

Mesoscopic Ordering of Polyelectrolyte Chains in Foam Films: Role of Electrostatic Forces

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Recent studies using a thin film balance of free-standing thin aqueous films (foam films) containing polyelectrolytes resulted in jump-like discontinuities in the film thickness with increasing outer pressure. These jumps in film thickness correspond to an oscillation of the disjoining pressure. The oscillation period of the disjoining pressure scales as $c^{-0.5}$ with the polyelectrolyte concentration c . A mesoscopic ordering of the chains in the film similar to that found in aqueous semidilute polyelectrolyte solutions is assumed. In experiments presented in this work, the electrostatic effect is investigated by adding low molecular salt and varying the degree of charge of the polyelectrolyte chains. The studies reveal that the amplitudes of the disjoining pressure oscillations are reduced with increasing ionic strength and decreasing degree of charge. The results show that the jumps in film thickness and therefore the structuring are due to the electrostatic repulsions between the polyelectrolyte chains.

Introduction

Interactions between polymers and surfactants in an aqueous medium are of great scientific interest because of their importance for many industrial applications. Polymers are used as stabilizers for foams and emulsions, for example. To use polymers in an efficient way in surfactant systems, it is necessary to control and to manipulate the properties of the colloidal mixture. Therefore, the behavior of the building blocks, i.e., the single surfactant films, must be well known. A single foam film consists of two surface layers separated by the film bulk phase. The elasticity of the surface layer is responsible for the film stability which can be enhanced by surface complexes formed by charged surfactants and oppositely charged polyelectrolytes.^{1,2} Furthermore, the stability of a thin film depends on the interactions between the two interfaces. The so-called disjoining pressure corresponds to the sum of all interactions between the interfaces such as electrostatic, van-der-Waals, or steric. Moreover, the volume between both interfaces of a free-standing film offers a cavity for studying the interaction between colloids such as latex particles³ or polyelectrolytes. The thickness of the foam films is between 5 and 150 nm and can be tuned in a specific way by using a thin film balance. Thus, the dimension of the film is of the same order as the characteristic lengths of colloidal systems such as the Debye length at a low ionic strength or the correlation length of transient polyelectrolyte networks (see below). The question is how polymers, e.g., interact in such a confined geometry.

The behavior of polyelectrolyte chains in semidilute, salt-free solutions (infinite geometry) is well described by the model of de Gennes,^{4–8} in which the entangled chains form an isotropic transient network. The characteristic length is the mesh size of the network, the so-called correlation length ξ . Small angle scattering experiments (ref 9 and references therein) at poly-

electrolyte solutions result in a broad peak of the scattering intensity profile related to the correlation length ($q_{\max} = 2\pi/\xi$). The correlation length scales with the polyelectrolyte concentration c as $c^{-0.5}$ ¹⁰ as predicted also by theoretical considerations. The Debye length, which is the measure of electrostatic screening, scales in the same way. This fact implies that the ordering of the polyelectrolyte chains in solution is induced by electrostatic repulsion between the chains.

Recent thin film balance studies on single foam films containing surfactants and polyelectrolytes have shown that the addition of polyelectrolytes leads to a film stratification.^{11,12} The films containing flexible² and rigid polyelectrolytes,¹³ respectively, show jumps in the film thickness with increasing outer pressure. This behavior can be generalized to films of polymer-like aggregates such as wormlike micelles.¹⁴ For all systems the jumps in film thickness scale with the polymer concentration c as $c^{-0.5}$. These results are in good agreement with a microscopic theory which predicts oscillatory solvation forces in polyelectrolyte solutions between two walls.¹⁵ The jumps in film thickness lead to the conclusion that there is a similar ordering of the polyelectrolyte chains in the confined geometry of foam films as in the infinite geometry of foam films.

Despite detailed investigations of surfactant/polyelectrolyte films there are many open questions. Specifically, it is not clear if the chains are squeezed out of the film into the Plateau borders during a jump or if they collapse inside the film. Furthermore, the influence of electrostatic forces on the chain ordering is not clarified in detail. This paper addresses these questions and presents experimental results on the influence of the polyelectrolyte concentration, the degree of charge and the amount of low molecular salt. The results indicate that the electrostatic repulsion between the polyelectrolyte chains plays an important role in the mesoscopic structuring of the polyelectrolyte chains in the confined geometry of free-standing films.

