

Tuning of Foam Film Thickness by Different (Poly)electrolyte/Surfactant Combinations[†]Branko Kolarić,[‡] Werner Jaeger,[§] Gabriele Heddicke,[‡] and Regine v. Klitzing^{*,‡}*Stranski-Laboratorium für Physikalische und Theoretische Chemie, Technische Universität Berlin, Strasse des 17. Juni 112, D-10623 Berlin, and Fraunhofer-Institut für Angewandte Polymerforschung, Golm**Received: January 7, 2003; In Final Form: May 7, 2003*

Disjoining pressure isotherms of free-standing liquid films (foam films) consisting of different polyelectrolyte/surfactant combinations are measured in a thin film pressure balance (TFPB). In dependence of the charge of polyelectrolyte and surfactant, a transition from an electrostatically stabilized common black film (CBF) to a sterically stabilized Newton black film (NBF) can be induced in some cases while for other polyelectrolyte/surfactant combinations the film is a CBF up to several thousands of pascals. The thinner NBF is less stable, and the film breaks after a few minutes. An exchange of the polymers by monomers leads to the same kind of film as that for the respective polymer, while the addition of, for example, simple salt leads always to a transition from CBF to NBF. The typical stratification of polyelectrolyte/surfactant films is not observed in monomer/surfactant films.

1. Introduction

Interactions between polyelectrolytes and surfactants in foams are of interest for many technical applications and in basic research. With respect to the industrial requests, different strengths of interactions between both compounds are requested. For instance, for decalcification processes a strong interaction between the polyanions and the surfactant is needed. On the other hand, in cosmetics the interactions between surfactants and polymers should be weak.

A foam consists of many single free-standing films (foam films) which are connected by so-called Plateau borders. The addition of polymers effects the interactions within the foam films and could lead to a change in film stability. The present paper deals with the influence of polyelectrolytes and polymers on the interactions between the film surfaces of a single horizontal foam film.

Recent studies of free-standing polyelectrolyte/surfactant films resulted in a stepwise thinning of the film, so-called stratification, above the polyelectrolyte overlap concentration. This is related to the formation of a transient network within the film, in analogy to the findings in polyelectrolyte solutions (e.g. refs 1–3), which induces structural forces. In this image, during one step, as much material as is contained in one mesh is pressed out of the film. The step size in film thickness is different for different polyelectrolytes,² but it is not affected by the choice of the surfactant.^{4,5} This means that the polyelectrolyte surfactant interactions do not affect the structural forces in the *film core*. But the question arises how the polyelectrolyte chains interact with the surfactant at the *film surfaces*. This is assumed to become important especially in thin films.

In the present paper the interactions within a foam film containing different combinations of polyelectrolytes and surfactants are investigated. To separate the effect of the chain character of the polyelectrolyte from its electrostatic properties,

the polyelectrolytes are replaced by their respective monomers in some experiments. The findings are related to the surface tension of the corresponding polyelectrolyte/surfactant solutions.

2. Scientific Background

A quantitative measure of this sum of the interactions is the disjoining pressure, which is the excess pressure between the pressure within the film and the pressure of the corresponding liquid due to interaction between the film surfaces. The contributions are van der Waals interaction, which is attractive for a symmetric system such as a foam film (gas/liquid/gas), electrostatic repulsion between the equally charged surfaces, and steric repulsion between the molecules adsorbed at the film surfaces:

$$\Pi = \Pi_{\text{vdW}} + \Pi_{\text{el}} + \Pi_{\text{steric}} + (\Pi_{\text{structural}}) + \dots \quad (1)$$

The interplay between these different interactions results in two different kinds of films: The so-called common black film (CBF) is determined by the DLVO forces (electrostatic and van der Waals forces), and the thinner Newton black film (NBF) is stabilized by steric repulsion and does not contain any free solvent molecules. A transition from CBF to NBF is induced by the addition of salt, leading to a screening of the surface charges. This confirms the electrostatic nature of the repulsive force stabilizing the CBF. The transition from CBF to NBF is due to the dominance of electrical double layer repulsion at medium film thickness and that of attractive van der Waals forces at small film thickness. This attractive part of the isotherm is mechanically unstable, and a step in film thickness from the thicker CBF to a thinner NBF is detected. This image describes a typical foam film with surfactant monomers in the film core between two surfactant layers. Above the critical micellization concentration (cmc) an oscillation of the disjoining pressure can be observed due to the expulsion of micelles out of the film.^{6–9} This paper deals with the question how the interactions between the surfaces can be influenced by polyelectrolytes.

