

Stability of Foam Films of Oppositely Charged Polyelectrolyte/Surfactant Mixtures: Effect of Isoelectric Point

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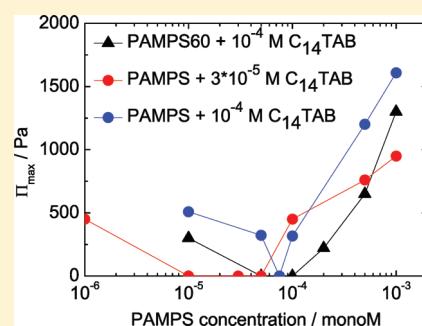
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 Supporting Information

ABSTRACT: In the present paper, the influence of the surfactant concentration and the degree of charge of a polymer on foam film properties of oppositely charged polyelectrolyte/surfactant mixtures has been investigated. To verify the assumption that the position of the isoelectric point (IEP) does not change the character of the foam film stabilities, the position of the IEP of the polyelectrolyte/surfactant mixtures has been shifted in two different ways. Within the first series of experiments, the foam film properties were studied using a fixed surfactant concentration of 3×10^{-5} M in the mixture. Due to the low surfactant concentration, this is a rather dilute system. In the second approach, a copolymer of nonionic and ionic monomer units was used to lower the charge density of the polymer. This gave rise to additional interactions between the polyelectrolyte and the surfactant, which makes the description of the foam film behavior more complex. In both systems, the same characteristics of the foam film stabilities were found: The foam film stability is reduced toward the IEP of the system, followed by a destabilization around the IEP. At polyelectrolyte concentrations above the IEP, foam films are very stable. However, the concentration range where unstable films were formed was rather broad, and the mechanisms leading to the destabilization had different origins. The results were compared with former findings on PAMPS/C₁₄TAB mixtures with an IEP of 10^{-4} M.¹



1. INTRODUCTION

Foams are dispersions from air bubbles in a liquid and are used in many applications, such as detergency, cosmetics, fire fighting, and enhanced oil recovery.² To investigate the properties of drained foams, it is generally accepted to examine the corresponding foam lamellas, which can be regarded as the main building blocks of the foam.^{3,4} The single foam film lamellas are stabilized by an excess pressure with respect to the bulk liquid normal to the film interfaces, which is called disjoining pressure Π .^{5,6} It arises from a thin transition region at the interface, whose properties derive from those of the two neighboring bulk phases.⁴ Since the disjoining pressure is an additive force, various components, such as electrostatic, van der Waals and steric forces, contribute to the stabilization of the foam film. Depending on the origin of the force, two different types of foam film can be formed. If the film is stabilized mainly by electrostatic forces, a common black film (CBF) is formed with a thickness of ~ 10 – 100 nm. On the other hand, Newton black films are stabilized mainly by steric forces and have a thickness of 5 – 10 nm in the case of foam films stabilized by low molecular weight surfactants.

Especially interactions between polyelectrolytes and surfactants are of great relevance in industry. Therefore, the present study deals with the characteristics of foam films from oppositely charged polyelectrolyte/surfactant mixtures. Depending on the type of polyelectrolyte and surfactant, the interactions can be of

different natures. In the case of charged polyelectrolyte/surfactant mixtures, either repulsive or attractive electrostatic interactions can occur between the components.^{7–9} Furthermore, when nonionic compounds or components that are accessible to hydrophobic interactions are used in a mixture, hydrophobic interactions play an important role, as well.^{10,11} All these forces have a strong influence on, for example, the properties of foam films or the hydrodynamic behavior of the bulk solution.

In the case of oppositely charged polyelectrolyte/surfactant mixtures, a strong electrostatic attraction is observed.^{12–16} The charges of the polyelectrolyte form complexes with surfactant molecules of opposite charge, which is entropically favorable due to the release of counterions.¹⁷ Depending on the ratio of the two compounds, the formation of these complexes can lead to hydrophobic aggregates located at the surface. Furthermore, the study of different polyelectrolyte/surfactant mixtures showed that the stability of foam films strongly depends on this ratio.^{1,18}

The stability of the foam films decreases when the isoelectric point (IEP) of the system is approached. When the IEP is crossed, foam films with a high stability are formed, which might indicate a charge reversal at the film surfaces. Surprisingly, the surface

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coverage gives no hint for a charge reversal at the interface. Below the IEP, the surface tension of the corresponding mixtures is low, indicating polyelectrolyte/surfactant complexes at the surface. However, once the IEP is crossed, a sudden release of the material from the surface is detected by the surface characterization methods, which implies that only a more or less pure surfactant layer is left at the interface. This indicates that not the surface layers of the foam films are crucial for foam film stability, but the net charge of the polyelectrolyte/surfactant complexes in the system plays an important role.^{1,18}

To verify the hypothesis that these findings are not unique for systems with an IEP at a polyelectrolyte and surfactant concentration of 10^{-4} M, it is important to investigate polyelectrolyte/surfactant mixtures with a different the IEP. For PAMPS/ C_{14} TAB systems, two different ways of changing the point of equal charges are possible. In the first series of experiments, the concentration of the surfactant is changed, leading to a system that is either more concentrated or more dilute than the system described in ref 1. Accordingly, only concentration effects are assumed to influence the interactions in foam films and, hence, their stability.

An alternative to the variation of the surfactant concentration is the use of a polyelectrolyte with a different degree of charge. Because only polymers with a charge density of 100% were studied in former investigations, a polymer with a lower degree of charge has to be used for this approach. For this purpose, a random copolymer of negatively charged and nonionic monomer units (namely, poly[tris(hydroxymethyl)methyl]acrylamide-co-acrylamido methyl propanesulfonate) is synthesized. Within this copolymer, the charged units are exchanged with nonionic but not very hydrophobic monomer units. In addition to electrostatic attraction between the charged components, now hydrophobic interactions between the nonionic monomer units and the surfactant or other polyelectrolyte chains can also occur.

