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Effects of Counterions and Co-ions on Foam Films Stabilized by Anionic Dodecyl Sulfate

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The influence of counterions and co-ions on the stability and thickness of foam films stabilized by anionic dodecyl sulfate (DS^-) has been studied in a thin film pressure balance. Particularly, the effect on the properties of foam films of (i) the counterions Li^+ , Na^+ , and Cs^+ of DS^- and (ii) monovalent inorganic salts added to sodium dodecyl sulfate solutions is considered. Generally, addition of salt improved the stability of the foam films. As a second order, an increasing ionic size led to an increased adsorption, which in the case of cations gave thinner and less stable films and in the case of anions led to thicker and more stable films. Hence, an effect of anions was observed though the film surfaces were already negatively charged by the anionic DS^- , leading to the conclusion that adsorption of anions to the film surface is governed by ion specific rather than electrostatic interactions. At a fixed surfactant and varying salt concentration, a maximum in film thickness could be identified at a salt concentration well below the surfactant concentration. We anticipate that (i) at low salt concentration salt mainly affects the charging of a film interface, whereas (ii) at high salt concentration salt mainly affects the screening of the electrostatic repulsion between the two interfaces of the film.

1. Introduction

The characteristics of foams play an important role in many industrial applications like flotation, dust control, fire control, tertiary oil recovery, food processing, personal care products, and foam materials. The stability of aqueous foams depends on bulk and surface viscosities, the Marangoni effect, disjoining pressure, and hydrophobic interactions as well as on surface tension (equilibrium and dynamic) and cmc.^{1–4} During foam formation, surfactant molecules adsorb at a freshly created air/water interface from the bulk. The properties of a monolayer of surfactant, which is a good indicator of foam stability, are sensitive to the concentration and nature of the salt.^{5–8} Gurkov et al. reported that the addition of inert NaCl increases the adsorbed amount of sodium dodecyl sulfate at the air/solution interface.⁷ The surface viscosity of a monolayer of *n*-alkylsuccinic anhydrides increases with an increase in NaCl concentration in contrast to a decrease in surface viscosity with an increase in NH_4NO_3 concentration.⁹

A proper understanding of ion specific effects on macroscopic foams is essential for applications such as ion flotation, which is used for ion separation (e.g., removal of heavy metal ions from wastewater). Much literature dealing with the effect of counterions on the properties of solutions of anionic surfactants (e.g., cmc, aggregation number, cloud point, and ionization number) can be found,^{10–19} but only a few publications deal with the counterion effect on the properties of foams. Pandey et al. investigated the foamability of aqueous solutions containing dodecyl sulfate surfactants with different counterions by using the shaking method, and the stability of these macroscopic foams increased from Li^+ , Na^+ , Cs^+ , to Mg^{2+} . The foam stability was controlled by the presence of stable micelles in the foam lamellae. The reduced ability of larger cations to screen the

electrostatic repulsion between the sulfate groups increases the stability of micelles in the order $\text{LiDS} < \text{NaDS} < \text{CsDS}$.²⁰

Foam stability in applications is often related to the stability of thin liquid films formed between two air bubbles. For thicknesses below ≈ 100 nm the film surfaces interact. This interaction causes an excess pressure normal to the film interfaces, called disjoining pressure, which is the sum of repulsive electrostatic (Π_{el}), attractive van der Waals (Π_{vdW}), and repulsive steric (Π_{st}) pressure. Adapted from these interactions two different types of thin films can be distinguished: common black films (CBF) stabilized by Π_{el} and Newton black films (NBF) stabilized by Π_{st} . The formation of a CBF or a NBF can be tuned by the type and concentration of the surfactant as well as by the type and concentration of (simple) salt.²¹

Most of the studies of anionic surfactant/salt systems published so far deal with the influence of electrolyte concentration on surfactant films at a fixed surfactant concentration that is relatively high and often close to the cmc. As a consequence, the salt concentrations used in most of the foam film studies were also relatively high (>10 mM).^{21–23} The influence of the electrolyte concentration on the stability of foam films from 1 mM sodium dodecyl sulfate (SDS) solution has been studied in detail by Exerowa et al.²⁴ The influence of the electrolyte concentration on the disjoining pressure isotherms of sodium *p*-(3-dodecyl)benzene sulfonate, sodium alkyl benzene sulfonate with an average alkyl chain length of C_{12} , and a commercial sulfonated glyceryl alcohol ethoxylate is in good agreement with the observations made for SDS.²⁵ Ion specific effects were not considered in these studies.^{22–28}

The importance of the choice of the anions and cations added to SDS films has been shown in dynamic measurements.²⁹ The influence of different sodium and magnesium salts at 24 mM on the thinning behavior of SDS films was studied. The main focus of this work was how the formation of dimers and complexes influences the molecular packing at the film surfaces and thus the lifetime of the films. The anion effects were classified by the authors along the hard and soft acids and bases

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(HSAB) concept. According to them, small and weakly polarizable anions like Cl^- , NO_3^- , and SO_4^{2-} (hard bases) lead to relatively unstable films as compared to films containing large and highly polarizable anions such as CO_3^{2-} and PO_4^{3-} (soft bases). Concerning the cation effect on the lifetime of SDS films, changing the counteracting cation from Na^+ to the divalent Mg^{2+} leads to more long-lasting films. It is claimed that in all cases the increase of stability is a consequence of interconnection of neighboring SDS headgroups. In the case of magnesium, the bridging is because of direct interactions between magnesium and the sulfate group, whereas for the large and highly polarizable anions it is due to formation of H-bonds with the headgroup. This linking of the sulfate groups results in a lower effective Coulomb repulsion between adjacent headgroups. Therefore, a closer molecular packing and higher surface concentration of SDS molecules is obtained, increasing the lifetime of the films.