Experimental Section

Materials. The polyelectrolyte used for the present studies is a statistic copolymer consisting of positively charged diallyl-

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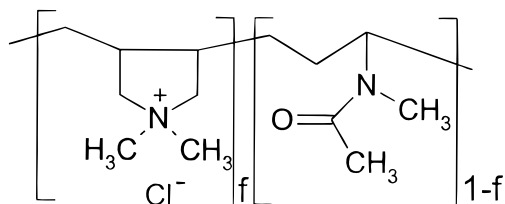


Figure 1. Structure of poly(DADMAC-co-NMVA) of different charge densities: $f = 0, 0.24, 0.5, 0.75, 1$.

dimethyl-ammoniumchloride (DADMAC) monomers and neutral *N*-methyl-*N*-vinylacetamide (NMVA) monomers. Details about the synthesis and characterization are described in ref 16 for poly(DADMAC) and in ref 17 for poly(NMVA) and the copolymers. In addition the pure poly(DADMAC) and the neutral poly(NMVA), chains with the linear charge density of $f = 0.75, 0.5$, and 0.24 were available. The structure is shown in Figure 1. The molecular weight is about 100 000 g/mol. As mentioned below, because of counterion condensation the effective charge density f_{eff} is smaller than the nominal charge density f . The surfactant C_{12}/C_{14} -alkylpolyglucoside (APG) was a gift from Henkel (Düsseldorf, Germany). It is a mixture of APGs with alkyl chains of 12 and 14 C atoms, respectively, and an average critical micelle concentration of 1.7 glycoside units. It is used at a fixed concentration of 0.045 g/L, below the critical micelle concentration (cmc) (0.2 g/L).

Methods. *Thin Film Balance.* The porous-plate technique developed first by Mysels¹⁸ and improved later by Exerova^{19,20} is used for measuring disjoining pressure isotherms. The film is formed on the hole (diameter of about 1 mm) of a porous glass. The glass plate with the film liquid is connected with a reservoir of a constant reference pressure P_r by a capillary tube. The film holder is placed in a closed plexiglass cell, which allows a constant pressure to be applied on the film using a syringe pump. The capillary pressure P_c in the film changes with the cell pressure. During the film drainage the capillary pressure causes a sucking of film liquid into the Plateau borders until the disjoining pressure begins to affect the dynamics. At equilibrium the capillary pressure and the disjoining pressure compensate each other. White light is focused perpendicularly onto the film. The behavior of the film can be observed directly by video microscopy. At the same time, the intensity reflected from the film is measured by a unit consisting of a 550 nm filter and a photomultiplier. The film thickness was determined by the interferometrical method of Scheludko.²¹ A detailed description of the apparatus used is included in ref 22. It was assumed that the equilibrium film thickness was reached when the reflected intensity stayed constant over a period of 20 min. The maximum imposed capillary pressure did not exceed the entry pressure for the porous plate.

Viscosity Measurements. The relative viscosity of the pure aqueous surfactant and the mixed polyelectrolyte/surfactant solutions was measured with a MicroUbbelohde viscometer (Schott, Mainz) using the Ostwald capillary method.

Surface Tension Measurements. The surface tension was measured by a Wilhelmy tensiometer (Krüss, Hamburg). The measurements were carried out in a Teflon trough (5 cm diameter) and by using the ring method.