2. EXPERIMENTAL SECTION

2.1. Materials. The cationic surfactant tetradecyltrimethylammonium bromide (C_{14} TAB) was purchased from Sigma-Aldrich (Steinheim, Germany) and recrystallized three times from acetone with traces of ethanol.¹⁹ The anionic polyelectrolytes poly(acrylamidomethyl propanesulfonate) sodium salt (PAMPS) and poly([tris(hydroxymethyl)methyl]acrylamide-co-acrylamidomethyl propanesulfonate) sodium salt (PAMPS60) (Figure 1) were prepared by an aqueous free radical polymerization with different charge fractions.²⁰ The first was synthesized with a nominal degree of charge of 100%, and the latter has a nominal charge fraction of 60%. Both polyelectrolytes were used as received. All solutions were prepared from Milli-Q water with a fixed surfactant concentration and different polyelectrolyte concentrations. All given polymer concentrations are related to the concentration of the respective monomer units.

2.2. Methods. **2.2.1. Thin Film Pressure Balance (TFPB).** A common method to measure disjoining pressure isotherms is the thin film pressure balance (TFPB).²¹ It was first developed by Mysels and Jones,²² later improved by Exerowa and co-workers,^{23–26} and allows the formation of horizontal, free-standing films. In this paper, the experiments were performed with the porous plate technique. The film is formed from a droplet in a hole (diameter ≈ 1 mm) that is drilled into a porous glass disk with a pore size of 10–15 μ m. The film holder is placed in the sealed stainless steel measuring cell that is equipped with a quartz glass window to monitor the film and a temperature control. It is connected to the

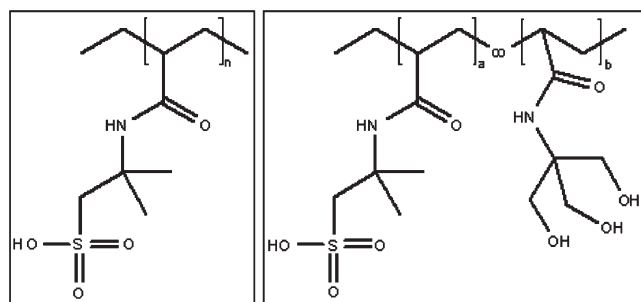


Figure 1. Chemical structure of the used polyelectrolytes. On the left, PAMPS; on the right, PAMPS60.

ambient reference pressure via a glass capillary. A reservoir of the sample solution is located in the cell to provide a saturated vapor pressure during the measurement. The pressure in the cell is adjusted via a motor-driven syringe pump. The corresponding film thickness is determined interferometrically by the method of Scheludko.^{27,28} Before the measurement, the film holder was immersed into the sample solution for 2 h to saturate the pores. Thirty min before starting the experiment, the holder was pulled out of the solution to give the surfaces of the droplet time to equilibrate. For each data point, the intensity of the light reflected from the film was recorded until it was constant for 20 min, which was then assumed to be in equilibrium. The experiments were carried out at 23 °C.

2.2.2. PB Calculation of the Disjoining Pressure Isotherms. The disjoining pressure isotherms are calculated with the PB program written by Per Linse²⁹ to get information about the surface potential of the foam films. In this program, the nonlinear Poisson–Boltzmann equation is solved under the assumption of constant surface potential. The numerical approach in the program considers two planar surfaces separated by the distance D and with their normals in the z direction. Since in the case of infinite, equally charged, and planar surfaces, the potential cannot change in the x and y directions because of the symmetry, only the variation in the z direction is important.³⁰ The intervening liquid is in equilibrium with a bulk electrolyte solution. Because of the symmetry of the thin film, only one-half of the system needs to be considered, $0 \leq z \leq b$, $b = D/2$. To obtain a unique solution, two boundary conditions are needed.^{5,6} The first one follows the symmetry requirement that the field must vanish at the midplane:

$$\left. \frac{d\Psi(z)}{dz} \right|_{z=b} = 0 \quad (1)$$

The second boundary condition derives from the requirement of electroneutrality, that is, that the total charge of the counterions between the two surfaces must be equal to the charge at the surface:

$$\left. \frac{d\Psi(z)}{dz} \right|_{z=0} = -\frac{\sigma}{\epsilon_0 \epsilon_r} \quad (2)$$

Before the calculation, the disjoining pressure isotherms are fitted with an exponential decay function of first order. From this fit, the Debye length and the corresponding ionic strength are calculated to get a good starting point for the PB calculation. Due to Manning condensation, only around one-third of the charged polymer units are dissociated. Therefore, the ionic strength cannot

be calculated by assuming 100% dissociation of all charged groups and has been derived from the fitting of the experimental disjoining isotherms. During the calculation process, the surface potential and the ionic strength are adjusted until the calculated curve coincides with the experimental data.

2.2.3. Surface Tension Measurements. Surface tension measurements were performed on a K11 tensiometer from Krüss (Hamburg, Germany) using the du Noüy ring method. The Teflon trough (diameter = 5 cm) with the respective sample solution was tempered for 15 min at 23 °C, and a lamella was pulled out of the solution to let the polyelectrolyte surfactant complexes adsorb at the surface.

2.2.4. Dynamic Surface Elasticity Measurements. The surface elasticity measurements were performed at a PAT1 (Sinterface Technologies, Berlin, Germany). The pendant drop was created at the tip of a capillary by a computer-driven dosing system. The drop was placed in a closed cuvette with a small reservoir of the sample solution at the bottom to prevent evaporation. Drop images were acquired with a CCD video camera, and from these images, the surface tension was calculated by drop shape analysis. After formation of the droplet, the surface was left to equilibrate for at least 2 h, then harmonic oscillations of the drop surface area were created with the computer-controlled dosing system, and both surface area A and surface tension γ were monitored as a function of time. The frequencies of the oscillation were varied between 0.005 and 0.1 Hz with at least six oscillations per frequency. All measurements were carried out at room temperature. The dilational surface elasticity, ε , was calculated according to the following equation,

$$\varepsilon(\omega) = \varepsilon_r + i\varepsilon_i = \frac{d\gamma}{d \ln A} \quad (3)$$

where ε , $d\gamma$, and $d \ln A$ are complex quantities. The elasticity modulus is determined from the amplitude ratio of the oscillating surface tension and surface area, whereas the dilational viscosity can be determined from the phase shift of the two dimensions.³¹

3. RESULTS

In the present work, we have investigated polyelectrolyte/surfactant mixtures of a fixed surfactant concentration and variable polymer concentration. In former studies, we have shown that with a surfactant concentration of 10^{-4} M, a complete destabilization¹ or at least a minimum in film stability¹⁸ occurred close to the IEP. To check whether the minimum in film stability is correlated to the IEP, experiments with mixtures of different IEP were performed. The term IEP refers to the composition of equal concentration of surfactant and charged monomers. In the following, the influence of the surfactant concentration and the charge degree of the polymer is shown.

