-220 / C₁₄TAB mixtures with $c_{sPSO_2-220} = 10^{-3}$ monoM and $c_{LiBr} = 10^{-4}$ M. The notation a) - j) denotes the progress of the stratification. The full event was finished after 2.5 s.

A.6 Appendix for chapter 6



FIGURE A.26: Images of sPSO₂-220 / C_{14} TAB mixtures 1 month after mixing. The samples contain 10^{-3} M LiBr and 3×10^{-5} monoM (a), 6.5×10^{-5} monoM (b) and 10^{-4} monoM sPSO₂-220 (c). d shows a close up of c.



FIGURE A.27: Formation of a NBF for $sPSO_2-220 / C_{14}TAB$ mixtures with $c_{sPSO_2-220} = 3 \times 10^{-5}$ monoM and $c_{LiBr} = 10^{-3}$ M. The notation a) - f) denotes the progress of the formation. Images were digitally post-processed to increase the contrast. The time from first appearance of the NBF until it ruptures was 0.3 s. The brighter areas of the foam film slow down and deform the spreading of the NBF.



FIGURE A.28: Close up of foam films of sPSO₂-220 / C₁₄TAB mixtures (*above* the BSMP, $c_{\rm sPSO_2-220} = 10^{-3}$ monoM, $c_{\rm C_{14}TAB} = 10^{-4}$ M) containing 10^{-3} M LiBr. The notation a) - d) denotes the progress of the disappearance of a white spot near the foam film rim. Images were digitally post-processed to highly increase the contrast.

A.7 Appendix for chapter 7



FIGURE A.29: Images of a foam film containing 0.5 mM BrijO10 and 100 mM NaCl,(a) before and (b) after post-proceeding. Inside the NBF flower-like domains of a condensed phase are formed.



FIGURE A.30: Disjoining pressure isotherms of 0.5 mM BrijO10 and 0.5 mM BrijO10 + 10 mM HSiW (a single measurement is shown). With 10 mM HSiW the foam film is nearly as incompressible as the NBF without HSiW implying a mainly steric stabilization. The higher thickness may result from trapped micelles. The inset shows the dark and corresponding thin foam film (digitally post-processed).



FIGURE A.31: Images of foam films of 0.5 mM BrijO10 in the presence of 0.5 mM HSiW at 388 Pa (a) and in the present of 2.5 mM HSiW at 373 Pa (b) without any further post processing. Color or brightness differences between the formed structures and the surrounding foam film are barely visible.



FIGURE A.32: BAM images: a) of the surface of 0.5 mM BrijO10 + 0.5 mM HSiW and b) of the surface of 0.5 mM BrijO10. The times refer to age of the surface after pouring the solution into the Teflon trough. Scale bar is 100 µm. Unlike the sample with HSiW, without HSiW no flower-like structures appeared at the surface over 20 min.

Bibliography

- A. Arzhavitina and H. Steckel. Foams for pharmaceutical and cosmetic application. Int. J. Pharm., 394(1-2):1--17, 2010. ISSN 03785173. doi: 10.1016/j.ijpharm.2010.04.028.
- Christopher Hill and Julian Eastoe. Foams: From nature to industry. Adv. Colloid Interface Sci., 247:496--513, 2017. ISSN 00018686. doi: 10.1016/j.cis. 2017.05.013.
- [3] Zhengchang Shen. Principles and Technologies of Flotation Machines. Springer Tracts in Mechanical Engineering. Springer Singapore, Singapore, 2021. ISBN 978-981-16-0331-0. doi: 10.1007/978-981-16-0332-7.
- [4] Douglas J. Durian and Srinivasa R. Raghavan. Making a frothy shampoo or beer. Phys. Today, 63(5):62--63, 2010. ISSN 00319228. doi: 10.1063/1.3431341.
- [5] Isabelle Cantat, Sylvie Cohen-Addad, Florence Elias, François Graner, Reinhard Höhler, Olivier Pitois, Florence Rouyer, Arnaud Saint-Jalmes, and Ruth Flatman. Foams: Structure and Dynamics. *Clim. Chang. 2013 - Phys. Sci. Basis*, 1(9):1--278, 2013. ISSN 1098-6596. doi: 10.1093/acprof: oso/9780199662890.001.0001.
- [6] B. Petkova, S. Tcholakova, M. Chenkova, K. Golemanov, N. Denkov, D. Thorley, and S. Stoyanov. Foamability of aqueous solutions: Role of surfactant type and concentration. *Adv. Colloid Interface Sci.*, 276:102084, 2020. ISSN 00018686. doi: 10.1016/j.cis.2019.102084.
- [7] Larissa Braun, Matthias Kühnhammer, and Regine von Klitzing. Stability of aqueous foam films and foams containing polymers: Discrepancies between different length scales. *Curr. Opin. Colloid Interface Sci.*, 50:101379, 2020. ISSN 18790399. doi: 10.1016/j.cocis.2020.08.004.

- [8] Ganesan Narsimhan and Ning Xiang. Role of Proteins on Formation, Drainage, and Stability of Liquid Food Foams. Annu. Rev. Food Sci. Technol., 9(1): 45--63, 2018. ISSN 1941-1413. doi: 10.1146/annurev-food-030216-030009.
- [9] Andrei Bureiko, Anna Trybala, Nina Kovalchuk, and Victor Starov. Current applications of foams formed from mixed surfactant-polymer solutions. Adv. Colloid Interface Sci., 222:670--677, 2014. ISSN 00018686. doi: 10.1016/j.cis. 2014.10.001.
- [10] Dotchi Exerowa, Georgi Gochev, Dimo Platikanov, Libero Liggieri, and Reinhard Miller, editors. Foam Films and Foam Fundamentals and Applicationss. CRC Press, 2018. ISBN 9781351117746. doi: 10.1201/9781351117746.
- [11] Sara Llamas, Eduardo Guzmán, Francisco Ortega, Nawel Baghdadli, Colette Cazeneuve, Ramón G. Rubio, and Gustavo S. Luengo. Adsorption of polyelectrolytes and polyelectrolytes-surfactant mixtures at surfaces: A physico-chemical approach to a cosmetic challenge. Adv. Colloid Interface Sci., 222:461--487, 2015. ISSN 00018686. doi: 10.1016/j.cis.2014.05.007.
- [12] Eduardo Guzmán. Polyelectrolyte-Surfactant Mixtures as the Model for Understanding the Performance of 2-in-1 Shampoo Formulations. Curr. Cosmet. Sci., 1(1):41--50, 2022. ISSN 26667797. doi: 10.2174/2666779701666220211145354.
- [13] E. D. Goddard. Polymer/surfactant interaction-Its relevance to detergent systems. J. Am. Oil Chem. Soc., 71(1):1--16, 1994. ISSN 0003021X. doi: 10.1007/BF02541467.
- [14] Maziar Veyskarami, Mohammad Hossein Ghazanfari, and Yousef Shafiei. Monitoring the behaviour of anionic polymer-anionic surfactant stabilized foam in the absence and presence of oil: Bulk and bubble-scale experimental analyses. Can. J. Chem. Eng., 97(S1):1386--1398, 2019. ISSN 1939019X. doi: 10.1002/cjce.23368.
- [15] Mahesh Budhathoki, Sai Hari Ram Barnee, Bor Jier Shiau, and Jeffrey H. Harwell. Improved oil recovery by reducing surfactant adsorption with polyelectrolyte in high saline brine. *Colloids Surfaces A Physicochem. Eng. Asp.*, 498:66--73, 2016. ISSN 18734359. doi: 10.1016/j.colsurfa.2016.03.012.
- [16] T. Ressler, U. Dorn, A. Walter, S. Schwarz, and A. H.P. Hahn. Structure and properties of PVMo11O40 heteropolyoxomolybdate supported on silica SBA-15
as selective oxidation catalyst. J. Catal., 275(1):1--10, 2010. ISSN 00219517. doi: 10.1016/j.jcat.2010.07.001.