The influence of organic counterions like tetraalkylammonium cations (TAA^+) on the stability of dilute aqueous solutions of SDS has also been studied.³⁰ Briefly, TAA^+ cations have a strong impact on the lifetime of foam films since they reduce the film stability because they act as antifoamer like tributyl phosphate.

So far, the influence of different ions has been investigated for macroscopic foams as well as by measurements of the drainage of foam films. However, an interpretation of the results regarding ion specific effects and a detailed study of equilibrium measurements of foam films stabilized by surfactant in the presence of various electrolytes are missing. Electrostatic properties such as surface potential and surface charge density dominate the film stability, and they can be only deduced from fitting the disjoining pressure isotherms of equilibrium systems by solving, e.g., the nonlinearized Poisson–Boltzmann equation.

The present work focuses on the specific effect of different ions on anionic surfactant films at low concentrations. Although the properties of foam films produced at low surfactant concentration are important for industrial application like froth flotation,³¹ only a few articles concerning this field have been published recently.^{26–28} The stability and thickness of 0.1 mM SDS films as a function of NaCl concentrations (1–400 mM) are reported by Wang.^{26,27} With increasing salt concentration, the film thickness decreased while the stability increased. The obtained disjoining pressure isotherms were compared with isotherms calculated with an extended DLVO theory.²⁶

As mentioned above, the knowledge of the influence of ions on foam films stabilized by anionic surfactant is important for wastewater treatment. Moreover, in a recent study it was demonstrated that the air/water interface showed a strong selectivity for both anions and cations.³² Since the air/water interface is negatively charged, the question arises if the impact of cations and anions on the properties of a film interface stabilized by SDS is similar to ion specific effects at the air/water interface. Therefore, our paper aims to answer the question of how the type of ion influences the properties of SDS foam films. Is the impact dominated by electrostatic interactions or due to the ion specificity, and what are the consequences regarding film stability and thickness? For this purpose, the influence of various anions as well as of cations on film stability and thickness are studied by (i) exchanging Na^+ of SDS to Li^+ or Cs^+ and (ii) adding monovalent salts to a 0.3 mM SDS solution. In the latter case, the ionic strength of the solutions varies only weakly since the salt concentration is around that of SDS.

2. Experimental Section

2.1. Substances and Cleaning Procedure. Sodium dodecyl sulfate (SDS) and lithium dodecyl sulfate (LiDS) were purchased from Sigma–Aldrich with purity >99.9% and used as received. Cesium dodecyl sulfate (CsDS) has been prepared in our lab with a modified procedure as given by Benrraou et al.¹⁰ using a strong cation-exchange resin (Merck Type I). Briefly, a 5 wt % SDS solution was stirred with the washed resin (acid form) and with CsOH (Aldrich, purity >99.95%) at 30 °C for 48 h. The capacity of the resin was at least double the amount of sodium ions from SDS to be exchanged. The resin was removed by filtration. The solid surfactant was received by freeze-drying the ion-exchanged solution. Static surface tension measurements were performed to check the surfactant purity. The electrolytes were obtained from Merck and roasted for 24 h at 500 °C to remove organic contaminants. All solutions were prepared with Milli-Q water. All glassware except the film holder was cleaned with Q9 from Ferak Berlin GmbH and rinsed thoroughly with water before use. Ethanol (10 times) and water (10 times) were pressed through the discs, and then the film holders were boiled for 48 h in water.

2.2. Thin Film Pressure Balance. All disjoining pressure isotherms were measured in a thin film pressure balance (TFPB) using the porous-plate technique,^{23,33,34} utilizing free-standing horizontal liquid foam films. The film was formed from a droplet in a hole of 1 mm in diameter that was drilled into the porous glass disk of the film holder. The film holder was placed in a hermetically sealed and temperature-controlled stainless steel cell such that the film was connected to the gas pressure P_g and the free end of the film holder's glass tube was exposed to the atmospheric pressure P_{atm} . The pressure difference $\Delta P = P_g - P_{\text{atm}}$ was adjusted via valves by a highly sensitive pressure transducer. By interferometrically measuring the film thickness after applying a fixed pressure P_{atm} in the cell, disjoining pressure isotherms $\Pi(h)$ were established. The film thickness has been assumed to have reached equilibrium when the reflected light intensity was constant for 20 min. Before the film is formed, the film holder is immersed into the solution for at least 2 h. All measurements were performed at 23 °C.

All disjoining pressure isotherms have been calculated at a constant surface potential by solving the nonlinear PB equation.³⁵ The surface charge densities were calculated by the Grahame equation³⁶ using the electrostatic potentials and the ionic strengths resulting from the model.