3.1. Effect of C_{14} TAB Concentration. In a first set of experiments, the IEP was shifted by changing the surfactant concentration in the PAMPS/ C_{14} TAB mixture. A surfactant concentration other than 10^{-4} M has to be carefully chosen. For a significantly different IEP, the surfactant concentration should not be too close to 10^{-4} M. On one hand, if the amount of surfactant is too high, the corresponding polyelectrolyte concentration crosses the overlap concentration, c^* , of the polyelectrolytes. In that case, the effect of the surface charge could be superposed by the stratification process, which would conceal surface effects. On the other hand, a certain surfactant concentration is needed to stabilize the foam film because this is a precondition for this type of investigation.

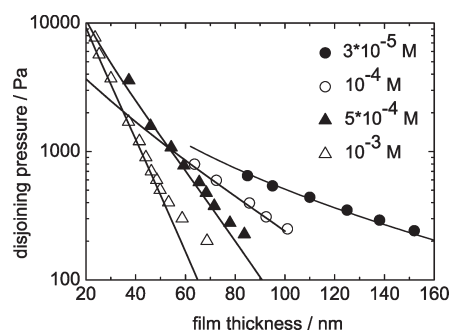


Figure 2. Disjoining pressure isotherms of pure C_{14} TAB films at different concentrations; the solid lines correspond to PB calculations at constant potential.

Table 1. Summary of the Surface Potentials, Ψ_0 , from the PB Calculation of the Disjoining Pressure Isotherms of C_{14} TAB Films at Different Surfactant Concentrations^a

C_{14} TAB concn (M)	Ψ_0 (mV)	κ_{PB}^{-1} (nm)	I_{PB} (M)	κ_{theo}^{-1} (nm)	I_{theo} (M)
3×10^{-5}	117	53.1	2.0×10^{-5}	55.9	3.0×10^{-5}
1×10^{-4}	78	29.3	1.0×10^{-4}	30.4	1.0×10^{-4}
5×10^{-4}	95	15.9	4.0×10^{-4}	13.7	5.0×10^{-4}
1×10^{-3}	98	10.3	1.0×10^{-3}	9.7	1.0×10^{-3}

^a The Debye length, κ_{PB}^{-1} , is calculated from a fit of the experimental data with an exponential decay function of first order; the ionic strength, I_{PB} , is derived from the PB calculation of the surface potential; κ_{theo}^{-1} and I_{theo} are calculated assuming 100% dissociation.

Figure 2 shows isotherms of pure C_{14} TAB films at different surfactant concentrations. It reveals that the foam films get thinner and the isotherms, steeper, with increasing surfactant concentration. This effect is related to the increasing ionic strength in the investigated surfactant solutions. The disjoining pressure isotherms are in good agreement with former findings by Exerowa et al. and Schulze-Schlarman et al.^{3,19} At the lowest investigated concentration, a thickness of 153 nm is observed at 220 Pa. With the addition of more surfactant, the film thickness considerably decreases from 101 nm at 10^{-4} M to 70 nm at 10^{-3} M at the same disjoining pressure due to the screening of the charges of the surfactant head groups at the surface. In addition to the film thinning, the stability of the foam films steadily increases from a Π_{max} of 700 Pa at 3×10^{-5} M C_{14} TAB to 8000 Pa at a surfactant concentration of 10^{-3} M. However, in contrast to the monotonic behavior of the disjoining pressure isotherms in terms of film thinning and stability increase, the surface potentials obtained from the PB calculations of the isotherms are not monotonic. In fact, the potential is strongly reduced from 117 to 78 mV when the surfactant concentration is increased from 3×10^{-5} to 10^{-4} M. At this concentration, a minimum potential is observed, and the potential rises again when more C_{14} TAB is added to the system. At 10^{-3} M, the surface potential reaches a value of almost 100 mV (see Table 1).

After these preliminary tests, the C_{14} TAB concentration was fixed at 3×10^{-5} M, which fulfils the above-described requirements of the experiment. This also determines the nominal IEP of this system, which is now 3×10^{-5} M. In Figure 3, disjoining pressure isotherms of PAMPS/ C_{14} TAB films at polyelectrolyte

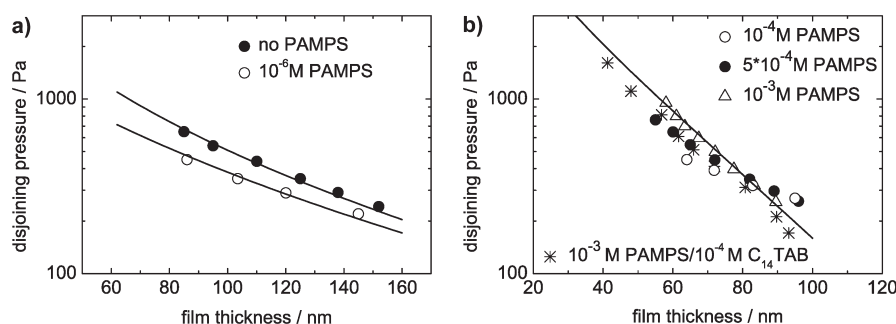


Figure 3. Disjoining pressure isotherms of PAMPS/ C_{14} TAB solutions with a fixed surfactant concentration of 3×10^{-5} M and with varied polyelectrolyte concentration (a) below the IEP and (b) above the IEP. The solid lines represent the PB calculation of the foam films at constant potential. For the sake of clarity, only some of the calculated isotherms are shown in the graph. For comparison, the stars indicate the data point of the disjoining pressure isotherm of 10^{-3} M PAMPS and 10^{-4} M C_{14} TAB.