- Bo Huang, Dong Hui Yang, and Bao Hang Han. Application of polyoxometalate derivatives in rechargeable batteries. J. Mater. Chem. A, 8(9):4593--4628, 2020. ISSN 20507496. doi: 10.1039/c9ta12679a.
- [18] Aleksandar Bijelic and Annette Rompel. The use of polyoxometalates in protein crystallography - An attempt to widen a well-known bottleneck. *Coord. Chem. Rev.*, 299:22--38, 2015. ISSN 00108545. doi: 10.1016/j.ccr.2015.03.018.
- [19] Max Hohenschutz, Isabelle Grillo, Charles Dewhurst, Philipp Schmid, Luc Girard, Alban Jonchère, Olivier Diat, and Pierre Bauduin. Superchaotropic nano-ions as foam stabilizers. J. Colloid Interface Sci., 603:141--147, 2021. ISSN 10957103. doi: 10.1016/j.jcis.2021.06.098.
- [20] G. Gochev, D. Platikanov, and R. Miller. Chronicles of foam films. Adv. Colloid Interface Sci., 233:115--125, 2016. ISSN 00018686. doi: 10.1016/j.cis.2015.08.009.
- [21] B. Derjaguin and L. Landau. Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. *Prog. Surf. Sci.*, 43(1-4):30--59, 1993. ISSN 00796816. doi: 10.1016/0079-6816(93)90013-L.
- [22] E J W Verwey. Theory of the Stability of Lyophobic Colloids. J. Phys. Colloid Chem., 51(3):631--636, 1947. ISSN 0092-7023. doi: 10.1021/j150453a001.
- [23] A. Scheludko and D. Exerowa. Über den elektrostatischen Druck in Schaumfilmen aus wässerigen Elektrolytlösungen. *Kolloid-Zeitschrift*, 165(2):148--151, 1959. ISSN 0303402X. doi: 10.1007/BF01809974.
- [24] Karol J. Mysels and Malcolm N. Jones. Direct measurement of the variation of double-layer repulsion with distance. *Discuss. Faraday Soc.*, 42(11):42, 1966.
 ISSN 0366-9033. doi: 10.1039/df9664200042.
- [25] D. Exerowa and A. Scheludko. Porous plate method for studying microscopic foam and emulsion films. CR Acad Bulg Sci, 24:47--50, 1971.
- [26] L. G. Cascão Pereira, C. Johansson, H. W. Blanch, and C. J. Radke. A bike-wheel microcell for measurement of thin-film forces. *Colloids Surfaces A Physicochem. Eng. Asp.*, 186(1-2):103--111, 2001. ISSN 09277757. doi: 10.1016/S0927-7757(01)00488-5.

- [27] Yiran Zhang, Subinuer Yilixiati, Collin Pearsall, and Vivek Sharma. Nanoscopic Terraces, Mesas, and Ridges in Freely Standing Thin Films Sculpted by Supramolecular Oscillatory Surface Forces. ACS Nano, 10(4):4678--4683, 2016. ISSN 1936086X. doi: 10.1021/acsnano.6b01012.
- [28] Yiran Zhang and Vivek Sharma. Domain expansion dynamics in stratifying foam films: Experiments. Soft Matter, 11(22):4408--4417, 2015. ISSN 17446848. doi: 10.1039/c5sm00066a.
- [29] Sébastien Andrieux, Pierre Muller, Manish Kaushal, Nadia Sofía Macias Vera, Robin Bollache, Clément Honorez, Alain Cagna, and Wiebke Drenckhan. Microfluidic thin film pressure balance for the study of complex thin films. *Lab Chip*, 21(2):412--420, 2021. ISSN 14730189. doi: 10.1039/d0lc00974a.
- [30] Jacob N. Israelachvili, editor. Intermolecular and Surface Forces (Third Edition).
 Academic Press, third edition edition, 2011. ISBN 978-0-12-375182-9.
- [31] Helmholtz. Ueber einige Gesetze der Vertheilung elektrischer Ströme in körperlichen Leitern mit Anwendung auf die thierisch-elektrischen Versuche. Ann Phys. Chemie, 89:211--233, 1853.
- [32] David Leonard Chapman. A contribution to the theory of electrocapillarity. London, Edinburgh, Dublin Philos. Mag. J. Sci., 25(148):475--481, 1913. ISSN 1941-5982. doi: 10.1080/14786440408634187.
- [33] Otto Stern. Zur Theorie der elektrolytischen Doppelschicht. Zeitschrift für Elektrochemie, 21-22(30):508--516, 1924. doi: 10.1002/bbpc.192400182.
- [34] Hans-Jürgen Butt and Michael Kappl. Surface and Interfacial Forces 2e.
 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, jun 2018. ISBN 9783527804351. doi: 10.1002/9783527804351.
- [35] D.F. Evans and H. Wennerström. The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology Meet. Advances in Interfacial Engineering. John Wiley & Sons, 1991. ISBN 978-0-471-24247-5.
- [36] Regine V. Klitzing. Effect of interface modification on forces in foam films and wetting films. Adv. Colloid Interface Sci., 114-115:253--266, 2005. ISSN 00018686. doi: 10.1016/j.cis.2004.12.004.
- [37] Jim W. Goodwin. Front Matter, volume 42. John Wiley & Sons, Ltd, Chichester, UK, 2004. ISBN 9780470093917. doi: 10.1002/0470093919.fmatter.

- [38] E Vanden-Eijnden. Soft Matter at Aqueous Interfaces, volume 917 of Lecture Notes in Physics. Springer International Publishing, 2016. ISBN 978-3-319-24500-3. doi: 10.1007/978-3-319-24502-7.
- [39] Muruganathan Ramanathan, Hans-Joachim Müller, Kaushik Vedula, Helmuth Möhwald, and Rumen Krastev. Basic properties of foam films stabilized with tetraethyl ammonium salt of perfluoro octane sulfonate (PFOS). *Colloids Surfaces A Physicochem. Eng. Asp.*, 354(1-3):1--7, 2010. ISSN 09277757. doi: 10.1016/j.colsurfa.2009.11.032.
- [40] R. von Klitzing, E. Thormann, T. Nylander, D. Langevin, and C. Stubenrauch. Confinement of linear polymers, surfactants, and particles between interfaces. *Adv. Colloid Interface Sci.*, 155(1-2):19--31, 2010. ISSN 00018686. doi: 10.1016/ j.cis.2010.02.003.
- [41] Enda Carey and Cosima Stubenrauch. A disjoining pressure study of foam films stabilized by mixtures of a nonionic (C12DMPO) and an ionic surfactant (C12TAB). J. Colloid Interface Sci., 343(1):314--323, 2010. ISSN 00219797. doi: 10.1016/j.jcis.2009.11.026.
- [42] Natascha Schelero, Gabi Hedicke, Per Linse, and Regine V Klitzing. Effects of counterions and co-ions on foam films stabilized by anionic dodecyl sulfate. J. Phys. Chem. B, 114(47):15523--15529, 2010. ISSN 1520-5207. doi: 10.1021/ jp1070488.
- [43] Judith Schulze-Schlarmann, Natalie Buchavzov, and Cosima Stubenrauch. A disjoining pressure study of foam films stabilized by tetradecyl trimethyl ammonium bromide C14TAB. Soft Matter, 2(7):584--594, 2006. ISSN 1744683X. doi: 10.1039/b602975b.
- [44] Pouria Amani, Stoyan I. Karakashev, Nikolay A. Grozev, Silviya S. Simeonova, Reinhard Miller, Victor Rudolph, and Mahshid Firouzi. Effect of selected monovalent salts on surfactant stabilized foams. Adv. Colloid Interface Sci., 295(March):102490, 2021. ISSN 00018686. doi: 10.1016/j.cis.2021.102490.
- [45] D. Exerowa, T. Kolarov, and Khr Khristov. Direct measurement of disjoining pressure in black foam films. I. Films from an ionic surfactant. *Colloids and Surfaces*, 22(2):161--169, 1987. ISSN 016666622. doi: 10.1016/0166-6622(87) 80218-4.

- [46] Haiyang Yuan, Wenjie Deng, Xiaolong Zhu, Guangming Liu, and Vincent Stuart James Craig. Colloidal Systems in Concentrated Electrolyte Solutions Exhibit Re-entrant Long-Range Electrostatic Interactions due to Underscreening. Langmuir, 2022. ISSN 15205827. doi: 10.1021/acs.langmuir.2c00519.
- [47] V. Bergeron and C. J. Radke. Equilibrium Measurements of Oscillatory Disjoining Pressures in Aqueous Foam Films. *Langmuir*, 8(12):3020--3026, 1992. ISSN 15205827. doi: 10.1021/la00048a028.
- [48] Subinuer Yilixiati, Rabees Rafiq, Yiran Zhang, and Vivek Sharma. Influence of Salt on Supramolecular Oscillatory Structural Forces and Stratification in Micellar Freestanding Films. ACS Nano, 12(2):1050--1061, 2018. ISSN 1936086X. doi: 10.1021/acsnano.7b05391.
- [49] Yan Zeng, Stefan Grandner, Cristiano L.P. Oliveira, Andreas F. Thünemann, Oskar Paris, Jan S. Pedersen, Sabine H.L. Klapp, and Regine Von Klitzing. Effect of particle size and Debye length on order parameters of colloidal silica suspensions under confinement. *Soft Matter*, 7(22):10899--10909, 2011. ISSN 1744683X. doi: 10.1039/c1sm05971h.
- [50] Natascha Schelero and Regine von Klitzing. Ion specific effects in foam films. *Curr. Opin. Colloid Interface Sci.*, 20(2):124--129, 2015. ISSN 13590294. doi: 10.1016/j.cocis.2015.03.006.
- [51] Natalie Buchavzov and Cosima Stubenrauch. A Disjoining Pressure Study of Foam Films Stabilized by Mixtures of Nonionic and Ionic Surfactants. *Langmuir*, 23(10):5315--5323, 2007. doi: 10.1021/la063642u.
- [52] Cosima Stubenrauch and Reinhard Miller. Stability of foam films and surface rheology: An oscillating bubble study at low frequencies. J. Phys. Chem. B, 108(20):6412--6421, 2004. ISSN 15206106. doi: 10.1021/jp049694e.
- [53] Felix Schulze-Zachau and Björn Braunschweig. C n TAB/polystyrene sulfonate mixtures at air-water interfaces: effects of alkyl chain length on surface activity and charging state. *Phys. Chem. Chem. Phys.*, 21(15):7847--7856, 2019. ISSN 1463-9076. doi: 10.1039/C9CP01107B.
- [54] Natascha Schelero, Reinhard Miller, and Regine von Klitzing. Effect of oppositely charged hydrophobic additives (alkanoates) on the stability of C14TAB foam films. *Colloids Surf. A*, 460:158--167, 2014. ISSN 09277757. doi: 10.1016/j. colsurfa.2014.03.091.