2.3. Surface Tension Measurements. The surface tension was measured at a K11 tensiometer (Krüss, Germany) under clean room conditions using the du Noüy ring method. The experiments were performed at 23 °C in a Teflon dish (diameter 5 cm) after thermal equilibration for at least 15 min.

3. Results

The influence of different anions and cations added to a SDS solution has been investigated at $c_{\text{DS}} = 0.3$ mM using salt concentrations $c_{\text{salt}} = 0.05$ – 0.5 mM. The film stabilities are characterized by the maximum pressure Π_{max} that can be applied to a film before it ruptures. Pressure isotherms from the nonlinear PB equation at constant surface potential were fitted to experimental ones with the surface potential as the only fitting parameter. Fitted surface potential, deduced surface charge density, and bulk Debye length were extracted from the result of the PB calculation for an improved description of the films.

3.1. Cation Effects. The specific effect of cations on foam films from DS^- was investigated in two ways: (i) by variation of the counteracting cation (counterion) of DS^- and (ii) by

TABLE 1: Experimental Maximum Pressure Applied to Foam Films Stabilized by LiDS, SDS, and CsDS at Different Surfactant Concentrations; Surface Potentials Φ , Surface Charge Densities σ , and Debye Lengths κ^{-1} Obtained by Fitting a Pressure Isotherm to a Single Surface Potential Using Solutions of the PB Equation; and the Debye Lengths $\kappa_{\text{ideal}}^{-1}$ of the Corresponding Bulk Solution Assuming Complete Dissociation Which Are Referred to As Ideal

salt	c_{DS^-} (mM)	Π_{max} (Pa)	Φ (mV)	σ (mC/m ²)	κ^{-1} (nm)	$\kappa_{\text{ideal}}^{-1}$ (nm)
LiDS	0.1	2165	85 ± 10	2.95 ± 0.5	30.4 ± 1	30.4
	1	6854	66 ± 10	6.17 ± 0.5	9.6 ± 1	9.6
	3.5	6738	50 ± 10	7.85 ± 0.5	5.1 ± 1	5.1
SDS	0.1	1053	70 ± 10	2.13 ± 0.5	30.4 ± 1	30.4
	1	4805	57 ± 10	5.0 ± 0.5	9.6 ± 1	9.6
	3.5	6760	40 ± 10	5.95 ± 0.5	5.1 ± 1	5.1
CsDS	0.1	1015	60 ± 10	1.7 ± 0.5	30.4 ± 1	30.4
	1	4040	47 ± 10	3.88 ± 0.5	9.6 ± 1	9.6
	3.5	6760	— ^a	— ^a	— ^a	5.1

^a No disjoining pressure isotherm could be fitted.

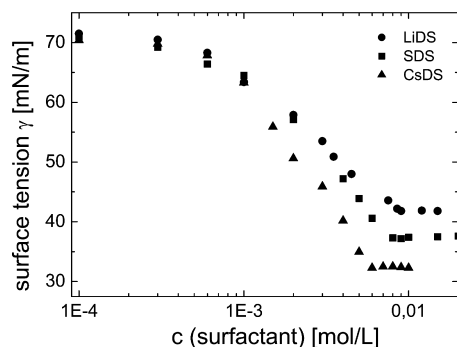


Figure 1. Surface tension γ versus surfactant concentration c_{DS^-} at 23 °C for LiDS (filled circles), SDS (filled squares), and CsDS (filled triangles).

addition of salt that contains cations different from the cation of SDS. The first approach has the advantage of having only one type of counterion present in the solution.

The influence of the counteracting cations Li^+ , Na^+ , and Cs^+ on the stability and thickness of foam films has been investigated by using dodecyl sulfates with different counterions. The corresponding results of the PB calculations performed are summarized in Table 1.

The surface tensions at 23 °C for different counterions are displayed in Figure 1. These measurements gave the bulk cmc's 8.9 mM (LiDS), 8.0 mM (SDS), and 6.0 mM (CsDS) in excellent agreement with literature values,^{10,20,37} and thus the cmc's decrease in the order $\text{LiDS} > \text{SDS} > \text{CsDS}$. The slope of the curves increases in the order of $\text{LiDS} < \text{SDS} < \text{CsDS}$, indicating the highest surface density in the case of CsDS. The plateau value above the cmc decreases in the order of $\text{LiDS} > \text{SDS} > \text{CsDS}$, implying that the energy needed to bring the surfactant molecule to the air/water interface decreases in the same order. Figure 2 displays the disjoining pressure isotherms for foam films of LiDS, SDS, and CsDS at $c_{\text{DS}^-} = 0.1, 1$, and 3.5 mM, respectively. All films show the classical behavior: (i) thinner foam film, (ii) more stable film, and (iii) larger slope of the $\Pi(h)$ isotherms at increasing ionic strength. In all cases the films are rather thick, 12–90 nm, and are thus classified as common black films.