Results

Effect of Polyelectrolyte Concentration. Figure 2 shows the disjoining pressure isotherms (disjoining pressure as a function of the film thickness) for the mixture of the fully charged poly-(DADMAC) and APG. The datapoints are measured in

equilibrium. The concentration of poly(DADMAC) was varied up to 2.1×10^{-2} mol/L. All polymer concentrations given in this paper refer to the concentration of monomer units. Obviously, the isotherm slope becomes steeper with increasing polyelectrolyte concentration. Steps in film thickness are observed. The number of jumps increases with the poly-(DADMAC) concentration and the step width from 75 nm for 1.33×10^{-3} mol/L to 15 nm for 2.1×10^{-2} mol/L. For a fixed polyelectrolyte concentration the size of the different jumps is almost the same. After the disjoining pressure is increased the film thins stepwise. However, the jumps are not reversible. By decreasing the pressure, the thickness increases along the branch and the jump to the neighbor branch is impossible. At all measured concentrations the thinnest film at high pressure has a thickness of about 5 nm. Because of this small thickness one can assume that it is a so-called Newton black film (NBF) which is stabilized by steric repulsion and does not contain any free solvent molecules. In most of the presented results the NBF film is unstable. In addition, the film collapses directly after the last jump from a common black film (CBF), which is stabilized by electrostatic interactions, to the NBF.

To illustrate the stepwise thinning, photographs of the film at different thicknesses are presented in Figure 3. The circular area in the middle of each photo is the plane parallel part of the film surrounded by the Plateau border. The intensity reflected from the film is homogeneous and bright before the first jump (Figure 3a). The film presents an interferometer as mentioned in the Experimental Section. In the present case the reflected intensity decreases with decreasing film thickness. During the transition the new film thickness spreads out in the form of darker spots (Figure 3b) which unify to a new homogeneous film thickness. When pressure is increased further, jumps occur (Figure 3c and d). The spots around the new film thickness in Figure 3d are drops and are thicker than the film. They are caused by hydrodynamic instabilities because the rate of extension of the smaller new thickness is faster than the liquid can be pressed out of the film.

In the studied regime, the surface tension was invariant with the polyelectrolyte concentration. There is no sign that the APG forms surface active complexes with the polyelectrolyte chains.

Effect of Degree of Charge. To get more detailed information about the origin of the jumps in film thickness the influence of the degree of charge was investigated. Figure 4 shows the isotherms at a fixed polyelectrolyte concentration of 1.06×10^{-2} mol/L but at different degrees of charges. Above a degree of charge of 50% the isotherms are very similar: The step width is constant and the film thicknesses between the steps are almost independent of the charge density. The jumps are induced at different pressures. Thus, only one transition can be observed at one time, and the transitions look similar to those shown in Figure 3. All thicknesses can be stabilized over the whole film and each data point is measured in an equilibrium condition. At a degree of charge of 24% the jumps are induced at the same low pressure. The different thicknesses cannot be stabilized and occur at the same time as shown in Figure 4f. The isotherm of the neutral chain is continuous without jumps. The film was unstable above 700 Pa. It is not clear if there is a transition at high pressure. But in general, the first jump occurred at a lower pressure than 700 Pa as demonstrated for the other charge densities.

The difference in stratification behavior at a different degree of charge is due to a change in chain conformation as discussed below. These changes in conformation are also observable in the polyelectrolyte bulk solution. Figure 5 shows the viscosity