- [55] Roland R. Netz and David Andelman. Neutral and charged polymers at interfaces. *Phys. Rep.*, 380(1-2):1--95, 2003. ISSN 03701573. doi: 10.1016/ S0370-1573(03)00118-2.
- [56] A. B. Kayitmazer, D. Shaw, and P. L. Dubin. Role of polyelectrolyte persistence length in the binding of oppositely charged micelles, dendrimers, and protein to chitosan and poly(dimethyldiallyammonium chloride). *Macromolecules*, 38(12): 5198--5204, 2005. ISSN 00249297. doi: 10.1021/ma050328i.
- [57] Michael V. Rapp, Stephen H. Donaldson, Matthew A. Gebbie, Yonas Gizaw, Peter Koenig, Yuri Roiter, and Jacob N. Israelachvili. Effects of Surfactants and Polyelectrolytes on the Interaction between a Negatively Charged Surface and a Hydrophobic Polymer Surface. *Langmuir*, 31(29):8013--8021, 2015. ISSN 15205827. doi: 10.1021/acs.langmuir.5b01781.
- [58] Jeffrey Penfold and Robert K. Thomas. Counterion Condensation, the Gibbs Equation, and Surfactant Binding: An Integrated Description of the Behavior of Polyelectrolytes and Their Mixtures with Surfactants at the Air-Water Interface. J. Phys. Chem. B, 124(28):6074--6094, 2020. ISSN 15205207. doi: 10.1021/acs.jpcb.0c02988.
- [59] C. D. Bain, P. M. Claesson, D. Langevin, R. Meszaros, T. Nylander, C. Stubenrauch, S. Titmuss, and R. von Klitzing. Complexes of surfactants with oppositely charged polymers at surfaces and in bulk. *Adv. Colloid Interface Sci.*, 155(1-2): 32--49, 2010. ISSN 00018686. doi: 10.1016/j.cis.2010.01.007.
- [60] Amália Mezei, Katalin Pojják, and Róbert Mészáros. Nonequilibrium features of the association between poly(vinylamine) and sodium dodecyl sulfate: The validity of the colloid dispersion concept. J. Phys. Chem. B, 112(32):9693--9699, 2008. ISSN 15206106. doi: 10.1021/jp802196c.
- [61] Dongcui Li, Manish S. Kelkar, and Norman J. Wagner. Phase behavior and molecular thermodynamics of coacervation in oppositely charged polyelectrolyte/surfactant systems: A cationic polymer JR 400 and anionic surfactant SDS mixture. *Langmuir*, 28(28):10348--10362, 2012. ISSN 07437463. doi: 10.1021/la301475s.
- [62] Laura Fernández-Peña, Eduardo Guzmán, Coral Fernández-Pérez, Irene Barba-Nieto, Francisco Ortega, Fabien Leonforte, Ramón G. Rubio, and Gustavo S. Luengo. Study of the Dilution-Induced Deposition of Concentrated Mixtures

of Polyelectrolytes and Surfactants. *Polymers (Basel).*, 14(7), 2022. ISSN 20734360. doi: 10.3390/polym14071335.

- [63] A. Naderi, P. M. Claesson, M. Bergström, and A. Dedinaite. Trapped nonequilibrium states in aqueous solutions of oppositely charged polyelectrolytes and surfactants: Effects of mixing protocol and salt concentration. *Colloids Surfaces A Physicochem. Eng. Asp.*, 253(1-3):83--93, 2005. ISSN 09277757. doi: 10.1016/j.colsurfa.2004.10.123.
- [64] Amália Mezei, Robert Mészáros, Imre Varga, and Tibor Gilányi. Effect of mixing on the formation of complexes of hyperbranched cationic polyelectrolytes and anionic surfactants. *Langmuir*, 23(8):4237--4247, 2007. ISSN 07437463. doi: 10.1021/la0635294.
- [65] Ágnes Ábrahám, Amália Mezei, and Róbert Mészáros. The effect of salt on the association between linear cationic polyelectrolytes and sodium dodecyl sulfate. *Soft Matter*, 5(19):3718--3726, 2009. ISSN 1744683X. doi: 10.1039/b903158h.
- [66] Amália Mezei, Ágnes Ábrahám, Katalin Pojják, and Róbert Mészáros. The impact of electrolyte on the aggregation of the complexes of hyperbranched poly(ethyleneimine) and sodium dodecyl sulfate. *Langmuir*, 25(13):7304--7312, 2009. ISSN 07437463. doi: 10.1021/la9003388.
- [67] Ágnes Ábrahám, Attila Kardos, Amália Mezei, Richard A. Campbell, and Imre Varga. Effects of ionic strength on the surface tension and nonequilibrium interfacial characteristics of poly(sodium styrenesulfonate)/ dodecyltrimethylammonium bromide mixtures. *Langmuir*, 30(17):4970-4979, 2014. ISSN 15205827. doi: 10.1021/la500637v.
- [68] Tommy Nylander, Yulia Samoshina, and Björn Lindman. Formation of polyelectrolyte-surfactant complexes on surfaces. Adv. Colloid Interface Sci., 123-126(SPEC. ISS.):105--123, 2006. ISSN 00018686. doi: 10.1016/j.cis.2006.07.005.
- [69] Richard A. Campbell, Marianna Yanez Arteta, Anna Angus-Smyth, Tommy Nylander, Boris A. Noskov, and Imre Varga. Direct impact of nonequilibrium aggregates on the structure and morphology of pdadmac/SDS layers at the air/water interface. *Langmuir*, 30(29):8664--8674, 2014. ISSN 15205827. doi: 10.1021/la500621t.
- [70] Larissa Braun, Martin Uhlig, Regine von Klitzing, and Richard A. Campbell. Polymers and surfactants at fluid interfaces studied with specular neutron

reflectometry. Adv. Colloid Interface Sci., 247(July):130--148, 2017. ISSN 00018686. doi: 10.1016/j.cis.2017.07.005.

- [71] Hernan Ritacco, Pierre-Antoine Albouy, Amitabha Bhattacharyya, and Dominique Langevin. Influence of the polymer backbone rigidity on polyelectrolyte-surfactant complexes at the air/water interface. *Phys. Chem. Chem. Phys.*, 2(22):5243--5251, 2000. ISSN 14639076. doi: 10.1039/b0046570.
- [72] Nirmesh J. Jain, Pierre Antoine Albouy, and Dominique Langevin. Study of adsorbed monolayers of a cationic surfactant and an anionic polyelectrolyte at the air-water interface. Role of the polymer charge density. *Langmuir*, 19(20): 8371-8379, 2003. ISSN 07437463. doi: 10.1021/la034842y.
- [73] D. Langevin. Polyelectrolyte and surfactant mixed solutions. Behavoir at surface and in thin films. Adv. Colloid Interface Sci., 89-90:467-484, 2001.
- [74] S. Trabelsi and D. Langevin. Co-adsorption of Carboxymethyl-Cellulose and Cationic Surfactants at the Air / Water Interface. *Langmuir*, 23(3):1248--1252, 2007. ISSN 0743-7463. doi: 10.1021/la062296d.
- [75] Atef Asnacios, Dominique Langevin, and Jean-François Argillier. Complexation of Cationic Surfactant and Anionic Polymer at the Air -- Water Interface. *Macromolecules*, 29(23):7412--7417, 1996. ISSN 0024-9297. doi: 10.1021/ ma960225n.
- [76] D. J.F. Taylor, R. K. Thomas, J. D. Hines, K. Humphreys, and J. Penfold. The adsorption of oppositely charged polyelectrolyte/surfactant mixtures at the air/water interface: Neutron reflection from dodecyl trimethylammonium bromide/sodium poly(styrene sulfonate) and sodium dodecyl sulfate/poly(vinyl pyridinium chloride). *Langmuir*, 18(25):9783--9791, 2002. ISSN 07437463. doi: 10.1021/la020503d.
- [77] D. J. F. Taylor, R. K. Thomas, P. X. Li, and J. Penfold. Adsorption of Oppositely Charged Polyelectrolyte/Surfactant Mixtures. Neutron Reflection from Alkyl Trimethylammonium Bromides and Sodium Poly(styrenesulfonate) at the Air/Water Interface: The Effect of Surfactant Chain Length. Langmuir, 19(9):3712--3719, 2003. ISSN 0743-7463. doi: 10.1021/la020709e.