One effect of polyelectrolytes in foam films is already well-investigated: Mixed films made from aqueous polyelectrolyte/

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surfactant solutions below the critical aggregation concentration (cac) drain stepwise above a certain polyelectrolyte concentration though there are no micelles inside.^{1,4,10} This behavior can be generalized to many different kinds of polyelectrolytes and polymer-like aggregates such as flexible and stiff chains² and wormlike surfactant micelles.¹¹ It is assumed that these steps are due to oscillations in the pressure and that structural forces which give an additional contribution to the disjoining pressure ($\Pi_{\text{structural}}$ in eq 1)^{6,12} are responsible for this kind of stratification. The steps in film thickness are of similar size to the correlation length of the corresponding polymer bulk solutions which are investigated by SANS.^{3,13} This indicates that the interactions which are responsible for the average interchain distance in the bulk solution are the same as those between the chains in the film core.

3. Experimental Section

3.1. Materials. In the present study different polymers and surfactants of different charges are used. The cationic one is poly(diallyldimethylammonium chloride) (PDADMAC), and the neutral one is poly(*N*-methyl-*N*-vinylacetamide) (PNMVA). Details about the synthesis and the characterization are described in ref 14 for poly(DADMAC) and in ref 15 for poly(NMVA). The respective monomers were obtained from Aldrich. The anionic poly(styrene sulfonate) (PSS) was purchased from Sigma. As surfactants the positively charged C₁₂TAB and C₁₆TAB (both from Sigma-Aldrich, Taufkirchen, Germany) are used and the nonionic α -C₁₂G₂ (dodecyl- α -maltoside) from Sigma-Aldrich is used. All solutions are prepared with Milli-Q water, and the concentrations are well below the cac and the cmc.

3.2. Methods. **3.2.1. Thin Film Pressure Balance (TFPB).** The measurements have been carried out in a thin film pressure balance using the porous plate technique. This method was developed by Mysels et al.¹⁶ and subsequently improved by Exerova^{17,18} for measuring the disjoining pressure $\Pi(h)$ in the film as a function of the film thickness h (disjoining pressure isotherm). The film is formed from aqueous polymer solution over the (1 mm) hole drilled in a porous plate. The film holder is enclosed in a metal cell with a quartz window, and the pressure inside the cell is changed using an O-ring pump. The film thickness is determined by an interferometric method.¹⁹ Further details of the apparatus are described elsewhere.⁶ To saturate the film surface, the film has been formed 30 min after pulling the fritted glass out of the solution. The equilibrium thickness is reached when the intensity is constant over a period of 20 min. The experiments have been carried out at 23 °C.

3.2.2. Surface Tension Measurements. The surface tension has been measured by a Wilhelmy tensiometer (Krüss, Hamburg). The measurements have been carried out in a Teflon trough (5 cm diameter) and by using the ring method. Before measuring the surface tension, a lamella has been moved out for 30 min. This allows the polyelectrolytes to adsorb at the enlarged surface.

4. Results

4.1. Thin Film Pressure Measurements. **4.1.1. Pure Surfactant Foam Films.** While pure C₁₆TAB foam films are stable at low surfactant concentrations, C₁₂TAB and α -C₁₂G₂ are not stable at the concentrations used in the present study. Only in combination with polymers do they become stable, even if no direct interaction like the formation of complexes between both compounds is detectable. This will be shown in the following.

4.1.2. Foam Films Containing Polymers. Figure 1 shows the disjoining pressure isotherms of free-standing aqueous films

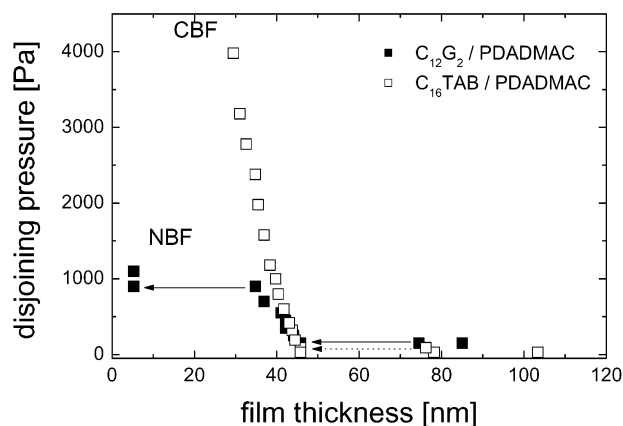


Figure 1. Disjoining pressure isotherms of films formed from PDADMAC/C₁₂G₂ or PDADMAC/C₁₆TAB solutions. The concentrations are as follows: PDADMAC, 5×10^{-3} mol/L; C₁₂G₂, 10^{-5} mol/L; C₁₆TAB, 10^{-4} mol/L.

