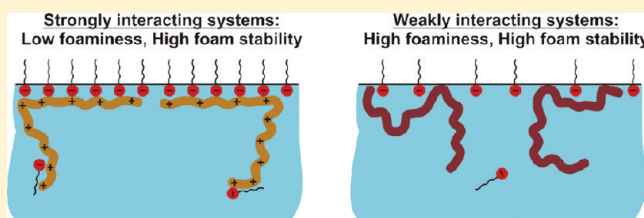# Foaming and Foam Stability for Mixed Polymer–Surfactant Solutions: Effects of Surfactant Type and Polymer Charge

R. Petkova, S. Tcholakova,* and N. D. Denkov

Department of Chemical Engineering, Faculty of Chemistry, Sofia University, 1 J. Bourchier Ave., 1164 Sofia, Bulgaria

ABSTRACT: Solutions of surfactant–polymer mixtures often exhibit different foaming properties, compared to the solutions of the individual components, due to the strong tendency for formation of polymer–surfactant complexes in the bulk and on the surface of the mixed solutions. A generally shared view in the literature is that electrostatic interactions govern the formation of these complexes, for example between anionic surfactants and cationic polymers. In this study we combine foam tests with model experiments to evaluate and explain the effect of several polymer–surfactant mixtures on the foaminess and foam stability of the respective solutions. Anionic, cationic, and nonionic surfactants (SDS, $C_{12}TAB$, and $C_{12}EO_{23}$) were studied to clarify the role of surfactant charge. Highly hydrophilic cationic and nonionic polymers (polyvinylamine and polyvinylformamide, respectivey) were chosen to eliminate the (more trivial) effect of direct hydrophobic interactions between the surfactant tails and the hydrophobic regions on the polymer chains. Our experiments showed clearly that the presence of opposite charges is not a necessary condition for boosting the foaminess and foam stability in the surfactant–polymer mixtures studied. Clear foam boosting (synergistic) effects were observed in the mixtures of cationic surfactant and cationic polymer, cationic surfactant and nonionic polymer, and anionic surfactant and nonionic polymer. The mixtures of anionic surfactant and cationic polymer showed improved foam stability, however, the foaminess was strongly reduced, as compared to the surfactant solutions without polymer. No significant synergistic or antagonistic effects were observed for the mixture of nonionic surfactant (with low critical micelle concentration) and nonionic polymer. The results from the model experiments allowed us to explain the observed trends by the different adsorption dynamics and complex formation pattern in the systems studied.

1. INTRODUCTION

Polymer–surfactant mixtures are widely used in many practical applications, such as the paper industry and home and personal care products.[1,2] Experimental studies have revealed the importance of subtle interactions between the components of the surfactant–polymer mixtures, both in the bulk and on the surface of their solutions. The surfactant–polymer interactions in the bulk solutions have been extensively studied for many years and are relatively well understood.[1–8] In contrast, the complex surface behavior of the polymer–surfactant mixtures, which is crucial for understanding the processes of foaming and foam stabilization in these systems, is less understood and attracts a rapidly increasing interest in recent years.[8–30]

In the course of their studies, researchers have distinguished between weakly interacting polymer–surfactant systems (usually comprising a neutral polymer and charged surfactant) and strongly interacting systems (containing surfactants and polymers with opposite charges).[12] The shape of the surface tension isotherms and the general behavior of the weakly interacting systems are relatively well understood.[8,11–13] The surface behavior of these systems is usually described in terms of the critical aggregation concentration (onset of polymer bound micellization) and the critical micelle concentration (formation of free surfactant micelles).[12]

The accumulated experimental results[12,16–18] evidence that the structure and composition of the adsorption layers in the strongly interacting systems depend on the competition

between the formation of surface complexes of type "polymer–surfactant monomers" and bulk complexes of type "polymer–surfactant micelle".[12] The behavior of the systems forming surface complexes of type polymer–surfactant monomers is usually not very different from the behavior of weakly interacting mixtures. In contrast, for the second type of systems (those forming bulk polymer–micelle complexes), it was observed that the solution surface tension passes through a deep minimum and subsequent maximum as a function of surfactant concentration (at fixed polymer concentration).[12,20] Recently,[29] it was shown that this minimum in the surface tension isotherms can be avoided by mechanical agitation of the solutions, which results in redispersion of the aggregates and supply of surface active material to the air/water interface, thus forming packed adsorption layer with low surface tension. The surface behavior of the strongly interacting systems depends significantly on the electrolyte concentration,[12] polymer charge density,[21] length of surfactant tails,[17] etc.