- [78] Robert K. Thomas and J. Penfold. Thermodynamics of the Air-Water Interface of Mixtures of Surfactants with Polyelectrolytes, Oligoelectrolytes, and Multivalent Metal Electrolytes. J. Phys. Chem. B, 122(51):12411--12427, 2018. ISSN 15205207. doi: 10.1021/acs.jpcb.8b10350.
- [79] Imre Varga and Richard A Campbell. General Physical Description of the Behavior of Oppositely Charged Polyelectrolyte/Surfactant Mixtures at the Air/Water Interface. *Langmuir*, asap:acs.langmuir.7b01288, 2017. ISSN 0743-7463. doi: 10.1021/acs.langmuir.7b01288.
- [80] Nora Kristen, Vasile Simulescu, Andrea Vüllings, André Laschewsky, Reinhard Miller, and Regine Von Klitzing. No charge reversal at foam film surfaces after addition of oppositely charged polyelectrolytes? J. Phys. Chem. B, 113(23): 7986--7990, 2009. ISSN 15206106. doi: 10.1021/jp902369d.
- [81] Ágnes Ábraham, Richard A. Campbell, and Imre Varga. New method to predict the surface tension of complex synthetic and biological polyelectrolyte/surfactant mixtures. *Langmuir*, 29(37):11554--11559, 2013. ISSN 07437463. doi: 10.1021/ la402525w.
- [82] Nora Kristen, Andrea Vüllings, André Laschewsky, Reinhard Miller, and Regine Von Klitzing. Foam films from oppositely charged polyelectolyte/surfactant mixtures: Effect of polyelectrolyte and surfactant hydrophobicity on film stability. Langmuir, 26(12):9321--9327, 2010. ISSN 07437463. doi: 10.1021/la1002463.
- [83] Martin Uhlig, Reinhard Miller, and Regine von Klitzing. Surface adsorption of sulfonated poly(phenylene sulfone)/C14 TAB mixtures and its correlation with foam film stability. *Phys. Chem. Chem. Phys.*, 18(27):18414--18423, 2016. ISSN 1463-9076. doi: 10.1039/C6CP02256A.
- [84] Heiko Fauser, Regine Von Klitzing, and Richard A. Campbell. Surface adsorption of oppositely charged C14TAB-PAMPS mixtures at the air/water interface and the impact on foam film stability. J. Phys. Chem. B, 119(1):348--358, 2015. ISSN 15205207. doi: 10.1021/jp509631b.
- [85] Martin Uhlig, Oliver Löhmann, Vargas Ruiz, Imre Varga, Regine Von Klitzing, and Richard A. Campbell. New structural approach to rationalize the foam film stability of oppositely charged polyelectrolyte / surfactant mixtures. *Chem. Commun.*, 56:952--955, 2020. doi: 10.1039/c9cc08470c.

- [86] B. Kolaric, W. Jaeger, G. Hedicke, and R. von Klitzing. Tuning of Foam Film Thickness by Different (Poly)electrolyte/Surfactant Combinations. J. Phys. Chem. B, 107(32):8152--8157, 2003. ISSN 1520-6106. doi: 10.1021/jp0340358.
- [87] César Márquez Beltrán, Samuel Guillot, and Dominique Langevin. Stratification phenomena in thin liquid films containing polyelectrolytes and stabilized by ionic surfactants. *Macromolecules*, 36(22):8506--8512, 2003. ISSN 00249297. doi: 10.1021/ma034599+.
- [88] Vance Bergeron, D. Langevin, and Atef Asnacios. Thin-Film Forces in Foam Films Containing Anionic Polyelectrolyte and Charged Surfactants. *Langmuir*, 12(6):1550--1556, 1996. ISSN 0743-7463. doi: 10.1021/la950654z.
- [89] Emil J. Burcik. The rate of surface tension lowering and its role in foaming. J. Colloid Sci., 5(5):421--436, 1950. ISSN 00958522. doi: 10.1016/0095-8522(50) 90034-1.
- [90] S. B. Aidarova, K. B. Musabekov, Z. B. Ospanova, and M. Guden. Foaming binary solution mixtures of low molecular surfactant and polyelectrolyte. J. Mater. Sci., 41(13):3979--3986, 2006. ISSN 00222461. doi: 10.1007/s10853-006-7573-9.
- [91] Irene Nalumansi, Grace Birungi, Brenda Moodley, and Emmanuel Tebandeke. Preparation and Identification of Reduced Phosphomolybdate Via, Molybdenum Blue Reaction. Orient. J. Chem., 36(04):607--612, 2020. ISSN 0970020X. doi: 10.13005/ojc/360403.
- [92] J. F. Keggin. The structure and formula of 12-phosphotungstic acid. Proc. R. Soc. London. Ser. A, Contain. Pap. a Math. Phys. Character, 144(851):75--100, mar 1933. ISSN 0950-1207. doi: 10.1098/rspa.1934.0035.
- [93] R. B. King. Aromaticity in Transition Metal Oxide Structures. J. Chem. Inf. Comput. Sci., 41(3):517-526, 2001. ISSN 00952338. doi: 10.1021/ci000074u.
- [94] Makoto Misono. Catalysis of heteropoly compounds (polyoxometalates), volume 176. Elsevier, 2013. ISBN 9780444538338. doi: 10.1016/B978-0-444-53833-8. 00004-1.
- [95] Billy B. Bardin, Shailendra V. Bordawekar, Matthew Neurock, and Robert J. Davis. Acidity of keggin-type heteropolycompounds evaluated by catalytic probe reactions, sorption microcalorimetry, and density functional quantum

chemical calculations. J. Phys. Chem. B, 102(52):10817--10825, 1998. ISSN 15206106. doi: 10.1021/jp982345y.

- [96] Aleksandar Kondinski and Tatjana N. Parac-Vogt. Keggin structure, Quō Vadis? Front. Chem., 6(AUG):1--7, 2018. ISSN 22962646. doi: 10.3389/fchem. 2018.00346.
- [97] Hasenknopf, Bernold. Polyoxometalates: introduction to a class of inorganic compounds and their biomedical applications. *Front. Biosci.*, 10(1-3):275, sep 2005. ISSN 10939946. doi: 10.2741/1527.
- [98] Rafael Zubrzycki, Jan Dirk Epping, and Thorsten Ressler. Role of Vanadium and Phosphorus in Substituted Keggin-Type Heteropolyoxo Molybdates Supported on Silica SBA-15 in Selective Propene Oxidation. *ChemCatChem*, 7(7):1112-1121, apr 2015. ISSN 18673880. doi: 10.1002/cctc.201402970.
- [99] Danica Bajuk-Bogdanović, Ivanka Holclajtner-Antunović, Marija Todorović, Ubavka B. Mioč, and Joanna Zakrzewska. A study of 12-tungstosilicic and 12-molybdophosphoric acids in solution. J. Serbian Chem. Soc., 73(2):197--209, 2008. ISSN 03525139. doi: 10.2298/JSC0802197B.
- [100] Julia Wienold, Olaf Timpe, and Thorsten Ressler. In Situ Investigations of Structure - Activity Relationships in Heteropolyoxomolybdates as Partial Oxidation Catalysts. *Chem. - A Eur. J.*, 9(24):6007--6017, 2003. ISSN 09476539. doi: 10.1002/chem.200305227.
- [101] Bappaditya Naskar, Olivier Diat, Véronique Nardello-Rataj, and Pierre Bauduin. Nanometer-Size Polyoxometalate Anions Adsorb Strongly on Neutral Soft Surfaces. J. Phys. Chem. C, 119(36):20985--20992, 2015. ISSN 19327455. doi: 10.1021/acs.jpcc.5b06273.
- [102] Cécile Monteux, Claudine E. Williams, and Vance Bergeron. Interfacial microgels formed by oppositely charged polyelectrolytes and surfactants. Part 2. Influence of surfactant chain length and surfactant/polymer ratio. *Langmuir*, 20(13):5367--5374, 2004. ISSN 07437463. doi: 10.1021/la049784a.
- [103] Elisabet Fuguet, Clara Ràfols, Martí Rosés, and Elisabeth Bosch. Critical micelle concentration of surfactants in aqueous buffered and unbuffered systems. *Anal. Chim. Acta*, 548(1-2):95--100, 2005. ISSN 00032670. doi: 10.1016/j.aca. 2005.05.069.