Table 2. Summary of the Surface Potentials, Ψ_0 , from the PB Calculation of the Disjoining Pressure Isotherms of PAMPS/ C_{14} TAB Films at a Surfactant Concentration of 3×10^{-5} M^a

PAMPS concn (monoM)	Ψ_0 (mV)	κ_{PB}^{-1} (nm)	I_{PB} (M)	κ_{theo}^{-1} (nm)	I_{theo} (M)
no PAMPS	117	53.1	2.0×10^{-5}	55.9	3.0×10^{-5}
1×10^{-6}	102	50.0	2.0×10^{-5}	55.0	3.1×10^{-5}
1×10^{-4}	70	33.8	5.0×10^{-5}	26.8	1.3×10^{-4}
5×10^{-4}	75	23.3	1.0×10^{-4}	13.2	5.3×10^{-4}
1×10^{-3}	90	16.5	2.5×10^{-4}	9.5	1.0×10^{-3}

^a The Debye length, κ_{PB}^{-1} , is calculated from a fit of the experimental data with an exponential decay function of first order; the ionic strength I_{PB} is derived from the PB calculation of the surface potential; κ_{theo}^{-1} and I_{theo} are calculated assuming 100% dissociation.

concentrations between 10^{-6} and 10^{-3} M PAMPS and of the foam film of the pure surfactant solution are shown. In Figure 3a, isotherms below the IEP are depicted. Note that the films are thicker now than for the system with a C_{14} TAB concentration of 10^{-4} M.¹ The addition of 10^{-6} M PAMPS reduces the thickness compared with the pure surfactant film by 10–142 nm at 220 Pa. Disjoining pressure isotherms of foam films with a PAMPS concentration larger than 10^{-4} M are shown in Figure 3b. In this case, an equilibrium thickness between 90 and 100 nm is found at low disjoining pressures, which is in good agreement with the measurements at higher surfactant concentration. The slope of the respective isotherms increases with increasing polyelectrolyte concentration. This phenomenon is related to the fact that a higher polyelectrolyte concentration leads to a higher ionic strength in the system. Furthermore, the ionic strengths of the mixtures (cf. Table 2) are in good agreement with the Manning concept of counterion condensation, which predicts for PAMPS that only one-third of the polyelectrolyte charges are dissociated.

In Figure 4, the stabilities of the foam films containing 5×10^{-5} M C_{14} TAB are marked by solid circles. The foam film stability is depicted by plotting Π_{max} versus the polymer concentration. Π_{max} is defined as the maximum disjoining pressure that can be applied to the foam films before they rupture. The pure C_{14} TAB foam film is stable up to a disjoining pressure of 700 Pa. With the addition of 10^{-6} M PAMPS, the Π_{max} of the foam film decreases to 480 Pa. These findings are supported by the corresponding potentials of the film surface. Foam films of a C_{14} TAB concentration of 3×10^{-5} M have a surface potential of 117 mV, which is very high compared with 78 mV of the film at 10^{-4} M C_{14} TAB.¹ The potential is reduced to 102 mV when

10^{-6} M PAMPS is added. In a concentration regime between 10^{-6} M and 10^{-4} M PAMPS, no stable film can be formed at all. This is a very broad concentration regime compared with the system of PAMPS/ C_{14} TAB with an IEP at 10^{-4} M (open circles in Figure 4), in which only one particular polyelectrolyte concentration leads to the destabilization of the foam film. The addition of more polyelectrolyte leads to an increase in film stability from 450 Pa at 10^{-4} M to almost 1000 Pa at a PAMPS concentration of 10^{-3} M. This is accompanied by an increase in surface potential up to 90 mV at 10^{-3} M PAMPS. All results of the PB calculations are summarized in Table 2.

For a better characterization of the surface properties of foam film stabilized by PAMPS/ C_{14} TAB mixtures at an IEP of 3×10^{-5} , surface tension measurements were performed. There are some approaches to measure the interfacial film tension directly;^{32,33} however, since it is not possible in our setup to measure the interfacial tension of the foam film, the corresponding polyelectrolyte/surfactant solution has been investigated. In fact, theoretical considerations predict a different surface coverage in the case of a foam film compared with the surface of the bulk solution.^{34,35} However, it is assumed that these changes are only minor so that they can be neglected, that is, the change in surface coverage is around 3% in the case of NBF.³⁴

As shown in Figure 5, the shape of the surface tension isotherm of PAMPS/ C_{14} TAB at 3×10^{-5} M resembles qualitatively that of the mixture at 10^{-4} M C_{14} TAB but shows less reduction in surface tension. The addition of a low amount of PAMPS (10^{-6} M) has almost no influence on the surface tension so that it corresponds to that of the pure surfactant solution. When the polyelectrolyte concentration is increased in the systems with 3×10^{-5} M C_{14} TAB, the surface tension decreases steadily until a

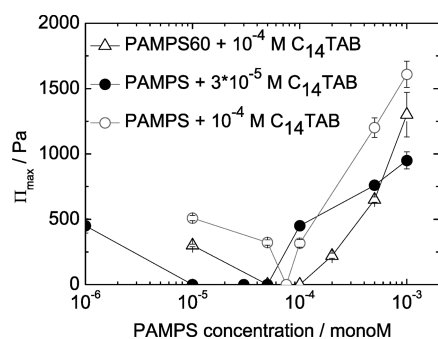


Figure 4. Stability of PAMPS/ C_{14} TAB films at different IEPs: IEP = 3×10^{-5} M (solid circles), IEP = 1.6×10^{-4} M (open triangles), IEP = 10^{-4} M (open circles), and maximum disjoining pressure Π_{\max} before film rupture versus polyelectrolyte concentration.