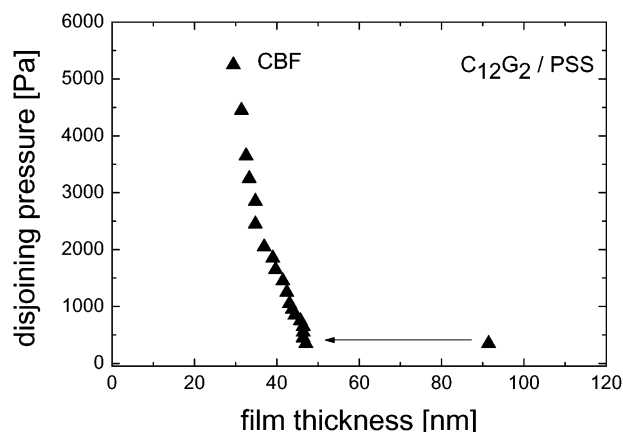


Figure 2. Disjoining pressure isotherm of a film formed from a PSS/C₁₂G₂ solution. The concentrations are as follows: PSS, 5×10^{-3} monomol/L; C₁₂G₂, 10^{-5} mol/L.

containing PDADMAC and either C₁₂G₂ or C₁₆TAB. Both isotherms show steps in film thickness, and the step size is the same for both surfactants. The isotherm branches are parts of an damped disjoining pressure oscillation induced by a networklike structuring of the polyelectrolyte chains, as mentioned in the Introduction. The present results confirm that the surfactant has no influence on the step size and therefore on the structuring of the polyelectrolytes within the film. But the choice of the surfactant affects the total film thickness at higher pressure. The PDADMAC/C₁₆TAB film is about 30 nm thick, which is an indication for a CBF. The CBF is very stable, and no transition to a NBF has been observed up to a pressure of 4000 Pa. If the positively charged C₁₆TAB is replaced by the nonionic C₁₂G₂, a CBF–NBF transition is already induced at a pressure of about 800 Pa, and the film is only several nanometers thick. The NBF is not stable, and it breaks after several minutes. On the other hand, if PDADMAC is replaced by PSS in the mixture with C₁₂G₂, a CBF of about 30 nm is obtained (Figure 2) and no NBF occurs up to a pressure of about 6000 Pa. If PSS is combined with the positively charged C₁₂TAB, the film is also stable and no CBF–NBF transition has been observed up to 1000 Pa (Figure 3). The stratification of the PSS/C₁₂TAB film which is also obvious in Figure 3 has already been discussed in ref 4 and is not the focus of the present paper. PDADMAC and PSS cannot be combined with the same cationic surfactant (either C₁₂TAB or C₁₆TAB), since PDAD-

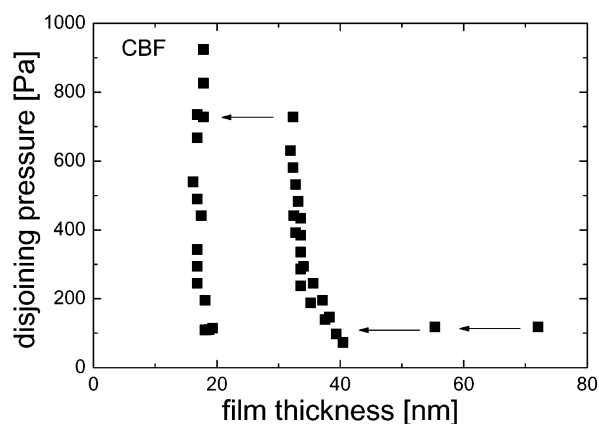


Figure 3. Disjoining pressure isotherm of a film formed from a PSS/ C_{12} TAB solution. The concentrations are as follows: PSS, 5×10^{-3} monomol/L; C_{12} TAB, 10^{-4} mol/L. Data from ref 4.