Along with the peculiar surface tension isotherms, the surfactant–polymer mixtures exhibit nontrivial surface rheological properties as well. It was shown that, at low surfactant concentrations, the adsorbed layers are viscoelastic and become fluid at high surfactant concentration.[30,31] The viscoelastic

region is larger at higher polymer concentrations and coincides with the appearance of turbidity of the bulk solution.[30,31] Monteux et al.[18] characterized the surface shear properties of strongly interacting system and showed that the surface shear modulus exhibits a maximum at surfactant−polymer ratio around one, which was explained with the formation of surfactant−polymer complex on the surface. This complex was found not to affect strongly the surface dilatational modulus of the mixed solution.[18] In a separate study, Noskov et al.[28] obtained somewhat different results for the same systems—the observed differences have been explained[22] by the different surface ages and frequency of oscillations in the two studies. On the other hand, both studies[18,28] reported strong variations of dynamic surface elasticity (passing through a maximum) in a narrow concentration range of surfactant, at constant polymer concentration. The significant drop of surface elasticity after the maximum was explained by Noskov et al.[22] with the formation of a heterogeneous adsorption layer containing micro-particles.[22] No correlation between surface elasticity and the measured ellipticity of the adsorption layer was determined in ref 18. Other studies, however, showed a strong effect of the formation of polymer−surfactant complexes on the surface dilatational elasticity—the latter was highest when larger amount of material was adsorbed on the solution surface.[32]

The foam film behavior of polymer−surfactant solutions has been also intensively studied in the context of foam stability.[9,21,32−36] It was shown that surface polymer−surfactant complexes are able to stabilize foam films with relatively large thickness, even at very low surfactant and polymer concentrations. At higher surfactant concentrations, polymer−surfactant aggregates are formed in the bulk solution, and as a consequence, foam films with uneven thickness are formed due to trapped aggregates.[33] In a recent paper[32] it was shown that the stability of foam films does not correlate with either of the surface tension or surface elasticity. The main results from the different studies of foam films stabilized by polymer−surfactant mixtures are summarized in ref 9.

The investigations of foam film properties are usually related to the stability of foams. A general assumption in these studies is that the foam stability increases when polymer−surfactant aggregates are trapped in the foam films.[8] Some correlation between surface shear elasticity and foam stability was also reported.[18] However, the actual results about the effect of polymer−surfactant interactions on the foam formation and stability are very limited.[8,11,18]

The major aim of the current study is to investigate more systematically the effects of polymer−surfactant interactions on the foamability and foam stability in mixed polymer−surfactant systems and to try to clarify the mechanisms governing these effects. To achieve our aims, we performed systematic series of experiments with two highly hydrophilic polymers (in the sense that these polymers do not reduce the surface tension even at relatively high weight concentration), one nonionic and one cationic, with three different types of surfactants: cationic, anionic, and nonionic. Along with foam tests, we determined the thickness and the stability of the foam films formed from the foaming solutions. The surface tension was also measured. Several of the most interesting systems were characterized by ellipsometry to measure the adsorption on the air−water interface.

The paper is organized as follows. The methods and materials are described in section 2. Section 3.1 presents the experimental results from the foam tests. The results from the model experiments are described in sections 3.2 and 3.3. The overall discussion about the mechanisms of foam stabilization is presented in section 3.4. The main conclusions are summarized in section 4.

2. MATERIALS AND METHODS

2.1. Materials. Two hydrophilic polymers were studied: cationic poly(vinylamine) (denoted as PVAm) and nonionic poly(N-vinyl-formamide) homopolymer (denoted in the text as PVFAm), both products of BASF. According to its producer, the positively charged PVAm consists of 95% units of vinylamine and 5% units of vinylformamide. The pK_a value of PVAm is around 8.6.[37,38] The molecular mass of PVAm was around 4.5×10^4, whereas the molecular mass of PVFAm was around 2×10^5.

As low-molecular-mass surfactants we used the anionic surfactant sodium dodecyl sulfate (SDS, product of Acros), the nonionic surfactant polyoxiethelene-23 dodecyl ether (Brij 35, product of Sigma, denoted as $C_{12}EO_{23}$), and the cationic surfactant dodecyltrimethyla-monium bromide (DTAB, product of Sigma, denoted as $C_{12}TAB$).

All surfactants and polymers were used as received. The aqueous solutions were prepared with deionized water, which was purified by a Milli-Q Organex system (Millipore). All solutions contained 10 mM NaCl (Merck, analytical grade) as a background electrolyte.