At $c_{\text{DS}^-} = 0.1$ mM, the thickness of foam films stabilized by SDS or CsDS is similar, while LiDS gives thicker films. The pressure at which the films rupture decreases with increasing

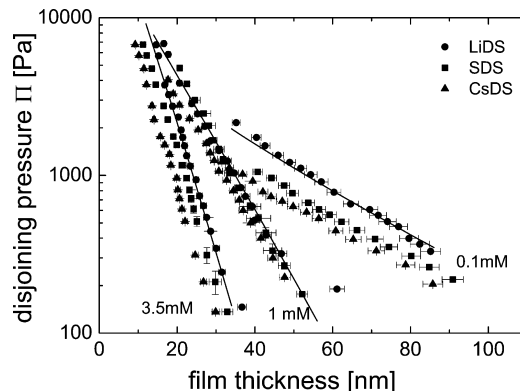


Figure 2. Disjoining pressure Π versus film thickness of LiDS (filled circles), SDS (filled squares), and CsDS (filled triangles) at $c_{\text{DS}^-} = 0.1, 1$, and 3.5 mM. Result from PB calculations are also given (solid curves), and for clarity, only some fitted isotherms are shown.

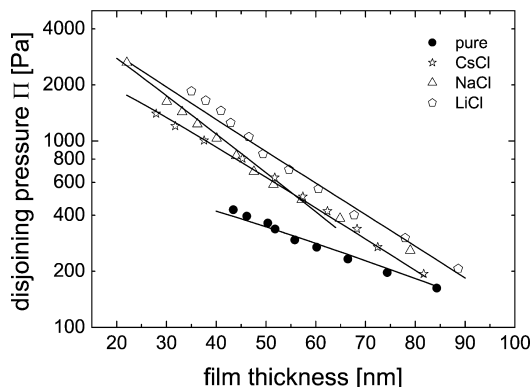


Figure 3. Disjoining pressure Π versus film thickness for a pure SDS film (filled circles) and SDS solutions containing CsCl (open stars), NaCl (open triangles), or LiCl (open pentagons) at $c_{\text{salt}} = 0.1$ mM. Throughout, $c_{\text{SDS}} = 0.3$ mM. Results from PB calculations are also given (solid curves).

counterion size from 2165 Pa (LiDS) to 1053 Pa (SDS) to 1015 Pa (CsDS). At $c_{\text{DS}^-} = 1$ mM only a minor difference between the $\Pi(h)$ curves of LiDS, SDS, and CsDS is observed. The maximum pressures which can be applied were $\Pi_{\text{max}} = 6854$ Pa (LiDS), 4805 Pa (SDS), and 4040 Pa (CsDS). At the largest surfactant concentration $c_{\text{DS}^-} = 3.5$ mM, the thickness decreases with increasing counterion size in the order $\text{Li}^+, \text{Na}^+, \text{and } \text{Cs}^+$. All disjoining pressure isotherms rupture at 6760 Pa. To summarize, the film thickness and stability decrease with increasing size of the counteracting cation from dodecyl sulfate surfactants from LiDS over SDS to CsDS.

The surface potential and surface charge density obtained from the PB calculations decrease with increasing size of the counterion of DS^- in the order $\text{Li}^+, \text{Na}^+, \text{and } \text{Cs}^+$. With increasing surfactant concentration, the surface potential Φ decreases while the surface charge density σ increases. For example, for LiDS Φ decreases from 85 to 50 mV and σ rises from 2.95 to 7.85 mC/m² at an increase of c_{DS^-} from 0.1 to 3.5 mM. All Debye lengths obtained from the PB calculations of the isotherms are similar to the ideal values which is an indication for complete dissociation of both components, at least in the bulk solutions.

Figure 3 displays the influence of cations of different chloride salts on foam films stabilized by SDS, and Table 2 summarizes the results of the PB calculations performed. These foam films are (i) thicker and (ii) more stable and (iii) possess steeper slopes of their disjoining pressure isotherms as compared to the pure SDS foam film. Furthermore, the film thickness decreases with

TABLE 2: Experimental Maximum Pressure Π_{\max} Applied to the Foam Films Stabilized by $c_{\text{SDS}} = 0.3$ mM; Surface Potentials Φ , Surface Charge Densities σ , and Debye lengths κ^{-1} Obtained by Fitting a Pressure Isotherm to a Single Surface Potential Using Solutions of the PB Equation and the Debye Lengths $\kappa_{\text{ideal}}^{-1}$ of the Corresponding Bulk Solutions Assuming Complete Dissociation

salt	c_{salt} (mM)	Π_{\max} (Pa)	Φ (mV)	σ (mC/m ²)	κ^{-1} (nm)	$\kappa_{\text{ideal}}^{-1}$ (nm)
—	0	429	47 ± 10	0.95 ± 0.5	39.3 ± 1	17.6
NaF	0.1	839	47 ± 10	1.73 ± 0.5	21.5 ± 1	15.2
NaCl	0.1	2631	59 ± 10	3.32 ± 0.5	19.2 ± 1	15.2
	0.2	2320	55 ± 10	2.43 ± 0.5	18.9 ± 1	13.6
	0.3	1167	37 ± 10	1.54 ± 0.5	18.2 ± 1	12.4
	0.5	1271	40 ± 10	1.74 ± 0.5	17.6 ± 1	10.8
NaI	0.1	3151	69 ± 10	3.43 ± 0.5	18.5 ± 1	15.2
	0.2	2783	65 ± 10	3.30 ± 0.5	17.6 ± 1	13.6
	0.3	1094	53 ± 10	2.48 ± 0.5	17.6 ± 1	12.4
	0.5	1782	36 ± 10	2.51 ± 0.5	10.8 ± 1	10.8
LiCl	0.1	2851	68 ± 10	3.42 ± 0.5	18.2 ± 1	15.2
CsCl	0.1	1404	56 ± 10	1.95 ± 0.5	24.1 ± 1	15.2
	0.2	1284	43 ± 10	1.43 ± 0.5	23.3 ± 1	13.6
	0.3	1103	40 ± 10	1.42 ± 0.5	21.5 ± 1	12.4
	0.5	7763	53 ± 10	3.39 ± 0.5	12.9 ± 1	10.8