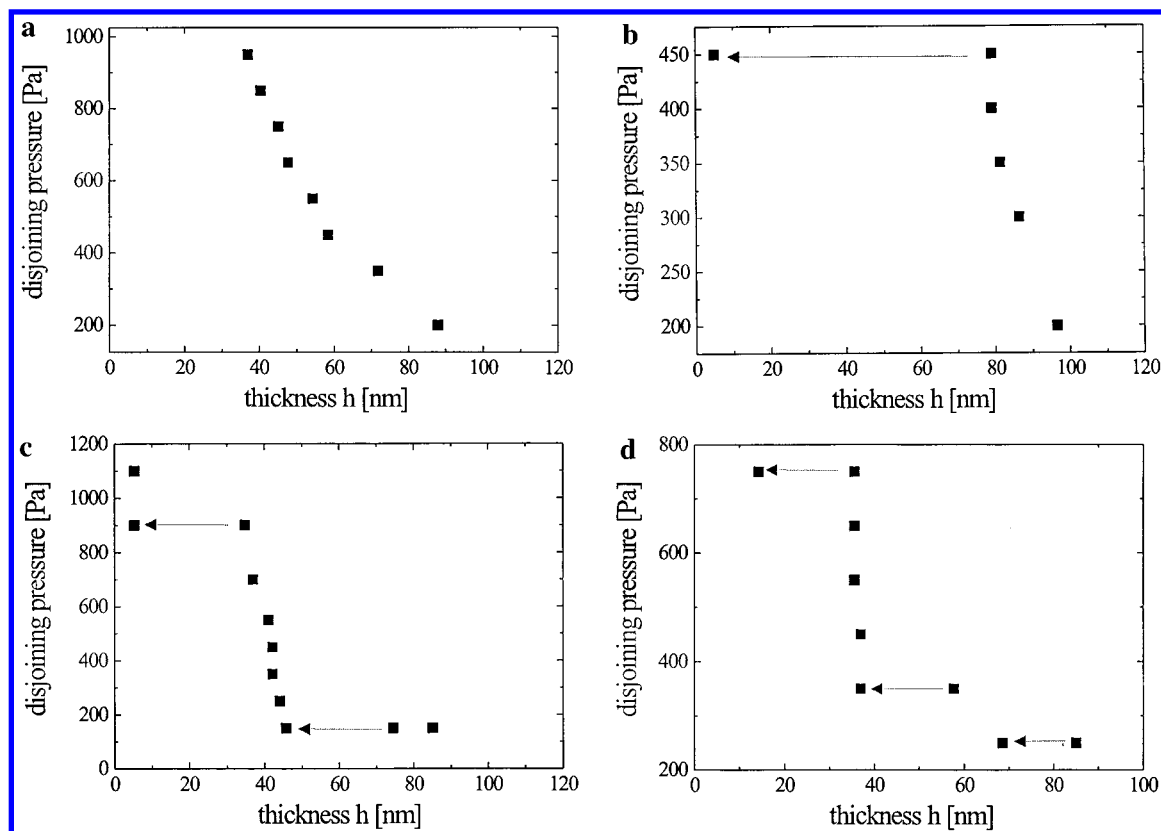


Figure 2. Disjoining pressure isotherms (disjoining pressure in dependence on or as a function of the film thickness) for the mixed system of C_{12}/C_{14} -APG and poly(DADMAC) ($f = 1.0$) at different poly(DADMAC) concentrations: (a) 5.33×10^{-7} mol/L, (b) 1.33×10^{-3} mol/L, (c) 5.33×10^{-3} mol/L, (d) 2.1×10^{-2} mol/L. The APG concentration was fixed at 0.045 g/L.

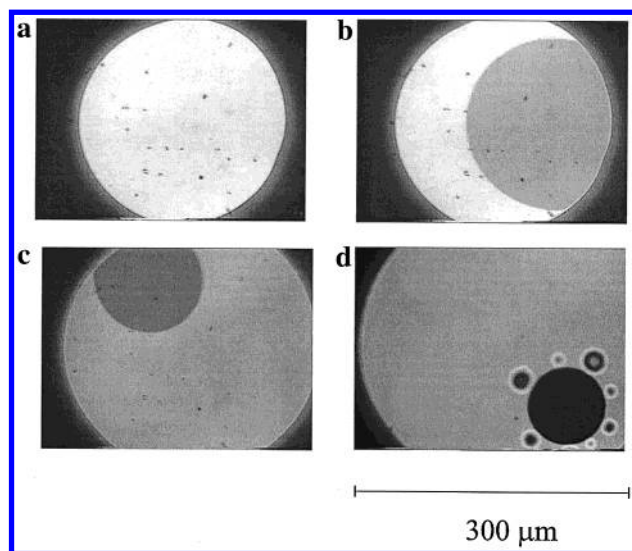


Figure 3. Photos of the film stratification at a poly(DADMAC) concentration of 8×10^{-3} mol/L: (a) before the first transition, (b) during the first transition, (c) during the second transition, (d) during the third transition.

in dependence on or as a function of the polyelectrolyte concentration at different degrees of charges. The viscosity increases with increasing polymer concentration and decreases with decreasing degree of charge. The results of both the stratification experiments and the viscosity measurements show the most obvious differences at the degree of charge below 50%, which indicates a distinct change in chain conformation.