Solutions of the individual polymers were prepared by the following procedure: A certain amount of polymer was added to the electrolyte solution and stirred at 35 °C for 1 h on magnetic stirrer. The concentration of PVAm in all foaming solutions was fixed at 0.35 wt %, whereas the concentration of PVFAm was fixed at 0.19 wt %. The solutions of PVAm had a viscosity of 2.2 mPa·s and pH ≈ 9.2 (which corresponds to ≈20% charged monomer units in the polymer chain[37]), whereas the solutions of PVFAm had a viscosity of 1.3 mPa.s and pH ≈ 6.1. Surfactant concentration in the foaming solutions was varied from 0 up to 1 mM. Note that the polymers were always in excess with respect to the weight concentration of surfactant in the studied mixed solutions.

To prepare mixed surfactant−polymer solutions, we first prepared separated stock solutions with doubled concentrations of surfactant and polymer. Afterward, we obtained the final mixed solutions with desired concentrations by mixing these stock solutions (1:1 by weight).

2.2. Experimental Methods.

2.2.1. Foam Test. To compare the foaminess and foam stability of the studied systems, we used a modification of the Bartsch test.[39] Briefly, 15 mL of the studied foaming solution was loaded in a glass cylinder with 75 mL total volume. To generate foam, 10 standard handshakes of the cylinder were applied. The initial foam volume and the subsequent foam decay were monitored during the following 15 min.

The solution foaminess is characterized by the volume of trapped air, V_0, immediately after shaking (at $t = 0$), while the foam stability is characterized by the defoaming time, which is defined as a time required for obtaining half of the solution surface free of bubbles.

2.2.2. Surface Properties of the Foaming Solutions. The surface tension of the foaming solutions was measured by the pendant drop method. The measurements were performed on apparatus DSA100 (Krüss GmbH, Hamburg, Germany) at 25.0 ± 0.5 °C. The kinetics of the surface tension relaxation, after a pendant drop has been formed rapidly on the capillary tip, was followed for 15 min.

2.2.3. Foam Films in Capillary Cell. Foam films of millimeter size were formed and observed in a capillary cell to obtain information about the film stability, equilibrium film thickness, and the film-thinning pattern. The observations were made in reflected light by using the method of Scheludko.[40] The films were formed from a biconcave drop, placed in a short capillary (i.d. 2 mm, height 3 mm) by sucking out liquid through a side orifice. The observations were performed in reflected light by means of an Axioplan microscope (Zeiss, Germany), equipped with a long-distance objective (Zeiss Epiplan 20×/0.40), CCD camera, video recorder, and monitor. The capillary pressure which drives the film thinning was increased in some

of the experiments by enlarging the radius of the foam film and/or by opening the capillary cell to the ambient atmosphere (so that water evaporation from the foam film was induced).[41]

2.2.4. Ellipsometry. The polymer adsorption on the air–water interface was determined by ellipsometry. The used instrument is a modification of a conventional null type ellipsometer (LEF 3M, Novosibirsk, Russia), which is adapted for kinetic measurements with time resolution of 1 s.[42] A solid state laser (λ = 532 nm, Compass 215M, Coherent), equipped with a light polarizer, emits a beam with a certain polarization state. All experiments are performed at 50° angle of incidence, which is close to the Brewster angle for water, 53.1°. After reflection from the sample surface, the light changes its polarization and enters the detector (photomultiplier, equipped with a rapidly rotating analyzer). The system is driven by a computer, and the raw data from the detector are instantaneously recomputed to give the two ellipsometric angles, Ψ and Δ, as functions of time. From the measured difference between the ellipsometric angles Δ for pure water and the studied polymer solution, we calculated the adsorption by using the relation[43,44]

$$\Gamma = K_{ell}(\Delta_{POL} - \Delta_{WATER}) \tag{1}$$

where $K_{ell} \approx 0.5$ mg m^{-2} deg^{-1} is an optical constant.

Equation 1 was derived in refs 43 and 44. Theoretical analysis of the complete set of equations for interpretation of ellipsometric data showed that for thin adsorption layers, when only one of the measured ellipsometric angles is sensitive to the changes of layer properties (this is the angle Δ in our experiments), the adsorbed amount can be calculated by eq 1, which represents eq 8 in ref 44:

The optical constant K_{ell} is defined by eq 8a in ref 44:

$$K_{ell} = \frac{n_{1x}{}^2}{A\frac{dn}{dc}(n_{1x}{}^2 - n_0{}^2)(n_{1x} + n_2)}$$

Here n_{1x} is the refractive index of the adsorption layer (assumed to be homogeneous), n_0 is the refractive index of the upper phase, and n_2 is the refractive index of the bottom (aqueous) phase. The value of the numerical prefactor A depends on the experimental conditions (see eq 5a in ref 44), and it is $A = 0.1396$ nm^{-1} for our experimental setup.