increasing cation size from Li⁺ to Na⁺ to Cs⁺. The maximal pressure before film rupture decreases from 2631 Pa (NaCl) to 1851 Pa (LiCl) to 1404 Pa (CsCl). The surface potential of a pure SDS film is $\Phi = 47$ mV and lower than that of SDS solutions containing alkali, and Φ decreases with increasing cation size from 68 mV (LiCl) to 59 mV (NaCl) to 56 mV (CsCl). The corresponding surface charge densities are $\sigma = 3.42$ mC/m² (LiCl), 3.43 mC/m² (NaCl), and 1.95 mC/m² (CsCl). The Debye lengths deduced from the PB calculations are 24.1 nm (CsCl), 19.2 nm (NaCl), and 18.2 nm (LiCl) and longer than the calculated ideal Debye lengths (15.2 nm).

3.2. Anion Effects. Figure 4 shows the disjoining pressure isotherms of foam films stabilized by SDS solutions containing different sodium salts (NaF, NaCl, and NaI) at $c_{\text{salt}} = 0.1$ mM. The film thickness and stability increase with increasing anion size from fluoride to chloride to iodide. In comparison to a pure SDS film, all films containing sodium halide are thicker and more stable, and the slope of their disjoining pressure isotherms is steeper. The maximum pressure before film rupture (Π_{\max}) was 429 Pa for the pure SDS film, and with salt added it increased to 839 Pa (NaF), 2631 Pa (NaCl), and 3151 Pa (NaI).

Table 2 shows that the predicted surface potential Φ and surface charge density σ increase with increasing anion size and

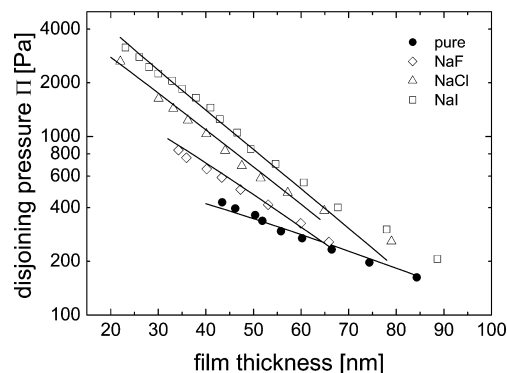


Figure 4. Disjoining pressure Π versus film thickness for a pure SDS film (filled circles) and SDS solutions containing NaF (open diamonds), NaCl (open triangles), or NaI (open squares) at $c_{\text{salt}} = 0.1$ mM. Throughout, $c_{\text{SDS}} = 0.3$ mM. Results from PB calculations are also given (solid curves).

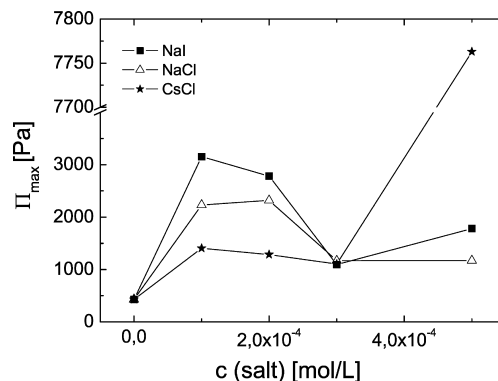


Figure 5. Maximum disjoining pressure Π_{\max} applied to the film versus salt concentration c_{salt} for $c_{\text{DS}^-} = 0.3$ mM SDS film with NaCl (open triangles), NaI (filled squares), and CsCl (filled stars).

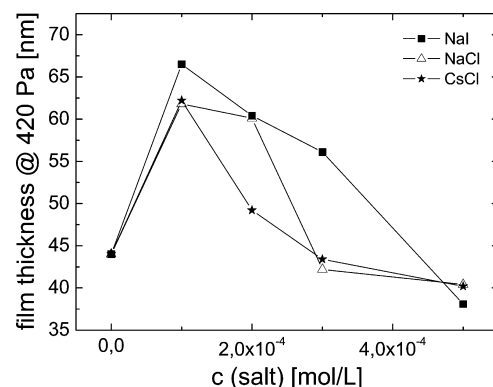


Figure 6. Film thickness at the disjoining pressure $\Pi = 420$ Pa versus salt concentration c_{salt} added to $c_{\text{DS}^-} = 0.3$ mM SDS film with NaCl (open triangles), NaI (filled squares), and CsCl (filled stars). All films were stable at 420 Pa.