TABLE 1: Type of Thinnest Free-Standing Film Observed by TFPB for Different Polyelectrolyte/Surfactant Combinations^a

	C_nG_m	C_nE_m	C_nTAB	SDS/AOT
PSS	CBF ³⁷	CBF ^{4,5}	CBF ^{2,4}	CBF ⁵ (SDS)
PAAS		CBF ⁵	CBF ^{1,10}	CBF ⁵ (SDS)
PAA (pH = 7)		CBF ³⁸	CBF ³⁸	
xanthan	CBF ²	unstable	unstable	unstable
CMcellulose				CBF ³⁹ (AOT)
CMchitine	CBF ³⁹			
PDADMAC	NBF ^{3,13,40}	unstable	CBF ³	unstable
PAH (pH = 5)		NBF ⁴¹	CBF ⁴¹	
PEI (pH = 4)		NBF	CBF ⁴²	
PNMVA	CBF ⁴⁰			
PVA				CBF ⁴³
PVP				CBF ⁴⁴

^a The polyanions are poly(styrene sulfonate) (PSS), poly(acryl amide sulfonate) (PAAS), and poly(acrylic acid) (PAA), and the polysaccharides are xanthan, carboxymethylcellulose, and carboxymethylchitine. The polycations are poly(diallyldimethylammonium chloride) (PDADMAC), poly(allylamine hydrochloride) (PAH), and poly(ethyleneimine) (PEI). The weak polyelectrolytes PAA, PAH, and PEI are considered in the pH regime where they are charged. Poly(*N*-methylvinylacetamide) (PVMMA), poly(vinyl alcohol) (PVA), and poly(vinylpyrrolidone) (PVP) are neutral polymers. Alkylglycosides (e.g. $C_{12}G_2$) and alkyl-ethylene oxides (e.g. $C_{12}E_5$ or $C_{12}E_6$) are nonionic surfactants, alkyl-trimethylammonium bromides (e.g. C_{12} TAB or C_{16} TAB) are positively charged, and sodium dodecyl sulfate (SDS) and dioctylsulfosuccinate (AOT) are anionic surfactants. The measurements are carried out without any additional salt.

MAC does not form stable films with C_{12} TAB and PSS does not form films with C_{16} TAB.

In the present study the CBF is always stable until high pressures, and it has to be destroyed mechanically. In contrast to that, a NBF breaks after a few minutes. These results of the TFPB measurements lead to the assumption that the charge combination is responsible for the appearance of a CBF–NBF transition. Data from the literature confirm this assumption. An overview of different combinations of surfactant and polyelectrolytes presented also by other groups is given in Table 1. Thereby, the thinnest film at high pressure is considered. The surfactants are nonionic ones (alkyl glycosides (C_nG_m) and alkyl ethylene oxide (C_nE_m)), cationic ones (C_nTAB), and anionic ones (SDS or AOT). The results show a CBF for polyanions, for example, PSS, PAAS, PAA, xanthan, carboxymethylcellulose, and carboxymethylchitine, in all surfactant combinations independent of the surfactant charge. In contrast to this, the surfactant charge plays an important role in foam films containing polycations (e.g. PDADMAC, PAH, PEI): In the case of

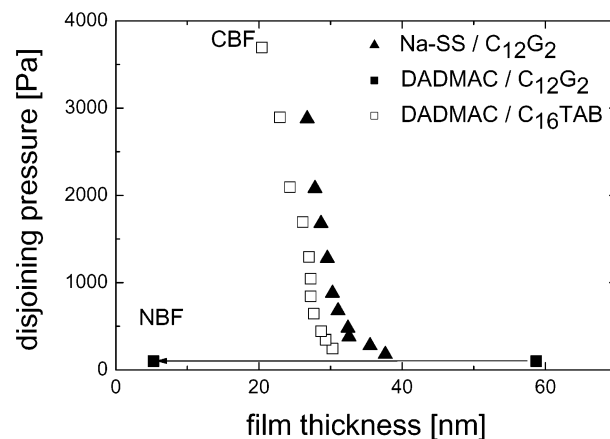


Figure 4. Disjoining pressure isotherms of films containing the monomers Na-SS and DADMAC at the corresponding monomer concentrations as in Figures 1 and 2. The concentrations are as follows: Na-SS, 5×10^{-3} mol/L; DADMAC, 5×10^{-3} mol/L; $C_{12}G_2$, 10^{-5} mol/L; C_{16} TAB, 10^{-4} mol/L.