Effect of Low Molecular Salt. The fact that the stepwise thinning seems to occur only in the case of charged polymers indicates an important role of the electrostatics for the ordering

of chains in the film. In addition to the degree of charge, the addition of low molecular salt influences the electrostatics. Figure 6 shows the disjoining pressure isotherm for the fully charged poly(DADMAC) at different concentrations of NaCl. With increasing salt concentration the pressure needed to induce a transition in film thickness decreases. Above a concentration of 5.32×10^{-4} mol/L the steps occur at the same pressure and the respective film thicknesses cannot be stabilized. At a NaCl concentration of $\geq 1.33 \times 10^{-3}$ mol/L the film thickness becomes inhomogeneous and the film drains more or less continuously.

Figure 7 shows the viscosity of the respective bulk solutions. The viscosity decreases with increasing salt concentration.

Discussion

Calculations show that the forces in polyelectrolyte solutions between interfaces correspond to oscillatory structural forces between two interfaces.¹⁵ Experimentally, only the thermodynamically stable points can be measured ($d\Pi/dh < 0$). Thus, the shown isotherm sections are considered to be parts of disjoining pressure oscillations. In analogy to the solvation forces between spherical particles (well-described in ref 23), the interface induces a lateral ordering of the polyelectrolyte chains. It is assumed that the stepwise thinning reflects this chain structuring. Figure 8 shows the step size as a function of the polyelectrolyte concentration. The fit by a power law results in an exponent of -0.5 , and the step size scales in the same way with the polyelectrolyte concentration as the correlation length in the bulk solution. Small-angle neutron scattering (SANS) experiments on the respective polyelectrolyte solutions result in the same correlation lengths of the bulk solution (infinite geometry).²⁴ This leads to the conclusion that the ordering of