- [104] Feng Liu, Zhongni Wang, Dezhi Sun, Xilian Wei, Wu Zhou, Ganzuo Li, and Gaoyong Zhang. Adsorption kinetics of Brij 97 at the air/solution interface. J. Dispers. Sci. Technol., 27(5):657--663, 2006. ISSN 01932691. doi: 10.1080/ 01932690600660624.
- [105] Michael Schuster, Klaus Dieter Kreuer, Henrik T. Andersen, and Joachim Maier. Sulfonated poly(phenylene sulfone) polymers as hydrolytically and thermooxidatively stable proton conducting ionomers. *Macromolecules*, 40(3): 598--607, 2007. ISSN 00249297. doi: 10.1021/ma062324z.
- [106] Michael Schuster, Carla C. De Araujo, Vladimir Atanasov, Henrik T. Andersen, Klaus Dieter Kreuer, and Joachim Maier. Highly sulfonated poly(phenylene sulfone): Preparation and stability issues. *Macromolecules*, 42(8):3129--3137, 2009. ISSN 00249297. doi: 10.1021/ma900333n.
- [107] Cosima Stubenrauch, Pierre Antoine Albouy, Regine V. Klitzing, and Dominique Langevin. Polymer/surfactant complexes at the water/air interface: A surface tension and X-ray reflectivity study. *Langmuir*, 16(7):3206--3213, 2000. ISSN 07437463. doi: 10.1021/la991277j.
- [108] Eduardo Guzmán, Laura Fernández-Peña, Francisco Ortega, and Ramón G. Rubio. Equilibrium and kinetically trapped aggregates in polyelectrolyte–oppositely charged surfactant mixtures. *Curr. Opin. Colloid Interface Sci.*, 48:91--108, 2020. ISSN 18790399. doi: 10.1016/j.cocis.2020.04.002.
- [109] Róbert Mészáros, Laurie Thompson, Martin Bos, Imre Varga, and Tibor Gilányi. Interaction of Sodium Dodecyl Sulfate with Polyethyleneimine: Surfactant-Induced Polymer Solution Colloid Dispersion Transition. Langmuir, 19(3): 609--615, 2003. ISSN 0743-7463. doi: 10.1021/la026616e.
- [110] A. Sheludko. Thin liquid films. Adv. Colloid Interface Sci., 1(4):391--464, 1967.
 ISSN 00018686. doi: 10.1016/0001-8686(67)85001-2.
- [111] Cosima Stubenrauch and Regine Von Klitzing. Disjoining pressure in thin liquid foam and emulsion films—new concepts and perspectives. J. Phys. Condens. Matter, 15237(1503):1197--1232, 2003. ISSN 0953-8984. doi: 10.1088/0953-8984/ 15/27/201.
- [112] Derek Y.C. Chan. A simple algorithm for calculating electrical double layer interactions in asymmetric electrolytes - Poisson-Boltzmann theory. J. Colloid

Interface Sci., 245(2):307--310, 2002. ISSN 00219797. doi: 10.1006/jcis.2001. 7942.

- [113] Tommy Nylander, Richard A Campbell, Pauline Vandoolaeghe, Marité Cárdenas, Per Linse, and Adrian R Rennie. Neutron reflectometry to investigate the delivery of lipids and DNA to interfaces (Review). *Biointerphases*, 3(2):FB64, 2008. ISSN 1559-4106. doi: 10.1116/1.2976448.
- [114] Toyoko Imae, editor. Neutrons in Soft Matter. John Wiley & Sons, Inc., New Jersey, 2011. ISBN 9780470933886. doi: 10.1002/9780470933886.ch7.
- [115] Jeffrey Penfold and Robert K. Thomas. Neutron reflectivity and small angle neutron scattering: an introduction and perspective on recent progress. *Curr. Opin. Colloid Interface Sci.*, 19(3):198--206, 2014. ISSN 13590294. doi: 10.1016/ j.cocis.2014.01.002.
- [116] Theyencheri Narayanan, Hanna Wacklin, Oleg Konovalov, and Reidar Lund. Recent applications of synchrotron radiation and neutrons in the study of soft matter. *Crystallography Reviews*, 23(3):160--226, 2017. doi: 10.1080/0889311X. 2016.1277212.
- [117] Heinz Kiessig. Untersuchungen zur Totalreflexion von Röntgenstrahlen. Ann. Phys., 402(6):715--768, 1931. ISSN 15213889. doi: 10.1002/andp.19314020607.
- [118] J. R. Lu, R. K. Thomas, and J. Penfold. Surfactant layers at the air/water interface: Structure and composition. Adv. Colloid Interface Sci., 84(1):143--304, 2000. ISSN 00018686. doi: 10.1016/S0001-8686(99)00019-6.
- [119] John Lekner. Theory of Reflection, volume 87 of Springer Series on Atomic, Optical, and Plasma Physics. Springer International Publishing, Cham, 2016. ISBN 978-3-319-23626-1. doi: 10.1007/978-3-319-23627-8.
- [120] Krishnan Chari, Young Soo Seo, and Sushil Satija. Competitive adsorption at the air-water interface from a self-assembling polymer-surfactant mixture. J. Phys. Chem. B, 108(31):11442--11446, 2004. ISSN 15206106. doi: 10.1021/jp049062s.
- [121] Mauro Moglianetti, Peixun Li, Fred L G Malet, Steven P. Armes, Robert K. Thomas, and Simon Titmuss. Interaction of polymer and surfactant at the air-water interface: Poly(2-(dimethylamino)ethyl methacrylate) and sodium dodecyl sulfate. *Langmuir*, 24(22):12892--12898, 2008. ISSN 07437463. doi: 10.1021/la8020468.

- [122] Larissa Braun, Martin Uhlig, Oliver Löhmann, Richard A Campbell, Emanuel Schneck, and Regine von Klitzing. Insights into Extended Structures and Their Driving Force: Influence of Salt on Polyelectrolyte/Surfactant Mixtures at the Air/Water Interface. ACS Appl. Mater. Interfaces, 2022. ISSN 1944-8244. doi: 10.1021/acsami.2c04421.
- [123] R. A. Campbell, H. P. Wacklin, I. Sutton, R. Cubitt, and G. Fragneto. FIGARO: The new horizontal neutron reflectometer at the ILL. *Eur. Phys. J. Plus*, 126 (11):107, 2011. ISSN 21905444. doi: 10.1140/epjp/i2011-11107-8.
- [124] Andrew Nelson. Co-refinement of multiple-contrast neutron/X-ray reflectivity data using MOTOFIT. Journal of Applied Crystallography, 39(2):273--276, 2006. doi: 10.1107/S0021889806005073.
- [125] Richard A. Campbell. Recent advances in resolving kinetic and dynamic processes at the air/water interface using specular neutron reflectometry. *Curr. Opin. Colloid Interface Sci.*, 37:49--60, 2018. ISSN 13590294. doi: 10.1016/j. cocis.2018.06.002.
- [126] Samantha Micciulla, Yuri Gerelli, Richard A. Campbell, and Emanuel Schneck. A Versatile Method for the Distance-Dependent Structural Characterization of Interacting Soft Interfaces by Neutron Reflectometry. *Langmuir*, 34(3):789--800, 2018. ISSN 15205827. doi: 10.1021/acs.langmuir.7b02971.
- [127] S. K. Sinha, E. B. Sirota, S. Garoff, and H. B. Stanley. X-ray and neutron scattering from rough surfaces. *Phys. Rev. B*, 38(4):2297--2311, 1988. ISSN 01631829. doi: 10.1103/PhysRevB.38.2297.
- [128] Philip Raymond Bevington and D. Keith Robinson. Data Reduction and Error Analysis for the Physical Sciences. MCGraw-Hill, Boston, 3 edition, 2003. ISBN 0072472278.
- [129] Hans-Jürgen Butt, Karlheinz Graf, and Michael Kappl. 02 Liquid Surfaces. Phys. Chem. Interfaces, pages 4--25, 2003. ISSN 3527602313. doi: 10.1002/ 3527602313.ch2.
- [130] P. Lecomte du Noüy. AN INTERFACIAL TENSIOMETER FOR UNIVERSAL USE. J. Gen. Physiol., 7(5):625--631, 1925. ISSN 1540-7748. doi: 10.1085/jgp. 7.5.625.

- [131] Hans-Dieter. Dörfler. Grenzflächen und kolloid-disperse Systeme : Physik und Chemie ; mit 88 Tabellen. Springer, Berlin [u.a.], 2002. ISBN 3540425470 9783540425472.
- [132] C. Huh and S. G. Mason. A rigorous theory of ring tensiometry. *Colloid Polym. Sci.*, 253(7):566--580, 1975. ISSN 0303-402X. doi: 10.1007/BF01753960.
- [133] Michael Bass and Optical Society of America, editors. Handbook of optics. McGraw-Hill, 2nd ed edition, 1995. ISBN 978-0-07-047740-7 978-0-07-047974-6 978-0-07-135408-0 978-0-07-136456-0.
- [134] Redouane Borsali and Robert ; Pecora. Soft Matter Characterization, volume 91.
 Springer Netherlands, Dordrecht, 2008. ISBN 978-1-4020-4464-9. doi: 10.1007/ 978-1-4020-4465-6.
- [135] Weiam Daear, Mark Mahadeo, and Elmar J. Prenner. Applications of Brewster angle microscopy from biological materials to biological systems. *Biochim. Biophys. Acta - Biomembr.*, 1859(10):1749--1766, 2017. ISSN 18792642. doi: 10.1016/j.bbamem.2017.06.016.
- [136] A. V. Delgado, F. González-Caballero, R. J. Hunter, L. K. Koopal, and J. Lyklema. Measurement and Interpretation of Electrokinetic Phenomena (IUPAC Technical Report). *Pure Appl. Chem.*, 77(10):1753--1805, 2005. ISSN 1365-3075. doi: 10.1351/pac200577101753.
- [137] I. M. Tucker, J. C.W. Corbett, J. Fatkin, R. O. Jack, M. Kaszuba, B. MacCreath, and F. McNeil-Watson. Laser Doppler Electrophoresis applied to colloids and surfaces. *Curr. Opin. Colloid Interface Sci.*, 20(4):215--226, 2015. ISSN 18790399. doi: 10.1016/j.cocis.2015.07.001.
- [138] Felix Schulze-Zachau and Björn Braunschweig. Structure of Polystyrenesulfonate/Surfactant Mixtures at Air–Water Interfaces and Their Role as Building Blocks for Macroscopic Foam. *Langmuir*, 33(14):3499--3508, apr 2017. ISSN 0743-7463. doi: 10.1021/acs.langmuir.7b00400.
- [139] Anna Slastanova, Richard A. Campbell, Tim Snow, Elizabeth Mould, Peixun Li, Rebecca J.L. Welbourn, Meng Chen, Eric Robles, and Wuge H. Briscoe. Synergy, competition, and the "hanging" polymer layer: Interactions between a neutral amphiphilic 'tardigrade' comb co-polymer with an anionic surfactant at the air-water interface. J. Colloid Interface Sci., 561:181--194, 2020. ISSN 10957103. doi: 10.1016/j.jcis.2019.11.017.