nonionic surfactants (e.g. C_nG_m and C_nE_m), a transition from a CBF to a NBF is observed. On the other hand, if the film contains cationic or anionic surfactant, the thinnest film is again a CBF. The addition of neutral polymer leads to a CBF as the thinnest film independent of the choice of surfactant. To summarize the different experiments, only with the combination of positively charged polyelectrolyte and nonionic surfactant is a transition from a CBF to a NBF observed. In all other polyelectrolyte/surfactant combinations the transition cannot be observed within the pressure regime investigated in the present studies.

It is important to emphasize that in the given examples the ionic strength within the films is low, that is, without any additional salt and at a polyelectrolyte concentration which is rather low (i.e. on the order of magnitude of the overlap concentration). At high ionic strength, in general a NBF occurs, since the electrostatic repulsion between the film surfaces is screened. In the case of weak polyelectrolytes, one has to take the pH into account. In the measurements presented in Table 1, the pH has been adjusted in the way that the polyelectrolytes are charged.

Furthermore, only foam films containing linear polyelectrolytes and surfactants are considered but not films of hydrophobically modified polymers, as described for instance in refs 20–25.

4.1.3. Foam Films Containing Monomers. The question arises which effect is related to the chain properties of polymers and which one is due to the influence of polymer charge. Therefore, foam films containing the respective monomers have been investigated (Figure 4). The main difference with respect to the films containing polymers is that the steps in film thickness within the regime of CBF vanish, which indicates that the steps are caused by the macromolecular character of the polymers. But again only for the combination of $C_{12}G_2$ and DADMAC monomers does a NBF occur in analogy to the PDADMAC/ $C_{12}G_2$ film. The step in film thickness corresponds to the transition from a CBF to a NBF which also occurs in foam films of pure surfactant solutions. This step has nothing to do with the multiple steps in thickness thinning of foam films containing polyelectrolytes. In the present case the film is quite unstable. Neither the CBF nor the NBF can be stabilized. The two other combinations DADMAC/ C_{16} TAB and Na-SS/ $C_{12}G_2$ result in a CBF.

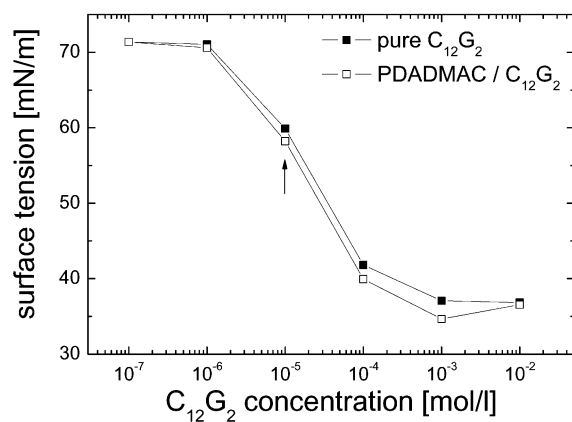


Figure 5. Surface tension of the pure $C_{12}G_2$ solution and a $C_{12}G_2$ solution containing 5×10^{-3} monomol/L PDADMAC. The arrow indicates the respective concentration which has been used for the experiments presented in Figure 1.

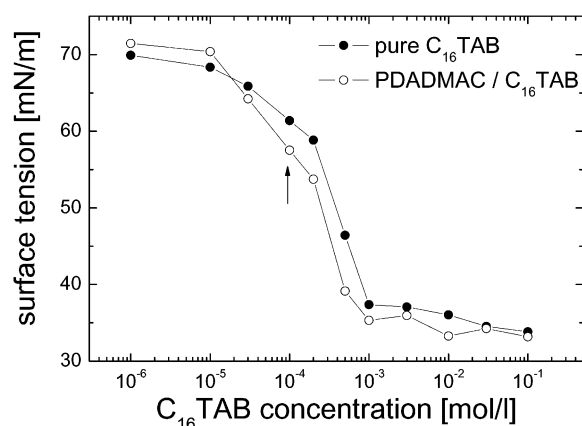


Figure 6. Surface tension of the pure $C_{16}TAB$ solution and a $C_{16}TAB$ solution containing 5×10^{-3} monomol/L PDADMAC. The arrow indicates the respective concentration which has been used for the experiments presented in Figure 1.