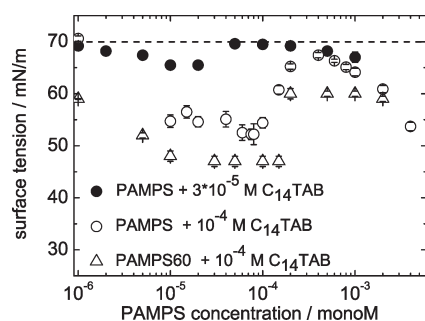


Figure 5. Surface tension of PAMPS/ C_{14} TAB solutions with fixed surfactant and variable PAMPS concentration at different IEPs: IEP = 3×10^{-5} M (solid circles), IEP = 10^{-4} M (open circles), and IEP = 1.6×10^{-4} M (open triangles). The dashed line corresponds to the surface tension of the pure surfactant at both concentrations.

minimum of 65 mN/m at 2×10^{-5} M is reached. This is less pronounced than in the case of a higher surfactant concentration and shifted to a lower PAMPS concentration. For PAMPS concentrations above the nominal IEP, the surface tension goes back to the value of the pure surfactant solution, which implies the release of material from the surface; however, polyelectrolyte concentrations larger than 2×10^{-4} M induce again the lowering of the surface tension.

3.2. Effect of PAMPS Charge Density. Another way to shift the IEP of the system is to change the degree of charge of the polyelectrolyte. So far, only polyelectrolytes with 100% charged monomer units have been investigated. Again, the type of polymer and the degree of charge need to be carefully chosen. On one hand, the degree of charge of the polyelectrolyte should be significantly different from 100% to get an IEP that can be distinguished from the former one. On the other hand, the reduction of charge density increases the hydrophobicity of the polymer, which can lead to the formation of aggregates and to a decrease in the solubility in water.³⁶ In the case of PAMPS at a degree of charge of 60%, no problems with solubility occur in the presence of 10^{-4} M C_{14} TAB, and the formation of aggregates is not very pronounced. The IEP in this system is 1.6×10^{-4} M.

In Figure 6, the disjoining pressure isotherms of the PAMPS60/ C_{14} TAB system are shown. In Figure 6a, isotherms without any polyelectrolyte and with a PAMPS60 concentration below the IEP are plotted, whereas in Figure 6b, isotherms above

the IEP are shown. The pure surfactant foam film at 10^{-4} M is stable up to a disjoining pressure of 900 Pa. The addition of 10^{-5} M PAMPS60 decreases the film stability drastically to 300 Pa. Between 10^{-5} and 2×10^{-4} M PAMPS60, which is slightly above the IEP of the system, no stable films can be formed. When the polyelectrolyte concentration is increased to 2×10^{-4} M, the corresponding foam film reaches a stability of 250 Pa, which is depicted in Figure 6b by a solid circle.

The stability of the foam films is shown in Figure 4. Further increase in the PAMPS60 concentration results in a strong increase in stability to 650 Pa at 5×10^{-4} M and 1200 Pa at 10^{-3} M. The foam film of the pure surfactant has a thickness of 101 nm at 220 Pa. The addition of 10^{-5} M PAMPS60 induces a slight increase in film thickness. At higher polymer concentration, the equilibrium film thickness at the same pressure is around 106 nm, which is high compared with other polyelectrolyte/surfactant systems. Furthermore, the slope of the isotherms increases with increasing ionic strength.

The shape of the stability curve is supported by the surface potentials that are calculated as specified in Table 3. The surface potentials of the foam films at 10^{-5} M and 2×10^{-4} M are not available, since there are too few data points to calculate the isotherm. The PB calculation of the isotherm at 5×10^{-4} M PAMPS60 results in a potential of 58 mV, which is considerably lower than that of the pure surfactant film. With increasing polyelectrolyte concentration, the surface potential rises and reaches a value of 72 mV at 10^{-3} M PAMPS60.

The shape of the surface tension isotherm of PAMPS60/ C_{14} TAB in Figure 5 is slightly different compared with PAMPS/ C_{14} TAB mixtures with fully charged PAMPS. The addition of polymer to the surfactant solution has a much larger influence on the surface tension, even though the degree of charge and the corresponding ability to form complexes with the surfactant is lower. At 10^{-6} M PAMPS60, the surface tension is already reduced to 68 mN/m compared with 70 mN/m of the pure surfactant solution. Further increasing the polymer concentration induces a strong reduction of surface tension until a plateau of 46 mN/m is reached at 5×10^{-5} M PAMPS60. The surface tension remains constant until the IEP of 1.6×10^{-4} M. The plateau is 6 mN/m below the minimum that is obtained for PAMPS/ C_{14} TAB with an IEP of 10^{-4} M. At higher polymer concentrations, a sudden increase in the surface tension can be observed, but in contrast to other polyelectrolyte/surfactant systems, the mixture does not reach the value of the pure surfactant. In fact, a second plateau is reached at 60 mN/m.

Since the surface tension measurements reveal rather unexpected properties of PAMPS60/ C_{14} TAB complexes at the surface, additional experiments have been carried out to characterize the free air/liquid interface. In Figure 7, the results of dilational surface elasticity measurements are shown. As suggested by the surface tension measurements, the surface elasticity increases upon polyelectrolyte addition compared with the value of the pure surfactant until a plateau is reached at 10^{-5} M PAMPS60. At the lowest measured polyelectrolyte concentration, the elasticity of the different frequencies varies between 25 and 40 mN/m. At the plateau of 60 ± 5 mN/m, the variation is smaller and is even more reduced close to the nominal IEP. Above the IEP, the surface elasticity drops to 38 ± 3 mN/m and stays constant up to a polymer concentration of 10^{-3} M, which is consistent with the surface tension measurements. However, the variation of the surface elasticity between the different frequencies increases continuously in this concentration regime.

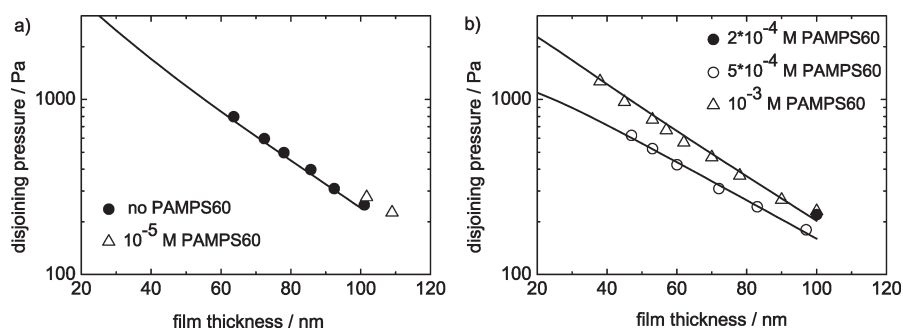


Figure 6. Disjoining pressure isotherms of PAMPS60/ C_{14} TAB solutions with fixed surfactant concentration (10^{-4} M) and varied polyelectrolyte concentration (a) below and (b) above the IEP. The solid lines represent the PB calculations of the foam films at constant potential.