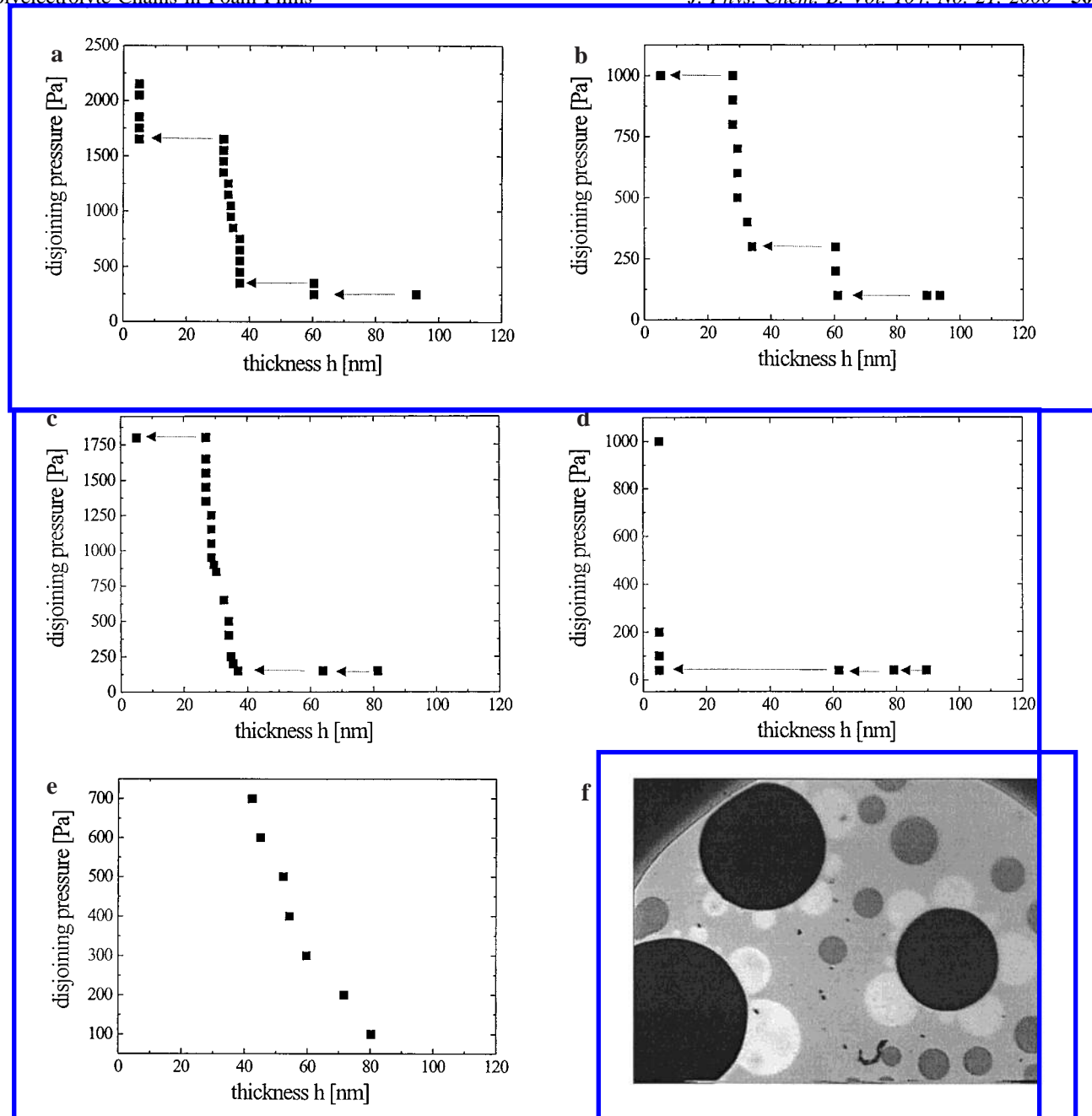


Figure 4. Disjoining pressure isotherms for the mixed system C_{12}/C_{14} -APG and polyelectrolyte at different charge densities: $f \equiv 1.0$ (a), 0.75 (b), 0.5 (c), 0.24 (d), 0 (e). (f) Photo of simultaneous transitions for $f = 0.24$. The polyelectrolyte concentration is 1.06×10^{-2} mol/L.

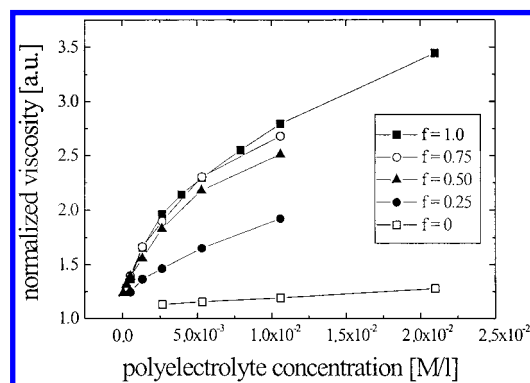


Figure 5. Viscosity normalized with respect to the viscosity of solvent (aqueous C_{12}/C_{14} -APG solution) as a function of the polyelectrolyte concentration at different charge densities.

polyelectrolyte chains in the confined geometry of the film is similar to that in the bulk solution.

For the theoretical calculations an isotropic distribution of monomers is assumed, which means an isotropic distribution of chain orientation. Because of the broken symmetry in the film, probably the chains are orientated parallel to the film surfaces and not perpendicular. It is concluded that the chains form transient two-dimensional networks parallel to the film interface. Two neighboring layers have a distance of the bulk correlation length ξ perpendicular to the film surface. The fact that the film thickness is about 5 nm (NBF) at the highest pressures indicates that there is at most one layer of polyelectrolyte chains in the film. This leads to the conclusion that the polyelectrolytes are squeezed out layer by layer, which is observed as steps in film thickness. Not only the molecular ordering normal to the surface but parallel to the surface is the decisive factor for oscillatory forces.²³ Thus, the decay in force amplitude in thicker films could be explained by the loss of lateral chain ordering with increasing distance from the surface. In the film bulk of thicker films (thicker than 150 nm) we