- [140] Peixun Li, Jeffery Penfold, Robert K. Thomas, and Hui Xu. Multilayers formed by polyelectrolyte-surfactant and related mixtures at the air-water interface. Adv. Colloid Interface Sci., 269:43--86, 2019. ISSN 00018686. doi: 10.1016/j.cis.2019.04.002.
- [141] Hua Wang, Heng Zhang, Shiling Yuan, Zhen Xu, and Chengbu Liu. Molecular dynamics study of the structure of an oppositely charged polyelectrolyte and an ionic surfactant at the air/water interface. *Colloids Surfaces A Physicochem. Eng. Asp.*, 454(1):104--112, 2014. ISSN 18734359. doi: 10.1016/j.colsurfa.2014. 04.009.
- [142] Richard A. Campbell, Marianna Yanez Arteta, Anna Angus-Smyth, Tommy Nylander, and Imre Varga. Multilayers at interfaces of an oppositely charged polyelectrolyte/ surfactant system resulting from the transport of bulk aggregates under gravity. J. Phys. Chem. B, 116(27):7981--7990, 2012. ISSN 15205207. doi: 10.1021/jp304564x.
- [143] Andrea Tummino, Jutta Toscano, Federica Sebastiani, Boris A. Noskov, Imre Varga, and Richard A. Campbell. Effects of Aggregate Charge and Subphase Ionic Strength on the Properties of Spread Polyelectrolyte/Surfactant Films at the Air/Water Interface under Static and Dynamic Conditions. *Langmuir*, 34 (6):2312--2323, 2018. ISSN 15205827. doi: 10.1021/acs.langmuir.7b03960.
- [144] Heiko Ahrens, Hubert Baltes, Johannes Schmitt, Helmuth Möhwald, and Christiane A. Helm. Polyelectrolyte adsorption onto insoluble monolayers at the air/water interface. *Macromolecules*, 34(13):4504--4512, 2001. ISSN 00249297. doi: 10.1021/ma001520h.
- [145] Eisuke Kanao, Takuya Kubo, Toyohiro Naito, Takatoshi Matsumoto, Tomoharu Sano, Mingdi Yan, and Koji Otsuka. Isotope Effects on Hydrogen Bonding and CH/CD-π Interaction. J. Phys. Chem. C, 122(26):15026--15032, 2018. ISSN 19327455. doi: 10.1021/acs.jpcc.8b04144.
- [146] Yuji Ono, Ryusuke Futamura, Yoshiyuki Hattori, Shigenori Utsumi, Toshio Sakai, and Katsumi Kaneko. Isotope effect on water adsorption on hydrophobic carbons of different nanoporosities. *Carbon N. Y.*, 119:251--256, 2017. ISSN 00086223. doi: 10.1016/j.carbon.2017.04.047.
- [147] S. Candau, E. Hirsch, and R. Zana. Effect of alcohol on the properties of micellar systems. IV. Effect of the isotopic composition of the system on the micellar

properties in the presence and absence of 1-pentanol. J. Colloid Interface Sci., 88(2):428--436, 1982. ISSN 00219797. doi: 10.1016/0021-9797(82)90271-5.

- [148] David Wade. Deuterium isotope effects on noncovalent interactions between molecules. *Chem. Biol. Interact.*, 117(3):191--217, 1999. ISSN 00092797. doi: 10.1016/S0009-2797(98)00097-0.
- [149] Jens Uwe Günther, Heiko Ahrens, and Christiane A. Helm. Two-dimensional lamellar phase of poly(styrene sulfonate) adsorbed onto an oppositely charged lipid monolayer. *Langmuir*, 25(3):1500--1508, 2009. ISSN 07437463. doi: 10.1021/la802987k.
- [150] Ksenija Kogej. Association and structure formation in oppositely charged polyelectrolyte-surfactant mixtures. Adv. Colloid Interface Sci., 158(1-2):68--83, 2010. ISSN 00018686. doi: 10.1016/j.cis.2009.04.003.
- [151] Nora Kristen and Regine Von Klitzing. Effect of polyelectrolyte/surfactant combinations on the stability of foam films. Soft Matter, 6(5):849--861, 2010.
 ISSN 1744683X. doi: 10.1039/b917297a.
- [152] D. Kovacevic, S. Van der Burgh, A. De Keizer, and Martien A. Cohen Stuart. Kinetics of formation and dissolution of weak polyelectrolyte multilayers: Role of salt and free polyions. *Langmuir*, 18(14):5607--5612, 2002. ISSN 07437463. doi: 10.1021/la025639q.
- [153] Roland R. Netz and Jean François Joanny. Adsorption of semiflexible polyelectrolytes on charged planar surfaces: Charge compensation, charge reversal, and multilayer formation. *Macromolecules*, 32(26):9013--9025, 1999. ISSN 00249297. doi: 10.1021/ma990263h.
- [154] René Messina. Effect of image forces on polyelectrolyte adsorption at a charged surface. Phys. Rev. E Stat. Physics, Plasmas, Fluids, Relat. Interdiscip. Top., 70(5):9, 2004. ISSN 1063651X. doi: 10.1103/PhysRevE.70.051802.
- [155] Philipp Buchold, Maor Ram-On, Yeshayahu Talmon, Ingo Hoffmann, Ralf Schweins, and Michael Gradzielski. Uncommon Structures of Oppositely Charged Hyaluronan/Surfactant Assemblies under Physiological Conditions. *Biomacromolecules*, 21(9):3498--3511, 2020. ISSN 15264602. doi: 10.1021/acs. biomac.0c00221.

- [156] Leonardo Chiappisi and Michael Gradzielski. Co-assembly in chitosan-surfactant mixtures: Thermodynamics, structures, interfacial properties and applications. Adv. Colloid Interface Sci., 220:92--107, 2015. ISSN 00018686. doi: 10.1016/j. cis.2015.03.003.
- [157] Elka S. Basheva, Peter A. Kralchevsky, Krassimir D. Danov, Rumyana D. Stanimirova, Neil Shaw, and Jordan T. Petkov. Vortex in liquid films from concentrated surfactant solutions containing micelles and colloidal particles. J. Colloid Interface Sci., 576:345--355, 2020. ISSN 10957103. doi: 10.1016/j.jcis. 2020.05.048.
- [158] Katharina Graessel, Christian Bächer, and Stephan Gekle. Rayleigh-Plateau instability of anisotropic interfaces. Part 1. An analytical and numerical study of fluid interfaces. J. Fluid Mech., 910, 2021. ISSN 14697645. doi: 10.1017/jfm. 2020.947.
- [159] Lord Rayleigh. On The Instability Of Jets. Proc. London Math. Soc., s1-10(1):
 4--13, 1878. ISSN 00246115. doi: 10.1112/plms/s1-10.1.4.
- [160] Jongju Lee, Alex Nikolov, and Darsh Wasan. Stepwise dynamics of an anionic micellar film – Formation of crown lenses. J. Colloid Interface Sci., 496:60--65, 2017. ISSN 10957103. doi: 10.1016/j.jcis.2017.01.110.
- [161] E. Pairam and A. Fernández-Nieves. Generation and stability of toroidal droplets in a viscous liquid. *Phys. Rev. Lett.*, 102(23):1--4, 2009. ISSN 00319007. doi: 10.1103/PhysRevLett.102.234501.
- [162] Heiko Fauser, Martin Uhlig, Reinhard Miller, and Regine Von Klitzing. Surface Adsorption of Oppositely Charged SDS:C12TAB Mixtures and the Relation to Foam Film Formation and Stability. J. Phys. Chem. B, 119(40):12877--12886, 2015. ISSN 15205207. doi: 10.1021/acs.jpcb.5b06231.
- [163] D. Exerowa, A. Nikolov, and M. Zacharieva. Common black and Newton film formation. J. Colloid Interface Sci., 81(2):419--429, 1981. ISSN 00219797. doi: 10.1016/0021-9797(81)90424-0.
- [164] Mengsu Peng, Timothy T. Duignan, and Anh V. Nguyen. Significant Effect of Surfactant Adsorption Layer Thickness in Equilibrium Foam Films. J. Phys. Chem. B, 124(25):5301--5310, 2020. ISSN 15205207. doi: 10.1021/acs.jpcb. 0c02883.