Table 3. Summary of the Surface Potentials Ψ_0 from the PB Calculation of the Disjoining Pressure Isotherms of PAMPS 60/ C_{14} TAB films^a

PAMPS60 concn (monoM)	Ψ_0 (mV)	κ_{PB}^{-1} (nm)	I_{PB} (M)	κ_{theo}^{-1} (nm)	I_{theo} (M)
no PAMPS	78	29.8	1.0×10^{-4}	30.4	1.0×10^{-4}
5×10^{-4}	58	28.0	1.0×10^{-4}	15.3	4.0×10^{-4}
1×10^{-3}	72	25.7	1.3×10^{-4}	11.6	7.0×10^{-4}

^aThe Debye length, κ_{PB}^{-1} , is calculated from a fit of the experimental data with an exponential decay function of first order; the ionic strength, I_{PB} , is derived from the PB calculation of the surface potential; κ_{theo}^{-1} and I_{theo} are calculated assuming 100% dissociation.

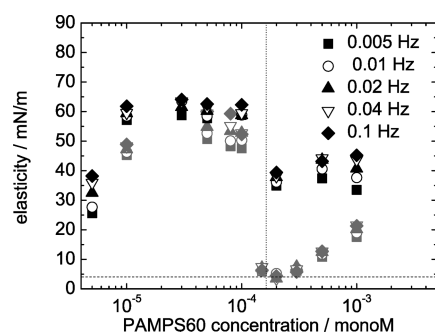


Figure 7. Surface elasticity of PAMPS60/ C_{14} TAB solutions with fixed surfactant (10^{-4} M) and variable PAMPS concentration at different frequencies. The dashed line corresponds to the elasticity of the pure surfactant; the vertical line illustrates the nominal IEP of the system. For comparison, the elasticities of PAMPS/ C_{14} TAB are shown in gray.

4. DISCUSSION

The foam film stability and surface properties of PAMPS/ C_{14} TAB with an IEP of 3×10^{-5} M and PAMPS/ C_{14} TAB with an IEP of 10^{-4} M show some systematic likenesses. The addition of small amounts of polyelectrolyte reduces the film stability until a total destabilization occurs in a concentration regime close to the respective IEP of each system. When the concentration of polyelectrolyte segments exceeds that of the surfactant, the films are significantly more stable than the pure surfactant films.

The mixtures described in this study show a broader concentration range in which unstable films occur than in the case of PAMPS/ C_{14} TAB with an IEP of 10^{-4} .¹ In addition, surface tension and elasticity measurements of PAMPS60/ C_{14} TAB show deviations from the findings of PAMPS/ C_{14} TAB so that the destabilization is presumably based on different mechanisms in the two cases.

4.1. Effect of Surfactant Concentration. The major difference between the PAMPS/ C_{14} TAB system with an IEP at 10^{-4} M and the one at 3×10^{-5} M is the surfactant coverage at the interface.

For example, the reduction of film stability of the pure surfactant film at 3×10^{-5} C_{14} TAB (700 Pa) compared with the film at a concentration of 10^{-4} M ($\Pi_{\max} = 900$ Pa) can be explained by this difference. However, since at both surfactant concentrations the surface tension is close to water, no difference in surface coverage is detectable.¹⁹ In contrast to that, the foam films of the two investigated surfactant concentrations show significantly different interactions between the film surfaces. At 3×10^{-5} M, the disjoining pressure isotherms of the foam film are flatter, which can be explained by the low ionic strength of the system. In this concentration regime, two effects counteract each other. On one hand, the electrostatic repulsion arising from the dissociated surfactant molecules is low. Yet, on the other hand, the screening of the electrostatic double layer is not very pronounced, as well. Both the film thickness and the surface potential are very high at 3×10^{-5} M C_{14} TAB. The film thickness is based on the high potential at the interface, since the two opposing interfaces repel each other strongly.

The surface potential, in turn, results from an interplay of several contributions, such as surfactant adsorption at the interface, degree of dissociation of the charged molecules, charge screening, and molecular conformation at the surface. Since experimental evidence gave rise to the assumption that the pure water/air interface is negatively charged,³⁷ the addition of cationic surfactant leads to a charge reversal at the interface.

One major drawback of the surface potential calculations of symmetric films is that no statement can be made on the sign of the potential so that other methods have to be taken into account. For example, a study on wetting films of C_{14} TAB solutions reported the point of zero charge of the surface to be at 10^{-6} M,³⁸ which is well below the concentrations investigated in this work.

This leads to the conclusion that all surface potentials of the investigated C_{14} TAB foam films are positive, which means that there is, indeed, a minimum potential and not a charge reversal at a surfactant concentration of 10^{-4} M. A possible explanation is given by Teppner et al.,³⁹ who found in an ellipsometry study that the counterion distribution changes near the interface, depending on the investigated surfactant concentration. At low surfactant concentrations, the counterions do not enter the adsorption layer but stay in the diffuse double layer near the interface so that no ion pairs can be formed and no reduction of the surface charge occurs. At higher concentrations, the counterions are situated in both the adsorption and the diffuse double layer so that charge screening starts to play a role. This would explain the surface potential of 117 mV at 3×10^{-5} M C_{14} TAB with the absence of ion pair formation at the interface. When the surfactant concentration is increased to 10^{-4} M, the surface potential is reduced to 78 mV because of the beginning charge screening and counterion condensation. Further addition of surfactant leads again to an increase in the surface potential, which could result from the increased adsorption of charged molecules at the interface.