By measuring the refractive index of a series of polymer solutions with Pulfrich refractometer (model PR2), we determined $dn/dc = 0.18 \pm 0.01$ cm^3/g for PVFAm and 0.17 ± 0.01 cm^3/g for PVAm. For calculation of K_{ell} we need also the value of n_{1x}. As far as we have only one measurable quantity (Δ) and two unknown characteristics of the adsorption layer (its thickness and its average refractive index), we should make some simplifying assumption about n_{1x}. As explained in ref 44, the variation of n_{1x} in the reasonable range between 1.332 and 1.5 results in a relatively small changes of K_{ell}. For PVFAm-containing solutions the value of K_{ell} varied between 0.44 and 0.6 mg m^{-2} deg^{-1}, whereas for PVAm-containing solutions it varied between 0.47 and 0.63 mg m^{-2} deg^{-1}, while n_{1x} is varied between 1.332 and 1.5. Therefore, in the following data analysis we assumed an average value of $K_{ell} \approx 0.5$ mg m^{-2} deg^{-1}.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Foam Formation and Stability.

3.1.1. Foamability. The initial foam volume, formed after shaking of the polymer solutions (without added surfactants), was 3 ± 1 mL for both polymers (PVAm and PVFAm). These foams contained relatively large, centimeter-sized bubbles and were very unstable—they completely disappeared within seconds. Such low foamability of the studied polymer solutions could be expected, as far as these polymers are very hydrophilic—they do not adsorb strongly on the solution surface and do not reduce the surface tension of the foaming solutions (see Figure 7).

The foamability of the surfactant solutions (without added polymers) was measured as a function of surfactant

concentration. The obtained results are shown in Figure 1 as empty symbols. One sees that V_0 increases almost linearly with
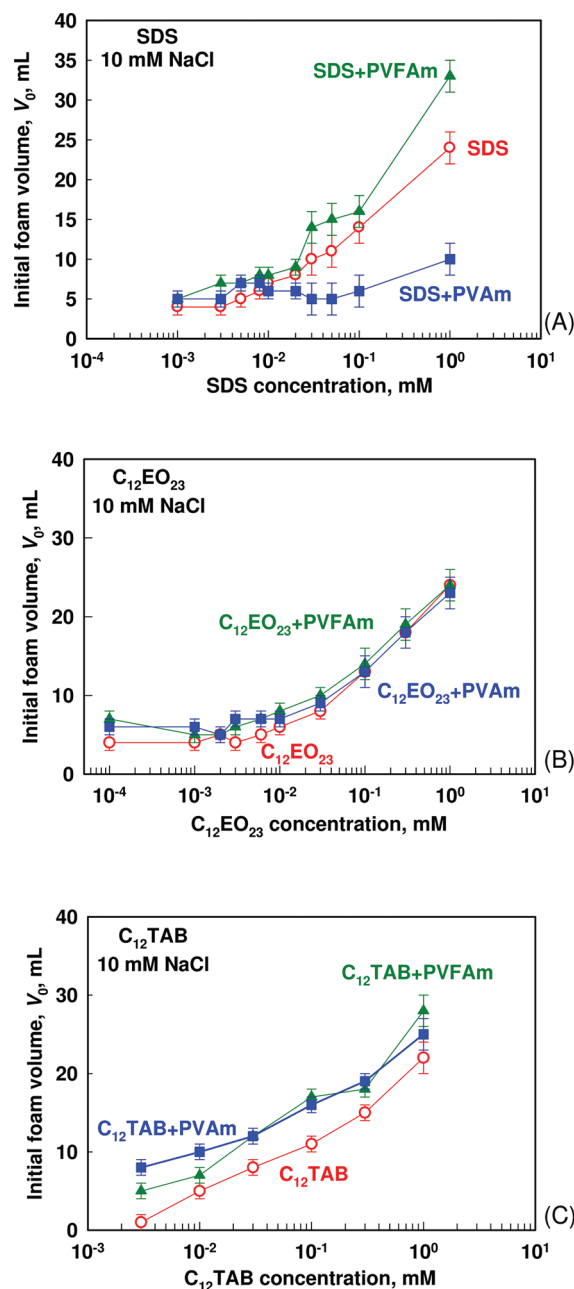