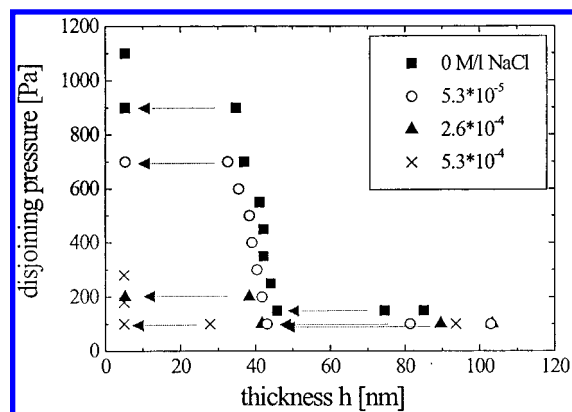


Figure 6. Disjoining pressure isotherms for the mixed system of C_{12}/C_{14} -APG and poly(DADMAC) at different NaCl concentrations. The polyelectrolyte concentration is 5.33×10^{-3} mol/L.

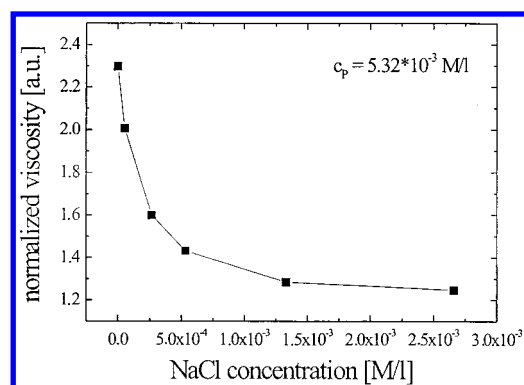


Figure 7. Viscosity of poly(DADMAC)-APG solutions normalized with respect to the viscosity of solvent (aqueous C_{12}/C_{14} -APG solution) as a function of the NaCl concentration. The polyelectrolyte concentration is 5.33×10^{-3} mol/L.

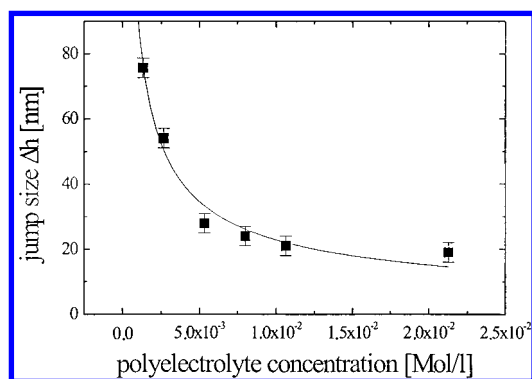


Figure 8. Measured jump size as a function of the polyelectrolyte concentration. The solid line corresponds to a fit by a power law, which results in an exponent of about -0.5 .

assume a structure which presents a transition between the two-dimensional network ordered parallel to the film surface and the three-dimensional isotropic network in the bulk solution. The decay in the amplitude is in good agreement with theoretical predictions about solvation forces between hard walls in polyelectrolyte solutions.¹⁵

This mesoscopic ordering of the chains is changed by the degree of charge. The linear charge density determines the chain conformation of polyelectrolytes in an important way. Strongly charged polyelectrolytes have a distance A between two charges smaller than the so-called Bjerrum length l_B (7.1 Å in water) and their conformation is determined by electrostatic interactions. In this regime counterion condensation must be taken into account.^{25,26} Thus, the effective charge density f_{eff} is smaller

TABLE 1: Nominal Charge Density (f), Distance between Two Charges (A) and the Effective Charge Density (f_{eff}) of the Polyelectrolytes Used in the Present Work, l_B Is the Bjerrum Length (7.1 Å in Water)

f	A [Å]	l_B/A	f_{eff}
1.00	3.8	1.87	0.53
0.75	5.1	1.39	0.53
0.50	7.6	0.93	0.5
0.24	15.2	0.47	0.25