- [165] Andrew Akanno, Eduardo Guzmán, Laura Fernández-Peña, Sara Llamas, Francisco Ortega, and Ramón G. Rubio. Equilibration of a Polycation-Anionic Surfactant Mixture at the Water/Vapor Interface. *Langmuir*, 34(25):7455--7464, 2018. ISSN 15205827. doi: 10.1021/acs.langmuir.8b01343.
- [166] Brandon K. Schabes and Geraldine L. Richmond. Helping Strands: Polyelectrolyte Assists in Surfactant Assembly below Critical Micelle Concentration. *Journal of Physical Chemistry B*, 124:234--239, 2019. ISSN 15205207. doi: 10.1021/acs.jpcb.9b08692.
- [167] Katalin Pojjaźk, Edit Bertalanits, and Roźbert Meźszaźros. Effect of salt on the equilibrium and nonequilibrium features of polyelectrolyte/surfactant association. Langmuir, 27(15):9139--9147, 2011. ISSN 07437463. doi: 10.1021/la2021353.
- [168] Narayan Chandra Mishra, Hans Joachim Müller, Helmuth Möhwald, and Rumen Krastev. Interactions and stability of foam films from pentaethyleneglycol monodecyl ether. *Colloids Surfaces A Physicochem. Eng. Asp.*, 282-283:92--98, 2006. doi: 10.1016/j.colsurfa.2005.12.014.
- [169] A. Holzwarth, S. Leporatti, and H. Riegler. Molecular ordering and domain morphology of molecularly thin triacontane films at SiO2/air interfaces. *Europhys. Lett.*, 52(6):653--659, 2000. ISSN 02955075. doi: 10.1209/epl/i2000-00488-0.
- [170] J Wang and A V Nguyen. Foam drainage in the presence of solid particles. Soft Matter, 12(12):3004--3012, 2016. ISSN 1744-683X. doi: 10.1039/C6SM00028B.
- [171] Denny Vitasari, Simon Cox, Paul Grassia, and Ruben Rosario. Effect of surfactant redistribution on the flow and stability of foam films. Proc. R. Soc. A Math. Phys. Eng. Sci., 476(2234), 2020. ISSN 14712946. doi: 10.1098/rspa. 2019.0637.
- [172] Max Hohenschutz, Isabelle Grillo, Olivier Diat, and Pierre Bauduin. How Nano-Ions Act Like Ionic Surfactants. Angew. Chemie - Int. Ed., 59(21):8084--8088, 2020. ISSN 15213773. doi: 10.1002/anie.201916193.
- [173] Thomas Buchecker, Philipp Schmid, Isabelle Grillo, Sylvain Prévost, Markus Drechsler, Olivier Diat, Arno Pfitzner, and Pierre Bauduin. Self-Assembly of Short Chain Poly-N-isopropylacrylamid Induced by Superchaotropic Keggin Polyoxometalates: From Globules to Sheets. J. Am. Chem. Soc., 141(17): 6890--6899, 2019. ISSN 15205126. doi: 10.1021/jacs.8b12181.

- [174] Philipp Schmid, Xaver Gra
 ß, Pratap Bahadur, Isabelle Grillo, Olivier Diat, Arno Pfitzner, and Pierre Bauduin. Polymeric Surfactant P84/Polyoxometalate α PW12O403- A Model System to Investigate the Interplay between Chaotropic and Hydrophobic Effects. *Colloids and Interfaces*, 6(1):16, 2022. ISSN 2504-5377. doi: 10.3390/colloids6010016.
- [175] Daiki Kobayashi, Hiromichi Nakahara, Osamu Shibata, Kei Unoura, and Hideki Nabika. Interplay of Hydrophobic and Electrostatic Interactions between Polyoxometalates and Lipid Molecules. J. Phys. Chem. C, 121(23):12895--12902, 2017. ISSN 19327455. doi: 10.1021/acs.jpcc.7b01774.
- [176] Khaleel I. Assaf, Merve S. Ural, Fangfang Pan, Tony Georgiev, Svetlana Simova, Kari Rissanen, Detlef Gabel, and Werner M. Nau. Water Structure Recovery in Chaotropic Anion Recognition: High-Affinity Binding of Dodecaborate Clusters to γ-Cyclodextrin. Angew. Chemie Int. Ed., 54(23):6852--6856, jun 2015. ISSN 14337851. doi: 10.1002/anie.201412485.
- [177] Sa Yao, Clément Falaise, Anton A. Ivanov, Nathalie Leclerc, Max Hohenschutz, Mohamed Haouas, David Landy, Michael A. Shestopalov, Pierre Bauduin, and Emmanuel Cadot. Hofmeister effect in the Keggin-type polyoxotungstate series. *Inorg. Chem. Front.*, 8(1):12--25, 2021. ISSN 2052-1553. doi: 10.1039/ d0qi00902d.
- [178] Alesya Mikhailovskaya, Li Zhang, Fabrice Cousin, François Boué, Pavel Yazhgur, François Muller, Cyprien Gay, and Anniina Salonen. Probing foam with neutrons. Adv. Colloid Interface Sci., 247(April):444--453, 2017. ISSN 00018686. doi: 10.1016/j.cis.2017.07.024.
- [179] Monique A V Axelos and François Boué. Foams As Viewed by Small-Angle Neutron Scattering. Langmuir, 19(17):6598--6604, 2003. ISSN 0743-7463. doi: 10.1021/la020965r.
- [180] Marcus D Hanwell, Donald E Curtis, David C Lonie, Tim Vandermeersch, Eva Zurek, and Geoffrey R Hutchison. Avogadro: an advanced semantic chemical editor, visualization, and analysis platform. J. Cheminform., 4(1):17, dec 2012. ISSN 1758-2946. doi: 10.1186/1758-2946-4-17.
- [181] Cosima Stubenrauch, Orlando J. Rojas, Judith Schlarmann, and Per M. Claesson. Interactions between nonpolar surfaces coated with the nonionic surfactant hexaoxyethylene dodecyl ether C 12E 6 and the origin of surface charges at the

air/water interface. Langmuir, 20(12):4977--4988, 2004. ISSN 07437463. doi: 10.1021/la0304060.

- [182] Cosima Stubenrauch and Brita Rippner Blomqvist. Foam Films, Foams and Surface Rheology of Non-Ionic Surfactants: Amphiphilic Block Copolymers Compared with Low Molecular Weight Surfactants, volume 1. WILEY-VCH, 2010. ISBN 9783527631193. doi: 10.1002/9783527631193.ch11.
- [183] Chrystian Ochoa, Shang Gao, Samanvaya Srivastava, and Vivek Sharma. Foam film stratification studies probe intermicellar interactions. *Proc. Natl. Acad. Sci.*, 118(25), jun 2021. ISSN 0027-8424. doi: 10.1073/pnas.2024805118.
- [184] Elka S. Basheva, Krassimir D. Danov, Gergana M. Radulova, Peter A. Kralchevsky, Hui Xu, Yee Wei Ung, and Jordan T. Petkov. Properties of the micelles of sulfonated methyl esters determined from the stepwise thinning of foam films and by rheological measurements. J. Colloid Interface Sci., 538: 660--670, 2019. ISSN 10957103. doi: 10.1016/j.jcis.2018.12.034.
- [185] Tianbo Liu. Hydrophilic macroionic solutions: What happens when soluble ions reach the size of nanometer scale? *Langmuir*, 26(12):9202--9213, 2010. ISSN 07437463. doi: 10.1021/la902917q.
- [186] Alla Malinenko, Alban Jonchère, Luc Girard, Sandra Parrès-Maynadié, Olivier Diat, and Pierre Bauduin. Are Keggin's POMs Charged Nanocolloids or Multicharged Anions? *Langmuir*, 34(5):2026--2038, 2018. ISSN 15205827. doi: 10.1021/acs.langmuir.7b03640.
- [187] Carlos Drummond, Leonor Pérez-Fuentes, and Delfi Bastos-González. Can polyoxometalates be considered as superchaotropic ions? J. Phys. Chem. C, 123(47):28744--28752, 2019. ISSN 19327455. doi: 10.1021/acs.jpcc.9b08324.
- [188] R. V. Klitzing, A. Espert, A. Asnacios, T. Hellweg, A. Colin, and D. Langevin. Forces in foam films containing polyelectrolyte and surfactant. *Colloids Surfaces A Physicochem. Eng. Asp.*, 149(1-3):131--140, 1999. ISSN 09277757. doi: 10.1016/S0927-7757(98)00307-0.
- [189] Krassimir D. Danov, Peter A. Kralchevsky, and Kavssery P. Ananthapadmanabhan. Micelle-monomer equilibria in solutions of ionic surfactants and in ionic-nonionic mixtures: A generalized phase separation model. Adv. Colloid Interface Sci., 206:17-45, 2014. ISSN 00018686. doi: 10.1016/j.cis.2013.02.001.