decrease with increasing salt concentration. The surface potential $\Phi = 47$ mV was obtained by applying the PB equation on a pure SDS foam film at $c_{\text{SDS}} = 0.3$ mM. Similar surface potential was obtained after adding NaF to $c_{\text{NaF}} = 0.1$ mM. In contrast, the addition of 0.1 mM NaCl or NaI increased the surface potential to 59 and 69 mV, respectively. The corresponding surface charge densities σ increased from 0.95 mC/m² (pure SDS film), 1.73 mC/m² (NaF), 3.32 mC/m² (NaCl) to 3.43 mC/m² (NaI). The Debye lengths extracted from the PB fittings ranged from 21.5 nm (NaF) to 19.2 nm (NaCl) to 18.5 nm (NaI) and were longer than the ideal value 15.2 nm obtained for a complete dissociation of both surfactant and salt. Note that in the case of cations the ion size has an opposite effect on the Debye length.

3.3. Effect of Salt Concentration. To further illustrate the influence of cations and anions on the stability and thickness of foam films stabilized by sodium dodecyl sulfate, Figure 5 shows the maximum pressure applied to the film with increasing salt concentration. Figure 6 depicts the film thickness as a function of the salt concentration at the disjoining pressure 420 Pa, at which all films remain stable. In the following, NaI is chosen to represent the anion influence while CsCl represents the cation influence on foam films stabilized by SDS (Figures 5 and 6), since iodide is the anion and cesium is the cation with the strongest adsorption at the air/water interface.^{32,38–43}

Independent of the type of salt, the maximum pressure versus salt concentration shows a maximum at $c_{\text{salt}} \approx 0.1$ mM. By increasing the salt concentration further, the stability decreases until it reaches a minimum for salt concentration equal to the surfactant concentration ($c_{\text{salt}} = 0.3$ mM). The film stability

decreases from NaI to NaCl to CsCl. For salt concentration above the surfactant concentration, the stability increases again. Now the order changes, and a film containing CsCl is the most stable one.

The characteristics of the film thickness at 420 Pa as a function of the salt concentration are different. After a rise of about 20 nm to a maximum thickness of 66.5 nm (NaI) and 62 nm (NaCl or CsCl) at 0.1 mM salt, the thickness decreases with increasing salt concentration (Figure 6).

According to PB calculations, the maximum and minimum in stability correlate with a maximum and minimum, respectively, of the surface charge density (Table 2). At equal salt and surfactant concentration, the surface charge density becomes $\sigma \approx 2.5 \text{ mC/m}^2$ (SDS/NaI) and $\approx 1.5 \text{ mC/m}^2$ (NaCl or CsCl).

4. Discussion

According to the PB theory, the type of ion should not affect the electrical double layer and hence neither the film stability at a fixed ionic strength. Furthermore, a counterion should be attracted to and co-ion repelled from the negatively charged film surfaces. We recall only Coulomb interactions are included in the PB theory.

The aim of this work was to clarify ion specific effects on the stability and film thickness of foam films stabilized by anionic dodecyl sulfate. Adding different monovalent ions has a pronounced effect on the stability and film thickness of such films. The comparison of these results points out that the affinity of the ions for the air/water interface and the direct interaction of the ions with the surfactant affect the stability and thickness of foam films. From the film studies the adsorption and ordering behavior of ions at the air/water interface can be indirectly deduced.

4.1. Cation Effect. The attraction between the dodecyl sulfate and the counterions increases in the order of $\text{Li}^+ < \text{Na}^+ < \text{Cs}^+$ (or $\text{LiDS} < \text{SDS} < \text{CsDS}$). This leads to the lowest degree of dissociation in the case of CsDS. As a consequence, the surfactant charge is smaller and the surface density of CsDS is larger than for SDS or LiDS close to the cmc as detected by surface tension measurements (Figure 1). Lateral screening of the surfactant charges in the interface seems to have a minor effect. The higher surfactant density might cause higher surface charge, which is not the case (Table 1). The surface charge density decreases in the order $\text{LiDS} > \text{SDS} > \text{CsDS}$, which means that the degree of dissociation is the dominant effect.

Generally, there exist three possible ways how the addition of different cations affects the thickness and stability of foam films stabilized by anionic surfactant. (1) Increased screening of the electrostatic repulsion between the two interfaces. By assuming a constant amount of adsorbed surfactant, fixed surface charge density, and reducing potential, this leads to a thinning of films as discussed in section 4.3. (2) Increased screening of the surfactant–surfactant repulsion in an interface (lateral screening) results in a higher surface charge if one assumes an increasing amount of adsorbed surfactant and a constant degree of dissociation. This has been observed upon addition of salt which will be further discussed in section 4.3, but not for different types of salt at a fixed salt concentration. (3) Adsorption of cations in the interfacial regions leading to a reduced surface charge density, which was here observed for different types of salt at a fixed salt concentration as further discussed in the following.