4.2. Surface Tension of Polyelectrolyte/Surfactant Solutions. As mentioned in the Introduction, the interplay between the different interactions between the surfaces decides whether a CBF–NBF transition takes place or not. One decisive factor could be the change in surface charge and therefore the electrostatic repulsion forces due to the adsorption of polyelectrolytes at the surface. To get an idea of the interactions between polyelectrolytes and surfactants at the film surfaces, the surface tension of the corresponding mixed solution has been measured. Figures 5 and 6 show the surface tension curves of the pure surfactants $C_{12}G_2$ and $C_{16}TAB$, respectively, and those for the mixed surfactant/PDADMAC solution. The mixed solutions are the same as those used for the experiments presented in Figure 1. The arrows indicate the respective concentrations investigated in the TFPB experiments. For both surfactants the addition of 5×10^{-3} monomol/L of PDADMAC has no effect on the surface tension within the experimental error. The surface tension of an aqueous solution containing 5×10^{-3} monomol/L of PDADMAC is the same as that of water.

In contrast to this, a pronounced effect on the surface tension is observed after the addition of PSS to the oppositely charged $C_{12}TAB$ (Figure 7). The surface tension of the mixed system is reduced and shows the typical plateau at intermediate surfactant concentrations which is related to the critical aggregation between polyelectrolyte and surfactant. The surface tension of this system is discussed in detail in refs 26 and 27. The addition of PDADMAC to the negatively charged surfactant SDS gives

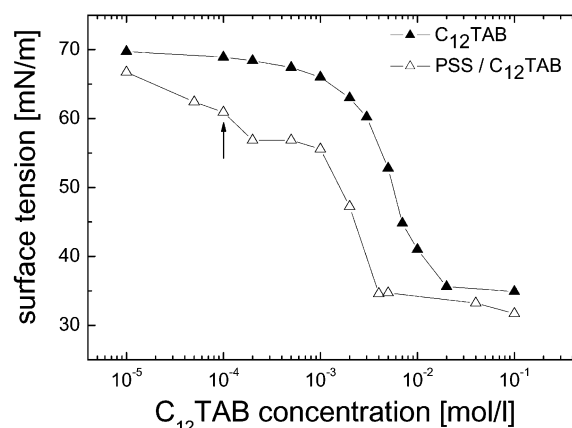


Figure 7. Surface tension of the pure $C_{12}TAB$ solution and a $C_{12}TAB$ solution containing 5×10^{-3} monomol/L PSS. The arrow indicates the respective concentration which has been used for the experiments presented in Figure 3.

qualitatively the same result. This system is not shown in the paper, since the corresponding foam films are not stable.

5. Discussion

The results show that the addition of polyelectrolytes leads to a change in disjoining pressure. This effect can be divided into two parts:

(1) The polyelectrolyte chains are assumed to form a transient network within the *film core* which results in structural forces. These reflect rather the interactions between the polyelectrolyte chains within the core than the interactions between the surfaces. An interaction between surfactant and polyelectrolytes is not detectable in the core at low surfactant concentrations (below the cac and the cmc), since the steps in film thickness are the same for different surfactants.

(2) In contrast to that, the choice of the surfactant has a pronounced influence on the total film thickness. This is due to the attraction/repulsion between polyelectrolytes and surfactant molecules at the *film surface*, which in turn affects the interactions between the surfaces.

The second point will be discussed in more detail in the following. First, the pure surfactant system without polyelectrolytes will be considered. An excess of surfactant molecules is detected at the surface by the decrease in surface tension with respect to the bare water surface tension. In pure surfactant foam films the adsorption of surfactant molecules is detected by changes in film thickness, that is, changes in interactions between the film surfaces. If the surface is charged, the repulsion between the surfaces is high enough to avoid a transition from a CBF to a NBF. The typical ζ potential is of the order of magnitude of 100 mV or even more.²⁸ The double layer potential increases with increasing surfactant adsorption in the range of small surfactant bulk concentrations.²⁹ At higher concentrations of the ionic surfactant, however, a saturation takes place due to the binding of counterions to the surface.³⁰ This is the opposite for films of nonionic surfactants, where the repulsion between the surfaces is reduced with increasing surfactant concentrations. At low surfactant concentrations the film shows a surface potential between 30 and 50 mV,^{10,31,32} which is high enough to stabilize a CBF. With increasing concentration the repulsion between the surfaces is reduced and a transition from a CBF to a NBF can be induced. The origin of surface charges in foam films of nonionic surfactants has not been clarified, yet, and it is still under discussion. Besides the adsorption of impurities and other negatively charged ions, the most favored explanation