Figure 1. Initial foam volume, V_0, as a function of surfactant concentration for (A) SDS, (B) $C_{12}EO_{23}$, and (C) $C_{12}TAB$-containing foams formed from surfactant solution alone (red circles), surfactant + PVAm (blue squares), and surfactant + PVFAm (red triangles). All solutions contain 10 mM NaCl. Polymer concentration is 0.35 wt % for PVAm and 0.19 wt % for PVFAm.

increasing the logarithm of surfactant concentration in the range between 0.01 and 1 mM, whereas at lower concentrations, the initial foam volume was $V_0 \approx 3$ mL or less. Interestingly, very similar results for the dependence $V_0(C_S)$ were obtained for all three surfactants studied, despite their different charges and molecular masses, up to 1 mM surfactant. This similarity indicates that the Marangoni effect, governed mostly by the number concentration of the adsorbed surfactant molecules during foaming, is the dominant effect for the initial

foam volume—the dynamic surfactant adsorption is expected to be similar for equal molar concentrations of the surfactants below their CMC. In contrast, the surface forces are expected to be very different for some of these molecules (e.g., nonionic vs ionic), which indicates that the surface forces had a secondary importance for the initial foam volume in this regime of foaming, realized at relatively low surfactant concentrations.

The foamability of the mixed polymer + surfactant solutions was also characterized as a function of surfactant concentration. The obtained results for SDS + polymer solutions are shown in Figure 1A. One sees that, at $C_S < 0.01$ mM, no significant effect of either of the polymers on V_0 could be detected—the foamability of SDS and SDS + polymer solutions coincide in the frame of our experimental accuracy. A significant difference in the foamability of the SDS solution, on one side, and SDS + polymer solutions, on the other side, is observed at $C_S \geq 0.03$ mM. At these higher concentrations, V_0 for the mixed SDS + PVFAm solutions is higher than V_0 for the SDS solution with the same concentration, C_S. In contrast, V_0 for the mixture of SDS with the cationic PVAm is significantly lower, compared to V_0 for SDS only. For example, V_0 is $\approx$10 mL for SDS + PVAm at the highest SDS concentration studied, $C_S = 1$ mM, whereas it is 22 and 32 mL for the SDS and SDS + PVFAm solutions, respectively, at the same surfactant concentration.

Therefore, we can conclude that, at $C_{SDS} > 0.02$ mM, the nonionic polymer PVFAm acts as foam booster (increases solution foaminess), whereas the cationic polymer PVAm acts as foam inhibitor (decreases the foaminess) with respect to SDS-stabilized foams. At $C_{SDS} < 0.02$ mM, no significant effect of these polymers on V_0 is observed.

Results for the initial volume of the foams, formed from $C_{12}EO_{23}$-containing solutions, are presented in Figure 1B. One sees that for these surfactant−polymer mixtures the foaminess of the polymer + surfactant solutions is virtually the same as that of the surfactant solutions without polymers. Therefore, the foaminess seems to be controlled entirely by the nonionic surfactant in the studied $C_{12}EO_{23}$ + polymer solutions.

Experimental results for $C_{12}TAB$-containing foams are presented in Figure 1C. Similarly to SDS foams, we observed almost linear increases of V_0 with $\log(C_S)$ for the foams formed from $C_{12}TAB$ solution (without polymer). Interestingly, we found that the addition of any of the studied polymers (the cationic PVAm or the nonionic PVFAm) to the cationic surfactant $C_{12}TAB$ increases V_0 for all surfactant concentrations studied. This effect is particularly well seen in the range of low and intermediate surfactant concentrations and becomes less pronounced at the highest $C_{12}TAB$ concentration. The results for the two polymers are very similar, despite the fact that one of them is cationic, whereas the other is nonionic, and they are mixed with a cationic surfactant.

From this series of experiments we can conclude that, at $C_S > 0.02$ mM, the cationic polymer PVAm decreases the foaminess of SDS solutions, has no significant effect on the foaminess for $C_{12}EO_{23}$ solutions, and increases the foaminess of $C_{12}TAB$ solutions. The nonionic polymer PVFAm has significant boosting effect for SDS and $C_{12}TAB$ solutions and has no significant effect for $C_{12}EO_{23}$ solutions. Some of these results are far from trivial and call for mechanistic explanations (see section 3.4).