A recent study demonstrated that the air/water interface shows a strong selectivity for both anions and cations.³² Furthermore, SFG measurements showed that the ion–interface affinity increases from Li^+ to Na^+ to Cs^+ .⁴² Thus, the large cations have

the largest tendency to be at or close to the air/water interface, similarly to the anions. While accumulation of anions leads to an enhancement of the negative surface potential and surface charge density of the air/solution interface, resulting in thicker and more stable films, the accumulation of cations reduces the negative surface potential and surface charge density, leading to thinner and less stable films (see Table 2). The film thickness and stability decrease with increasing size from Li^+ to Na^+ to Cs^+ . The ion charge density of Li^+ is smaller compared to the other alkaline cations. Li^+ possesses the highest charge density and thus the largest hydration shell. This increases the contact distance between cations and anions/headgroups, leading to an attenuation of the Coulomb interaction. Foam films stabilized by 0.3 mM SDS in 0.1 mM LiCl are thicker than SDS foam films containing NaCl or CsCl.

The presented results are in good agreement with the findings reported by Sentenac and Benattar. They studied the influence of LiCl and CsCl on aerosol-OT (AOT) films at a fixed surfactant concentration close to the cmc.⁴⁴ The $\Pi(h)$ isotherm containing LiCl equals the curve with CsCl at $c_{\text{salt}} = 50 \text{ mM}$. However, for salt concentrations $>50 \text{ mM}$, the addition of LiCl leads to about 10 nm thicker films than in the case of CsCl. The separation of 10 nm between both films remains approximately constant, even if the electrolyte concentration is increased further. The disjoining pressure isotherms of the AOT/CsCl systems can be described by the classical DLVO approach, while it fails in the case of LiCl. Apparently, an additional repulsion arises on the LiCl containing the $\Pi(h)$ isotherm. The authors argue that the additional repulsion in the case of AOT/LiCl films is a consequence of the reduced screening perpendicular to the film surfaces due to the large hydration shell of Li^+ . Another explanation could be that the adsorption density of Li^+ in the subsurface layer is lower because of its large hydration radius. The hydration radius of the lithium cation (3.82 Å) is larger than the hydration radius of sodium (3.58 Å) and of cesium (3.29 Å).

According to Collin, the interaction between a headgroup and a counterion depends on their surface charge densities.⁴⁵ Vlachy and co-workers classified anionic surfactants along the charge density of their headgroups resulting in a headgroup sequence, which resembles the Hofmeister anion series.⁴⁶ According to the authors, headgroups with a high charge density like carboxylates will form close ion pairs with cations of similar charge density like lithium, while headgroups with lower charge densities like sulfates or sulfonates will form ion pairs with cations with lower charge densities like cesium or ammonium.⁴⁶ This means for the present system that the addition of CsCl to a SDS solution leads to a partial exchange of Na^+ by Cs^+ . Furthermore, Cs^+ and DS^- are thought to form ion pairs. Indeed, the film thickness and stability are the lowest for the system with the highest probability for ion pairing, namely, CsDS solution or SDS solution containing CsCl.

The comparison of foam films stabilized by 0.1 mM CsDS (Figure 2) with foam films from 0.3 mM SDS in 0.1 mM CsCl (Figure 3) indicates that the surface and film properties of the SDS/CsCl system are dominated by the addition of CsCl, since both disjoining pressure isotherms are almost congruent and the surface potential and surface charge density of both foam films are similar within the PB calculations. The presented results strengthen the assumption that Na^+ is exchanged by Cs^+ . However, the precise composition of the adsorption layer cannot be deduced from film studies. In contrast, the comparison of foam films stabilized by LiDS with foam films from 0.3 mM SDS in 0.1 mM M LiCl shows no concurrence between both

disjoining pressure isotherms. According to literature, the exchange of the counterion of SDS (Na^+) by Li^+ is not favorable.^{20,37,45,46}

To summarize, the specific cation effect on film stability and thickness of foam films from anionic dodecyl sulfate surfactants is dominated by the strength of the interaction between the headgroup and its counterion. The addition of different cations can lead to an exchange of the counterion near the sulfate headgroup. The stronger the interaction between counterion and headgroup, the lower the stability and the film thickness.

4.2. Anion Effect. There are many experimental observations that anions adsorb on the charged air/water interface. The accumulation of larger ions, such as Cl^- and I^- , at the air/water interface has been probed by surface sensitive techniques like second harmonic generation (SHG) and sum frequency generation (SFG)^{38,47–53} as well as by computational methods.^{39,43,54–61} Furthermore, the investigation of ion specific effects on the (de)stability and functionality of thin aqueous wetting films with a TFPB showed that ions of the same valence but increasing size display a stronger tendency to adsorb at the surface.^{32,41} The enhancement of anions at the air/water interface leads to an increase in stability and thickness of aqueous wetting films, whereas the adsorption of cations has the reversed effect. The sign of the air/water interface is controversially discussed, but most of the experiments indicate a negative net charge.^{41,62,63}

The addition of various sodium halides to 0.3 mM SDS solutions caused (i) an enhancement of the film stability and thickness and (ii) the enhancement increasing with increasing anion size from F^- to Cl^- to I^- (Figure 4). The order of the halides is the same as that seen for aqueous wetting films of the pure sodium salt solutions on bare silicon⁴¹ and for halides at the air/water interface.