for negative surface charges is the adsorption of OH^- ions at the air/water interface due to the dissociation of water. The adsorption mechanism itself is still under discussion, and only qualitative explanations, for example, steric aspects, can be given.^{33,34}

5.1. Polyelectrolyte and Surface of the Same Charge. *5.1.1. Polyelectrolyte and Surfactant of the Same Charge.* In the present case the addition of positively charged polyelectrolytes has no influence on the surface tension if the solution contains positively charged surfactant. This means that no PDADMAC adsorbs at the surface of the solution, which has been expected due to electrostatic repulsion between both classes of compounds. In the foam film the repulsion between surfactant and polyelectrolytes results in an enhanced repulsion between the film surfaces, which avoids in turn the transition from a CBF to a NBF. One reason for the enhanced repulsion could be the depletion of polymer near the film surface, which would lead to a higher polymer concentration within the film center. This in turn could lead to an additional osmotic pressure term.

5.1.2. Polyanion and Nonionic Surfactant. Under the assumption that the surface is slightly negatively charged at low concentrations of nonionic surfactants, the polyelectrolyte is repelled from the interface and the situation is similar to the one described above.

5.1.3. Charged Surfactant and Nonionic Polymer. The uncharged polymer does not reduce the electrostatic repulsion of the charged surfaces. Therefore, a CBF is formed and no transition to a NBF is observed.

5.1.4. Polyelectrolyte and Surfactant of Opposite Charge. The addition of polyelectrolytes to a solution of oppositely charged surfactants leads to a decrease in surface tension, which is an indication for the formation of surface active complexes, as described elsewhere (e.g. refs 26 and 27). The adsorption of polyelectrolytes reduces the surface charge with respect to the charge of the pure surfactant surface layer, and the charge can be even reversed if enough polyelectrolyte is adsorbed. Charge reversal would lead again to the same situation as described above, where polyelectrolyte and surface have the same charge. This would mean that, also in the case where polyelectrolyte and surfactant are oppositely charged, the polyelectrolyte is repelled from the interface, which results in a CBF. It is assumed that, at PSS concentrations near the threshold of charge reversal, a NBF would occur, since the surface charge would be quite low. To our knowledge, up to now no NBF has been observed for the system PSS/ C_{12}TAB . Above a PSS concentration of 5×10^{-3} monomol/L, the thickness of the CBF decreases with increasing PSS concentration. But this is rather due to the increasing ionic strength and the electrostatic screening, and it is not related to a charge reversal.⁴ Between a PSS concentration of 5×10^{-4} and 5×10^{-3} monomol/L, the CBF thickness is constant. The trial to find the assumed threshold of charge reversal by decreasing the polyelectrolyte concentration was not successful, because the film was not stable below a PSS concentration of 5×10^{-4} monomol/L. (Since the pure C_{12}TAB films are not stable, they need a certain amount of oppositely charged polyelectrolyte to be stabilized, and this required minimum concentration seems to be above the charge reversal threshold.) Both kinds of films, where polyelectrolyte and surfactant have the same charge or where both compounds are oppositely charged, are sketched in Figure 8. Due to the strong electrostatic interaction between the interfaces, the electrostatic barrier cannot be overcome and no transition from a CBF to a NBF takes place.

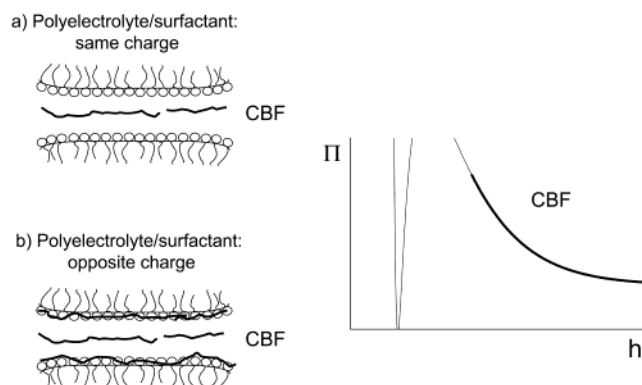


Figure 8. Model of a film for which the film surface and the polyelectrolytes have the same sign of charge. This can be adjusted (a) if polyelectrolyte and surfactant have the same sign of charge or (b) if they are oppositely charged and the surface charge is reversed by the adsorption of polyelectrolytes. Right-hand side: schematic disjoining pressure curve of the CBF.