3.1.2. Foam Stability. To evaluate the foam stability, the foam volume was measured as a function of time after foam generation. Representative experimental curves are shown in Figure 2. One sees that the curves $V_F(t)$ for the surfactant−
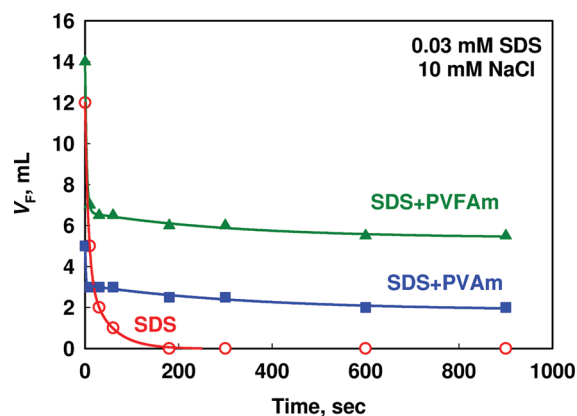

Figure 2. Foam volume as a function of time for 0.03 mM SDS (red symbols), 0.03 mM SDS + 0.35 wt % PVAm (blue squares), and 0.03 mM SDS + 0.19 wt % PVFAm (green triangles). All solutions contain 10 mM NaCl.

polymer mixtures typically consist of two well-defined regions: fast foam decay during the first 10 s and much slower decrease of the foam volume during the following period (up to 900 s in these experiments). As mentioned in the Materials and Methods section, we characterized the foam stability by using the so-called "defoaming time", t_{DEF}, defined as the time, required to obtain half of the solution surface free of bubbles. It should be mentioned that solutions that have higher foamaibility may have lower foam stability and vice versa. Such an example is shown in Figure 2. The foamability of 0.03 mM SDS solution is higher than V_0 for the mixed 0.03 mM SDS + 0.35 wt % PVAm solution; however, the defoaming time for SDS is 150 s, whereas a fraction of the foam formed in SDS + PVAm solution remains stable even after 900 s (residual foam ≈2 mL). Therefore, the foamability and foam stability are governed, at least partially, by different factors and should be explained separately (see section 3.4).

The defoaming time for foams, formed in polymer solutions (no added surfactant), was below 10 s for both polymers studied. Therefore, the foams formed from 0.35 wt % PVAm or 0.19 wt % PVFAm solutions were very unstable due to the highly hydrophilic nature of these polymers.

The defoaming time for SDS + polymer solutions is shown in Figure 3A as a function of SDS concentration. One sees that t_{DEF} increases with the increase of C_S for all foams studied. The threshold surfactant concentration, above which $t_{DEF} > 900$ s and the foam could be considered as stable, is the highest for SDS-stabilized foams without polymer, 0.1 mM for this system. The threshold surfactant concentration decreases by about 5 times for PVAm + SDS solutions (down to 0.02 mM SDS) and 3 times for SDS + PVFAm stabilized foams (down to 0.03 mM SDS). Therefore, both studied polymers—the cationic PVAm and the nonionic PVFAm—increase significantly the foam stability of SDS-containing foams. Let us emphasize again that opposite effects of PVAm are observed with respect to foamability and foam stability in the case of SDS—this cationic polymer decreases the volume of the initial foam but increases its stability. In contrast, the nonionic polymer increases both the initial foam volume and foam stability.

To compare quantitatively the stable foams with $t_{DEF} > 900$ s, we determined also the ratio of the residual to the initial foam, $p = V_F(t = 900 \text{ s})/V_0$, which characterizes the fraction of initial foam remaining stable after 900 s (see Figure 3B). These results
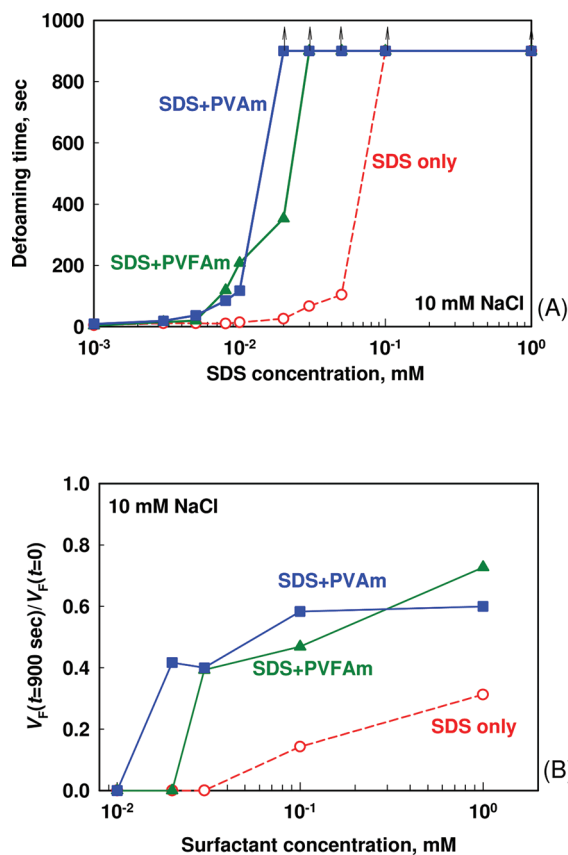
Figure 3. (A) Defoaming time as a function of surfactant concentration for foams formed from SDS (red symbols), SDS + PVAm (blue squares), and SDS + PVFAm (red triangles). (B) Fraction of residual foam after 900 s for the stable foams with defoaming time longer than 900 s. All solutions contain 10 mM NaCl and polymer concentration is 0.35 wt % for PVAm and 0.19 wt % for PVFAm.