When polyelectrolytes are added to the system, the characteristics of the foam films change. As in the case of PAMPS/ C_{14} TAB with an IEP of 10^{-4} M, the addition of low amounts of PAMPS leads to a reduction of both the film stability and the surface potential. Furthermore, this is accompanied by a decrease in film thickness, implying that the polyelectrolytes, now situated at the surface, change the distribution of the counterions in the Helmholtz layer.³⁹ Since the polyelectrolytes and surfactants are oppositely charged, both compounds form surface-active complexes and thereby release their counterions, which leads to a gain in entropy. In analogy to the transition from a negatively charged air/water interface to a positively charged one after the addition of C_{14} TAB, one would expect a charge reversal due to the addition of oppositely charged polyelectrolytes, which would be indicated by the increase in stability and surface potential above the IEP. However, surface tension and elasticity contradict this assumption.

The surface tension shows the same characteristics as for the PAMPS/ C_{14} TAB system with an IEP of 10^{-4} M. However, the reduction in surface tension is less pronounced and the breaking point is shifted to the new IEP of 3×10^{-5} M. The reduced adsorption to the surface can easily be explained by the lower amount of surface complexes in this concentration regime. In a concentration regime between 10^{-5} and 8×10^{-5} M PAMPS, no stable films can be formed at all, even though the surface coverage changes significantly according to the surface tension. A maximum coverage is found below 3×10^{-5} M, and a reduced amount of material at the surface is measured above this concentration. This indicates that the surface coverage plays only a minor role in stabilizing the foam film and that the net charge of the dissociated polyelectrolyte chain is more important in this case.

In the described concentration range, the surface charge is obviously too low to stabilize a foam film and a sufficiently high charge in the system is not reached until the addition of 10^{-4} M PAMPS. At this point, stable foam films are formed again with a stability of almost 1000 Pa at 10^{-3} M PAMPS. This is more stable than the pure surfactant film, but less stable compared to PAMPS/ C_{14} TAB investigated before, although the polyelectrolyte concentration is the same. However, this phenomenon is not reflected in the surface potentials since they are in the same range as those of foam films of PAMPS/ C_{14} TAB with an IEP of 10^{-4} M. From this, the conclusion can be drawn that the stabilization of

foam films is affected by two individual parameters: the initial surfactant concentration and the polyelectrolyte/surfactant ratio in the system. This is in good agreement with former findings in which it was shown that the stability of the foam films depends on the electrostatic repulsion of the polyelectrolyte/surfactant complexes within the film and not necessarily on that of the film surfaces.¹

4.2. Effect of a Lower Degree of Polymer Charge. The effect of PAMPS60/ C_{14} TAB mixtures is even more complex. In addition to the broader destabilization range, the surface tension and elasticity measurements reveal characteristics that differ significantly from the typical polyelectrolyte/surfactant curves discussed in refs 1 and 18. On both sides of the IEP (namely, between 10^{-5} and 10^{-4} M PAMPS60 and between 10^{-4} and 10^{-3} M), a plateau in both surface tension and elasticity can be observed. In the surface tension measurements, the plateau below the IEP is significantly lower than that above this point. However, the surface tension does not go back to the value of the pure surfactant, as it does in the case of 100% charged PAMPS. This means that not all polyelectrolyte/surfactants are released from the surface. These findings are supported by surface elasticity measurements. Below 10^{-5} M PAMPS60, the elasticity is 30 mN/m, whereas the pure surfactant surface has an elasticity of 4 mN/m. The evolution of the elasticity isotherm suggests that, at this concentration, polyelectrolyte/surfactant complexes and unbound surfactant molecules are adsorbed to the surface. The surface elasticity increases up to a PAMPS concentration of 10^{-5} M. The constant elasticity implies that the density at the surface remains the same, even when more polyelectrolyte is added. Above the IEP of 1.6×10^{-4} M, the adsorbed material is drastically reduced. However, the measured values again remain constant over a concentration range of 1 order of magnitude.

Since PAMPS60 has both negatively charged and nonionic monomer units, the interactions between the polymer and the surfactant are very complex. They can arise from electrostatic attraction between the oppositely charged compounds but also from interactions between the surfactant and the nonionic unit. The aggregation of charged surfactants and nonionic polymers is widely known in the literature^{11,40} and is usually based on hydrophobic interactions or the formation of hydrogen bonds. For the occurrence of hydrophobic interactions, a surfactant with a sufficiently long alkyl chain is needed: the threshold is reported to be more than 12 C atoms in the hydrophobic tail in the C_n TAB series.¹¹

The strongly reduced surface tension indicates that the polyelectrolyte/surfactant complexes at the surface are more hydrophobic than complexes containing 100% charged polyelectrolytes. The increased surface activity arises from the lower degree of charge, which makes the polymer less water-soluble.³⁶ For example, at a charge fraction below 20%, the solubility of a polymer is significantly reduced.^{41,42} In addition, the surface elasticity measurements reveal a strong interaction between the surfactant and the polyelectrolyte, even at low polymer concentration. However, the increased adsorption cannot arise from hydrophobic interactions between surfactant and polymer in the complex. In that case, the alkyl chain of the surfactant would interact with the polymer backbone and the charged headgroup would be exposed to the surrounding water phase, which would make the complex more hydrophilic and not surface-active.

O'Driscoll et al.⁴³ observed an interaction between the non-ionic monomer unit and the charged headgroup of the surfactant. The described effect arises from an interaction between the dipole

of the nonionic monomer unit and the surfactant, which leaves the hydrophobic tail of the surfactant exposed to the surrounding. Together with the more hydrophobic character of the polymer, these interactions could be responsible for the increased surface activity of the complexes. In general, nonionic polymers interact more strongly with negatively charged surfactants, such as sodium dodecyl sulfate, and show only weak interactions with cationic surfactants. This is interpreted as a more favorable interaction of anionic surfactants with the hydration shell of the polymer or the unfavorable bulkiness of the cationic headgroup.⁴⁴ Nevertheless, interactions between nonionic polyelectrolytes and C_n TAB have been reported in the literature^{10,43,44} and are supposed to be stronger for more hydrophobic polymers.