The fact that anions adsorb at the negatively charged air/water interface demonstrates that interactions beyond the Coulomb one can overcompensate the Coulomb repulsion and hence are important for the adsorption of co-ions at the air/water interface.^{32,38–42,64} In particular, small and intermediately polarizable anions with a large hydration shell like fluoride prefer to stay in water, while highly polarizable ions with a smaller hydration shell like iodide favor the hydrophobic air/water interface.^{65–67}

Additional negative charges can adsorb onto a negatively charged surface by two possible ways, which cannot be distinguished by the presented experiments. (i) The first effect is through available space at the air/water interface. In the concentration regime considered here, the interface is not saturated by DS^- . This means that more anions can adsorb at the interface. According to literature, there are three possible ways how the affinity of ions for the air/water interface can be explained. (1) The ions' affinity for an interface arises from the favorable interaction of the polarizability of an ion with the interfacial electric field due to the mean orientation of interfacial water molecules.^{68,69} (2) The interfacial affinity of ions can be explained by an adapted version of the standard theory of hydrophobic solvation.⁷⁰ According to that theory, the free energy cost to solvate a small neutral cavity is a measure of the cavity volume. This suggests that the adsorption of ions at the air/water interface is dominated by the size of the ion, and thus by its hydrophobic nature.⁶⁴ (3) Collective dipole-moment fluctuations of water are suppressed near an ion which applies a force on the ion that attracts it to regions where the density of dipole-moment fluctuations is lower than in bulk water, i.e., regions of lower relative permittivity.⁷¹

The specific influence of anions on the thickness and stability of foam films stabilized by SDS should be only visible at SDS concentrations where the interface is not completely covered by anions. Specific anion effects have been observed for foam films from SDS at 3 mM.⁷² This indicates that anion adsorption at the interface takes place in all concentrations considered here. However, at high surface coverage there is smaller fraction of anion-free interface, and thus, the charging of the surface due to anion adsorption is not pronounced enough to overcome the screening perpendicular to the film surfaces. This point will be further discussed in section 4.3.

The second effect arises due to the fact that anions can enter the hydrophobic area of the monolayer.⁷³ The ability of individual anions to penetrate into the alkyl chain portion follows the Hofmeister series.^{73–76} A possible explanation as to why anions penetrate into the alkyl chain portion could be their polarizability. Due to the high polarizability of large anions, a dipole is induced in the otherwise spherical anion at the surface. The attractive interaction between the induced surface dipoles, the surrounding water molecules, and the headgroups compensates the electrostatic repulsion and loss of solvation energy. That was not explicitly cross-checked for cations, but there are hints that it could also happen there.⁷²

4.3. Effect of Salt Concentration. The qualitative dependencies of salt concentrations on film stability and thickness do not strongly depend on the type of salt. For all salts, the stability shows (i) a local maximum at a salt concentration of about 0.1 mM and (ii) a minimum at a salt concentration equal to the surfactant concentration (Figure 5). Furthermore, all thicknesses at the pressure 420 Pa increase up to the salt concentration of 0.1 mM and thereafter display a monotonous decrease (Figure 6). A qualitatively similar effect of the salt concentration was also found for cationic surfactants at varied salt concentrations.⁷² The increase in film thickness at low salt concentrations is explained by a charging effect of the film interfaces. Since the addition of all salts causes an increased film thickness, it is assumed that the screening of the electrostatic surfactant–surfactant repulsion leads to a higher surface charge. At $c_{\text{salt}} > 0.1$ mM, screening of the electrostatic repulsion between the two film interfaces becomes the leading contribution to the thinning of foam films.

5. Conclusion

The choice of additional co-ions and counterion of surfactant is a powerful tool to tune the foam film (de)stability of surfactant solutions. The aim of this work was to clarify the ion specific effect on the stability and film thickness of foam films stabilized by dodecyl sulfates. Adding different monovalent ions has a pronounced effect on the stability and film thickness of SDS films. Even anions show a strong effect on the properties of foam films from SDS. Negatively charged ions can still adsorb at the air/solution interface, although it is already negatively precharged.

The tendency for adsorption at the film surfaces increases with increasing ion size. This leads to more stable and thicker films in the case of anions and the opposite effect for cations, which was also supported by the results of the PB calculations of the experimental data. The type of counterion affects the degree of dissociation of the surfactants.

The addition of cations which differ from the original counterion of the surfactant molecules leads to competitive cation adsorption at the sulfate headgroups. This could result in an exchange of the native counterion of the surfactant. The type of the counterion of dodecyl sulfates directly influences

the foam film thickness and its stability. With increasing cation size the interaction between the sulfate headgroup and the counteracting cation increases. This enhances the adsorption of surfactant molecules at the foam film interface. Simultaneously, the surface charge density and the resulting electrostatic repulsion decrease. The comparison of the presented results points out that the ion specific effect on the film thickness and stability of foam films from sodium dodecyl sulfate is dominated by the ion size, at least for alkali and halides.

By varying the salt concentration, a maximum of the stability and thickness of SDS films at a salt concentration below the surfactant concentration is observed. At low salt concentrations charging of the surfaces takes place, while above the maximum screening perpendicular to the film surfaces dominates.

Acknowledgment. Financial support from the DFG (KI 1165-10/1 and 10/2) SPP 1273 “Kolloidverfahrenstechnik” and the Swedish Research Council (VR) through the Linnaeus Center of Excellence on Organizing Molecular Matter (OMM) is gratefully acknowledged.

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