show no significant difference in the fraction of remaining stable foam in the presence of the cationic PVAm and nonionic PVFAm polymers, when SDS is used as a surfactant. The observed very high stability of the foams, formed in SDS + PVAm and SDS + PVFAm solutions, at SDS concentration well below the CMC of this surfactant, demonstrates the strong synergistic effect for both types of mixed solutions: nonionic polymer + anionic surfactant and cationic polymer + anionic surfactant with respect to foam stability.

A similar series of experiments was performed with $C_{12}EO_{23}$-containing solutions (see Figure 4). The addition of any of the studied polymers had a relatively small effect for $C_{12}EO_{23}$. The threshold surfactant concentration, above which the foam remains stable for 900 s, is ≈0.005 mM, and it decreases down to ≈0.003 mM when PVAm or PVFAm is present in the solution. Note that the $C_{12}EO_{23}$ concentration, at which the foam becomes stable without polymer, is around an order of magnitude lower than that for SDS (cf. Figures 3 and 4). This latter difference is certainly related to the different CMC values of these surfactants which are ≈3.5 mM for SDS and ≈0.2 mM for $C_{12}EO_{23}$ (measured at 10 mM NaCl) and, hence, to the different surfactant adsorption at given surfactant concentration. Note that for both surfactants stable foams are observed at concentrations which are 30−40 times lower than the CMC of the respective surfactant.
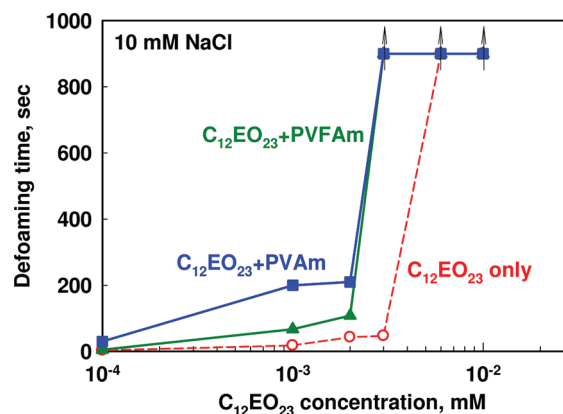

Figure 4. Defoaming time as a function of surfactant concentration for foams formed from $C_{12}EO_{23}$ (red symbols), $C_{12}EO_{23}$ + PVAm (blue squares), $C_{12}EO_{23}$ + PVFAm (red triangles). All solutions contain 10 mM NaCl, and polymer concentration is 0.35 wt % for PVAm and 0.19 wt % for PVFAm.

Results for the defoaming time of $C_{12}TAB$-cotaining foams are shown in Figure 5. One sees that this surfactant is unable to
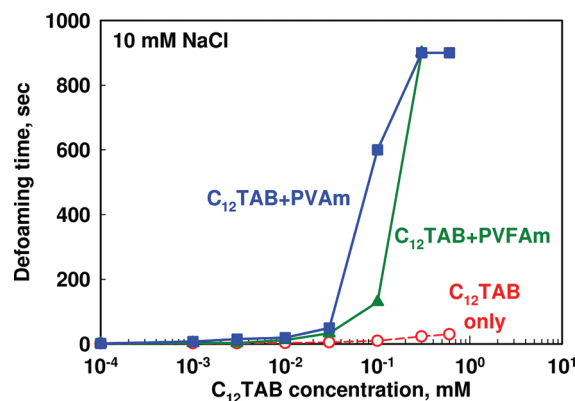

Figure 5. Defoaming time as a function of surfactant concentration for foams formed from $C_{12}TAB$ (red symbols), $C_{12}TAB$ + PVAm (blue squares), and $C_{12}TAB$ + PVFAm (red triangles). All solutions contain 10 mM NaCl, and polymer concentration is 0.35 wt % for PVAm and 0.19 wt % for PVFAm.

stabilize the foam for more than 20 s even at concentrations up to 1 mM, which is due to its large headgroup and the related high CMC ≈ 14 mM (at 10 mM NaCl). Surprisingly, we observed that the addition of the cationic polymer PVAm to the cationic surfactant $C_{12}TAB$ increases very significantly the foam stability, and stable foams are formed even at C_S = 0.2 mM surfactant (see Figure 5). Therefore, we see a strong synergistic effect between the cationic surfactant and the cationic polymer with respect to both foam stability and foamability. The nonionic polymer PVFAm also increases significantly the defoaming time for these foams.