than the nominal charge density f . The behavior of weakly charged polyelectrolytes is dominated by entropic effects. In addition to the effect on chain conformation, a decrease in charge density reduces the electrostatic repulsion between chains because of the smaller electrostatic potential of the chains. In Table 1 the values of l_B/A and f_{eff} are given for different degrees of charge. At $f = 0.5$ – 1.0 the distance between two charges is smaller or equal to the Bjerrum length. Thus, the effective charge of the chains and the amount of uncondensed counterions are nearly constant in this regime, which results in the same film thicknesses between the steps in this concentration regime. This fact is also reflected by the results of viscosity measurements and leads to the conclusion that the investigated strongly charged chains have a similar conformation. It is assumed that the chains are extended at a degree of charge above 50% because of the electrostatic repulsion along the chain. The disjoining pressure isotherms for the three highest degrees of charge show that the step size is invariant to the charge density, which means that the chain ordering in the film is similar. SANS experiments using semidilute polyelectrolyte solution show also that the bulk correlation length above the condensation threshold is independent of the charge density.^{10,24}

Below a degree of charge of 50% the effective charge is reduced. The electrostatic repulsion along the chain and between two chains decreases. The chains begin to coil, which is reflected in a smaller viscosity of the bulk solution. These weaker electrostatic interactions induce a less-ordered structure of polyelectrolyte chains parallel and normal to the film surface. The energy barrier which has to be overcome for a layer of polyelectrolyte to be squeezed out is reduced. In other words, the amplitude of the pressure oscillations is reduced with decreasing effective charge. The ordering seems to be completely lost in films of neutral polymer chains. Scattering experiments on polyelectrolyte solutions show that below the condensation threshold the correlation peak is shifted toward higher scattering vector and then levels off with decreasing charge density.²⁷ In our thin film balance experiment the different isotherm sections for the CBF cannot be stabilized at a charge density of 0.24. Therefore we cannot make any conclusion about the step size and its dependence on the charge density below the condensation threshold.

The addition of salt leads to a screening of the charges along the polyelectrolyte chains which results in a reduced electrostatic repulsion along the chain and therefore in a coiling of the chain. The worsening of the solvent quality induces a nonhomogeneous transition from an extended chain to a coiled one by forming several blobs (coils) along the chain. Molecular dynamics simulations of strongly charged flexible chains in poor solvents predict such a kind of transition by increasing the monomer density²⁸ corresponding to an increasing concentration of counterions. A similar model can be also applied to the present situation of constant monomer density but increasing salt concentration.²⁹ In addition, the screening of charge reduces the electrostatic interaction between two neighboring chains. It is assumed that both the decrease in intra- and interchain repulsion

destroy the mesoscopic ordering of polyelectrolyte chains in the film. The reduced entanglements of the chains lead to a decrease in viscosity. Furthermore, the steps in film thickness are induced at lower pressures than in the salt-free case. This is in good agreement with theoretical calculations of forces between surfaces immersed in polyelectrolyte solutions at different salt concentrations.¹⁵ They predict a decreasing amplitude of the oscillations of solvation forces with decreasing Debye length. Thus, the effect on the amplitude of the pressure oscillations is qualitatively the same as in the case of decreasing effective charge.

Conclusions

Thin film balance measurements were carried out on free-standing films made from aqueous mixed surfactant/polyelectrolyte solutions. Above the critical chain overlap concentration c^* a stepwise thinning occurs. The different isotherm sections between the steps are parts of disjoining pressure oscillations. The step size scales with the polyelectrolyte concentration c as $c^{-0.5}$. This is in good agreement with theoretical models of other authors and an ordering of polyelectrolyte chains in the confined geometry of foam films is assumed. At charge densities above the threshold of counterion condensation the step size is constant, indicating a renormalization of the effective charge. Below the condensation threshold the amplitude of the disjoining pressure oscillations decreases with decreasing degree of charge and disappears for neutral polymer chains. A decrease in pressure amplitude is also noticed after addition of low molecular salt. Both the decrease in charge density and the increasing ionic strength reduce the electrostatic interactions and destroy the chain layering. We conclude that the mesoscopic ordering of polyelectrolyte chains in aqueous films is caused by electrostatic repulsion between the chains.

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