- [190] Michael Ludwig and Regine von Klitzing. Untangling superposed double layer and structural forces across confined nanoparticle suspensions. *Phys. Chem. Chem. Phys.*, 23(2):1325--1334, 2021. ISSN 1463-9076. doi: 10.1039/ D0CP05631F.
- [191] T. Kolarov, A. Scheludko, and D. Exerowa. Contact angle between black film and bulk liquid. *Trans. Faraday Soc.*, 64:2864--2873, 1968. ISSN 00147672. doi: 10.1039/TF9686402864.
- [192] Charles Tanford. Micelle shape and size. J. Phys. Chem., 76(21):3020--3024, 1972. ISSN 00223654. doi: 10.1021/j100665a018.
- [193] Rossen Sedev and Dotchi Exerowa. DLVO and non-DLVO surface forces in foam films from amphiphilic block copolymers. Adv. Colloid Interface Sci., 83 (1):111--136, 1999. ISSN 00018686. doi: 10.1016/S0001-8686(99)00007-X.
- [194] K. Lunkenheimer, K. Malysa, K. Winsel, K. Geggel, and S. Siegel. Novel method and parameters for testing and characterization of foam stability. *Langmuir*, 26 (6):3883--3888, 2010. ISSN 07437463. doi: 10.1021/la9035002.
- [195] V. Bergeron. Disjoining Pressures and Film Stability of Alkyltrimethylammonium Bromide Foam Films. *Langmuir*, 13(13):3474--3482, 1997. ISSN 0743-7463. doi: 10.1021/la970004q.
- [196] Afshin Asadzadeh Shahir, Dimitrinka Arabadzhieva, Hristina Petkova, Stoyan I. Karakashev, Anh V. Nguyen, and Elena Mileva. Effect of Under-Monolayer Adsorption on Foamability, Rheological Characteristics, and Dynamic Behavior of Fluid Interfaces: Experimental Evidence for the Guggenheim Extended Interface Model. J. Phys. Chem. C, 121(21):11472--11487, 2017. ISSN 19327455. doi: 10.1021/acs.jpcc.7b02483.
- [197] Dominique Langevin. On the rupture of thin films made from aqueous surfactant solutions. Adv. Colloid Interface Sci., 275:102075, 2020. ISSN 00018686. doi: 10.1016/j.cis.2019.102075.
- [198] Philipp Schmid, Max Hohenschutz, Xaver Gra
 ß, Michael Witzmann, Didier Touraud, Olivier Diat, Arno Pfitzner, and Pierre Bauduin. Counterion effect on α-Keggin polyoxometalates in water: The peculiar role of H+ on their salting-in effect and co-assembly with organics. J. Mol. Liq., 359:119214, 2022. ISSN 01677322. doi: 10.1016/j.molliq.2022.119214.

- [199] Raphaël Poryles, Théo Lenavetier, Emmanuel Schaub, Adrien Bussonnière, Arnaud Saint-Jalmes, and Isabelle Cantat. Non linear elasticity of foam films made of SDS/dodecanol mixtures. *Soft Matter*, 18(10):2046--2053, 2022. ISSN 17446848. doi: 10.1039/d1sm01733k.
- [200] Javier Carrascosa-Tejedor, Andreas Santamaria, Andrea Tummino, Imre Varga, Marina Efstratiou, M. Jayne Lawrence, Armando Maestro, and Richard A. Campbell. Polyelectrolyte/surfactant films: from 2D to 3D structural control. *Chem. Commun.*, 2022. ISSN 1359-7345. doi: 10.1039/d2cc03766a.
- [201] Georgi G. Gochev, Ernesto Scoppola, Richard A. Campbell, Boris A. Noskov, Reinhard Miller, and Emanuel Schneck. β-Lactoglobulin Adsorption Layers at the Water/Air Surface: 3. Neutron Reflectometry Study on the Effect of pH. J. Phys. Chem. B, 2019. ISSN 15205207. doi: 10.1021/acs.jpcb.9b07733.
- [202] Paulo A.R. Pires and Omar A. El Seoud. Benzyl (3-acylaminopropyl) dimethylammonium chloride surfactants: Structure and some properties of the micellar aggregates. Prog. Colloid Polym. Sci., 133(May):131--141, 2006. ISSN 0340255X. doi: 10.1007/2882_072.

Abbreviations

ACMW	Air Contrast Matched Water
BAM	Brewster Angle Microscopy
BSMP	Bulk Stoichiometric Mixing Point
$C_{12}TAB$	dodecyltrimethylammonium bromide
$C_{14}TAB$	tetradecyltrimethylammonium bromide
cm-C ₁₄ TAB	\mathbf{c} ontrast \mathbf{m} atched tetradecyltrimethylammonium bromide
d-C ₁₄ TAB	deuterated tetradecyltrimethylammonium bromide
h-C ₁₄ TAB	protonated tetradecyltrimethylammonium bromide
cac	\mathbf{c} ritical \mathbf{a} ggregation \mathbf{c} oncentration
CBF	$\mathbf{C}\mathbf{o}\mathbf{m}\mathbf{m}\mathbf{o}\mathbf{n}\mathbf{B}\mathbf{l}\mathbf{a}\mathbf{c}\mathbf{k}\mathbf{F}\mathbf{i}\mathbf{l}\mathbf{m}$
cmc	\mathbf{c} ritical \mathbf{m} icelle \mathbf{c} oncentration
CP-AFM	Colloidal Probe Atomic Force Microscopy
c*	overlap concentration
DLVO theory	theory named after \mathbf{D} erjaguin, Landau, Verwey, and Overbeek
DODA	dioctadecyldimethyl ammoimum bromide
FWHM	$\mathbf{Full} \ \mathbf{W} \mathrm{idth} \ \mathrm{at} \ \mathbf{H} \mathrm{alf} \ \mathbf{M} \mathrm{aximum}$
HSiW	silicotungstic acid $\mathbf{H}_{4}\mathbf{SiW}_{12}\mathbf{O}_{40}$
$l_{ m p}$	intrinsic persistence length
NBF	Newton Black Film

NR	Neutron Reflectometry
Р	Polyelectrolyte
PAMPS	poly(acrylamido methyl propanesulfonate)
PB eq.	\mathbf{P} oisson- \mathbf{B} oltzmann equation
PDADMAC	poly (diallyldimethylammonium chloride)
POM	Polyoxometalate
PSS	sodium $poly(styrenesulfonate)$
S	\mathbf{S} urfactant
SANS	$\mathbf{S} \mathbf{mall} \ \mathbf{A} \mathbf{ngle} \ \mathbf{N} \mathbf{eutron} \ \mathbf{S} \mathbf{cattering}$
SAXS	$\mathbf{S}\text{mall} \ \mathbf{A}\text{ngle} \ \mathbf{X}\text{-ray} \ \mathbf{S}\text{cattering}$
SDS	\mathbf{S} odium \mathbf{D} odecyl \mathbf{S} ulfate
SiW	silicotung state $\mathbf{SiW}_{12}\mathbf{O}_{40}^{4-}$
SLD	\mathbf{S} cattering Length Density
$sPSO_2-220$	monosulfonated poly(phenylene sulfone)
TFPB	Thin Film Pressure Balance
UV-vis	\mathbf{u} ltra \mathbf{v} iolet- \mathbf{v} isible

Danksagungen

Zunächst möchte ich bei Prof. Regine v. Klitzing für die Möglichkeit bedanken meine Dissertation in ihrem Arbeitskreis anzufertigen. Ihre Unterstützung und Ratschläge sowie die Möglichkeit zu Konferenzen zu reisen, haben mir während meiner gesamten Arbeit geholfen.

Bei Prof. Emanuel Schneck möchte ich mich sowohl für die Übername des Zweitgutachtens sowie für seine Hilfe bei der Auswertung der Neutronendaten herzlichst bedanken. Bei allen, die mir bei dem Prozess hin zu dieser Arbeit geholfen haben -- sei es bei den Arbeiten im Labor, dem Auswerten der Daten oder dem Schreiben von Papern -möchte ich mich herzlichst bedanken.

Bei der gesamten Arbeitsgruppe "Soft Matter at Interfaces" möchte ich mich für die mir zur zuteilgewordenen Unterstützung und die überaus angenehme Arbeitsatmosphäre bedanken. Sei es der wissenschaftliche Austausch, die Kaffeepausen / Feierabendbiere oder die gemeinsamen Spieleabende - ohne euch wären die vergangenen Jahre deutlich weniger erträglich gewesen. Trotz der fortlaufenden Mängelliste haben wir es es geschafft im "neuen" S2/04 unsere Kisten auszupacken und mit dem Forschen loszulegen. (Möge Patrick auf immer in der Teeküche bleiben.)

Mein besondere Dank gilt Sandra und Cassia -- mit euch fahre ich gerne noch mal in den Urlaub...ähh zur ECIS.

Bei meiner Familie, meinen Freunden und bei Alex möchte ich für eure großartige Unterstützung währen meines Studiums und der Promotion bedanken. Ihr wart immer für mich da, wenn ich Trost, ein zuhörendes Ohr oder Ablenkung bei lauter Musik oder rollenden Würfeln brauchte.