The polymer complexes form coils with a small hydrodynamic radius⁴⁵ when all charges form complexes; that is, no repulsion occurs between the polymer segments. In this case, a highly packed polyelectrolyte/surfactant film can arise⁴³ at the interface. This is supported by a relatively high surface elasticity of 60 mN/m, which gives rise to the assumption that the complexes form an interconnected network at the surface. The interaction between the nonionic monomer units and the surfactant can lead to the shielding of the charged head groups. The shielded surfactant cannot contribute to the surface charge anymore, which is therefore reduced.

As described in the previous section, a certain amount of unbound surfactant is needed to stabilize a CBF. In the case of PAMPS60/ C_{14} TAB, this prerequisite seems not to be fulfilled in a broad concentration range. The films are already destabilized at low polyelectrolyte concentration of 5×10^{-5} M because of the headgroup shielding. In addition, the foam film measurements showed that aggregates are formed in the bulk at 10^{-4} M PAMPS60, indicating that close to the IEP, 1:1 complexes occur that precipitate. However, this is not reflected in the surface tension or elasticity, which means that the aggregates do not adsorb at the interface and, hence, do not influence the surface properties.

At high surfactant concentrations, several conformations of the complexes at the surface are possible. One possibility is that the bulk aggregates adsorb at the surface because they are in the course of a phase separation at the interface, which is postulated, for example, by O'Driscoll et al.⁴³ In that case, the micelles would remain in the core of the polymer coil with no contact with the air phase. Another possible mechanism would be that the aggregates change the conformation during the adsorption so that the more hydrophobic surfactant tails are exposed to the air. This phenomenon is also observed for proteins that accumulate their hydrophobic domains in the core and expose them to the air when they are attached to the surface.⁴⁶ The latter mechanism is more likely in our case, since no phase separation is observed for PAMPS60.

When the polymer concentration crosses the IEP of the system, the complexes at the interface are rearranged as follows from the surface characterization. Both the surface tension and the elasticity measurements indicate that a part of the polyelectrolyte complexes is released from the surface, and the influence of unbound surfactant molecules increases again. Above the IEP, the concentration of the charged polymer segments exceeds that of the surfactant so that not all charged units can be complexed by the surfactant. This affects the surface complexes in two ways: First, the internal repulsion of the likely charged polymer segments increases, resulting in a larger persistence length, that is, in larger coils. The higher hydrodynamic radius, in turn, leads to a reduced packing at the surface^{43,45} due to a higher surface area per complex. Furthermore, fewer surfactant molecules decorate

one polymer chain, thereby reducing the hydrophobicity of the complex. However, due to the nonionic monomer units, the complexes are still amphiphilic enough that they remain adsorbed on the surface. The surface tension and elasticity do not change upon polyelectrolyte addition, possibly because the surface is already saturated and new polymer chains adsorb underneath, forming a thicker layer at the surface.

At polymer concentrations above 10^{-4} M, stable films are formed again. In this concentration regime, the negative charges of the polyelectrolyte strongly affect the film stability, and the surfactant shielding does not play a role anymore. Comparing the film stabilities with former results, the films are less stable than those from PAMPS/ C_{14} TAB at the same concentration, which is also reflected in a lower surface potential. The latter is considerably lower compared with foam films from 100% charged polyelectrolyte. This can easily be explained by the fact that the amount of charged monomer units is 40% lower at the same polyelectrolyte concentration. Hence, the repulsion that arises from the charged polymer segments is weaker, and the corresponding foam films are less stable. However, compared with the foam films with a similar charge density (for example, 5×10^{-4} M PAMPS and 10^{-3} M PAMPS60), the stabilities are in the same range. This supports the assumption that the stability arises from the charged polyelectrolyte in the films, no matter where they are situated, since one remarkable difference between the two systems is that in the latter case, the polyelectrolyte is adsorbed to the interface.

5. CONCLUSION

In the present paper, the effect of the nominal IEP of anionic polyelectrolytes/ C_{14} TAB mixtures on foam film stability and surface properties is presented. For that purpose, foam film stabilities of PAMPS/ C_{14} TAB with an IEP of 3×10^{-5} M and PAMPS60/ C_{14} TAB with an IEP of 1.6×10^{-4} M have been investigated and compared with former results of PAMPS/ C_{14} TAB with an IEP of 10^{-4} M. The behavior of foam films in both systems shows strong similarities to the former systems, and the destabilization is shifted according to the IEP. However, one remarkable difference is observed between the systems: in the case of an IEP unequal to 10^{-4} M, the range of unstable foam films is much broader.

In a first set of experiments, the surfactant concentration which determines the IEP was reduced, which leads to a more dilute system. In the dilute system, the critical concentration at which no stable films are formed is reached at a polyelectrolyte concentration far below the IEP, although the surface tension measurements show the same characteristics as PAMPS/ C_{14} TAB with an IEP of 10^{-4} M. This implies that below the IEP, a certain amount of unbound surfactant is needed to stabilize a CBF. Furthermore, the foam film stabilities reveal that Π_{\max} strongly depends on the polyelectrolyte concentration but also on the initial surfactant concentration.

In a second approach, the degree of charge of the polyelectrolyte was varied. For this reason, a random copolymer of anionic and nonionic monomer was used, which makes the explanation of the interactions in the foam film more complex. The analysis of the results shows that the formed complexes are more hydrophobic. In addition, the surfactant interacts with the dipole of the nonionic polymer segments. The latter leads to a shielding of the surface charge and a destabilization of the foam films already at low polymer concentrations. Above the IEP, some of

the polyelectrolyte/surfactant complexes are released from the interface, but there is still material left at the surface. Furthermore, stable films are formed again at this point, meaning that no matter where polyelectrolyte is situated in the film, it contributes to the stabilization of the film.

In general, one can conclude that the stability curve and the isotherms of the surface properties look qualitatively the same. Minima and maxima of Π_{max} , surface tension, and elasticity are shifted according to the differences in the nominal IEP; However, in the case of PAMPS60 the nonionic monomer units have an additional influence.

■ ASSOCIATED CONTENT

S Supporting Information. A comparison of the surface tension of the Du Noüy ring method and the drop shape analysis is shown in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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