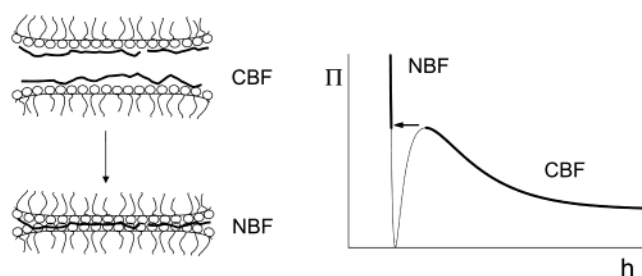


Figure 9. Model of a film for which the film surface and the polyelectrolytes are oppositely charged. This can only be adjusted by mixing negatively charged polyelectrolytes and nonionic surfactant. Right-hand side: schematic disjoining pressure curve of the CBF–NBF transition.

5.2. Polyelectrolyte and Surface of Opposite Charge. The addition of PDADMAC to a solution containing nonionic surfactant has no effect on the surface tension, which means that no complexation between both classes of compounds takes place and that the PDADMAC does not adsorb itself at the interface. Under the assumption that OH^- ions adsorb at the surface, it should be slightly negatively charged and therefore oppositely charged with respect to the polyelectrolyte. This would mean that the surface attracts the polyelectrolyte, but no complexes are formed with the surfactant. The polyelectrolyte chains would reduce the surface potential. The electrostatic barrier can be overcome, and a NBF is formed (see Figure 9).

5.3. Films Containing Monomers. The films containing the monomers DADMAC and Na-SS show qualitatively the same behavior concerning the thinnest accessible thickness as that of the corresponding polyelectrolyte films. This result is remarkable, since usually the addition of low molecular weight salts such as NaCl leads to the formation of a NBF. Therefore, it is assumed that the adsorption or depletion of the monomers plays an important role for the final film thickness. This means that the monomers cannot be considered as simple salts.

5.4. Film Stability. As mentioned at the beginning of section 4, only the pure C_{16}TAB is stable at such low surfactant concentrations as are studied in the present paper. Neither the pure C_{12}G_2 nor the pure C_{12}TAB film is stable. It should be noticed that $\beta\text{-C}_{12}\text{G}_2$ forms stable films at these low concentrations^{32,36} but not $\alpha\text{-C}_{12}\text{G}_2$ that has been used in the present experiments. This means that the steric effect of the surfactant headgroup plays an important role for the stability. The stability of C_{12}TAB is discussed in ref 35. The stabilization of C_{12}TAB

films by oppositely charged polyelectrolytes is easy to understand. The polyelectrolytes screen the charges of the headgroups and increase the packing of the surfactant molecules. But it is not obvious why a polyelectrolyte stabilizes a film if there is no detectable interaction at the surface by surface tension measurements (e.g. PDADMAC/C₁₂G₂ or PSS/C₁₂G₂). In the case of PSS/C₁₂G₂, the additional electrostatic repulsion between the PSS and the slightly negative charged surface might increase the stability. This could not be the reason for the PDADMAC/C₁₂G₂ film. There, structural forces might enhance the stability. The stratification hampers the drainage process. An indication for this assumption could be the relatively unstable DADMAC/C₁₂G₂ film of monomers, where no stratification due to structural forces occurs.

6. Conclusions

The results of the present paper lead to the conclusion that the film can be divided into three regions: the two interfacial regions with an excess of surfactant and the film core containing a geometrically confined polyelectrolyte solution. The interactions (attraction or repulsion) between the polyelectrolytes and surfactant at the film surfaces affect the total film thickness. The structuring of the polyelectrolyte chains within the film core induces structural forces. Films which contain the corresponding monomers show a similar CBF/NBF behavior to that of the films which contain polymers. This confirms the important role of charges for the final thickness of the film.

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