From these series of experiments we can conclude that strong synergistic effect with respect to foam stability is observed in the solutions of (1) anionic surfactant (SDS) and nonionic (PVFAm) polymer, (2) anionic surfactant and cationic (PVAm) polymer, (3) cationic surfactant ($C_{12}TAB$) and cationic polymer (PVAm), and (4) cationic surfactant and nonionic polymer. When the nonionic surfactant $C_{12}EO_{23}$ is used, no synergy with the studied polymers was observed.

3.2. Surface Properties. To clarify the mechanisms governing the observed effects on foam behavior, we performed several series of model experiments. The results from the surface tension and surface adsorption measurements are described in section 3.2. The results from the related foam film observations are described in section 3.3.

3.2.1. Surface Tension. The surface tension of 0.35 wt % PVAm and 0.19 wt % PVFAm solutions was measured by drop shape analysis. The experimental results showed that the surface tension of PVFAm is ≈71 mN/m and does not change with time up to 900 s. The surface tension of PVAm also starts from 71 mN/m and decreases by less than 0.2 mN/m for 900 s (see Figure 7). Therefore, the studied polymers have very low surface activity. These results correlate well with the low foamability and foam stability for the solutions containing polymer only.

The surface tension of SDS solutions (without polymers) is ≈71 mN/m at $C_S \leq 0.1$ mM, which is in a good agreement with the results obtained by other authors.[45−48] Therefore, there is no need of low surface tension to obtain stable foam for SDS solutions—the foams are stable for 15 min at 0.1 mM SDS (Figure 3) while the surface tension of the respective foaming solution is still very high (see section 3.4 for explanation).

The results for the surface tension of SDS + PVFAm and SDS + PVAm solutions are presented in Figures 6A and 6B, respectively. One sees that the adsorption curves differ very significantly for these two solutions. The equilibrium surface

tension of SDS + PVFAm solutions is reached very quickly, and no significant further decrease is observed up to the end of our measurements (900 s). The surface tension of PVFAm + SDS solutions, at $C_{SDS} \leq 0.02$ mM, coincides with the surface tension of PVFAm alone. Significantly lower surface tension of the mixed solution is measured at 0.1 mM and higher concentrations of SDS. Therefore, PVFAm + SDS behaves as a mixture of weakly interacting polymer and surfactant, and the studied surfactant concentrations are below the critical aggregation concentration in the bulk.[12]

The results for the surface tension kinetics of PVAm + SDS solution, at $C_{SDS} < 0.01$ mM, also coincided with the results for the pure polymer (see Figure 6B). However, at $C_S = 0.01$ mM, the surface tension decreases significantly after a long induction period (up to 100 s). Similar behavior is observed at 0.03 mM SDS, with shorter induction period (≈30 s), and the surface tension decreases down to 35 mN/m, thus indicating the formation of dense adsorption layer. At 0.1 mM SDS, the induction period is shorter than 2 s, and the surface tension decreases down to ≈30 mN/m. Such low surface tensions were reported before for strongly interacting polymer−surfactant systems.[12,38] Therefore, we can conclude that SDS + PVAm is a strongly interacting system and that the kinetic curves of surface tension consists of two well-defined regions: the surface tension coincides with that of the pure polymer in the first region, whereas a sharp decrease is observed during the second period, reflecting the formation of denser surfactant−polymer complexes on the solution surface.

The comparison between the measured surface tensions, on one side, and the foamability and foam stability of the SDS + polymer solutions, on the other side, does not reveal any obvious correlation. The weakly interacting system PVFAm + SDS, with higher equilibrium surface tension, showed much better foamability compared to the strongly interacting system PVAm + SDS. The most probable explanation for this behavior is that the concentration of free SDS molecules, which can adsorb rapidly on the solution surface during foaming, is much lower in the strongly interacting system (as compared to the weakly interacting system) because the main fraction of SDS molecules is bound to the cationic PVAm molecules in the bulk solution. As a consequence, the foamability of PVAm + SDS is worse compared to PVFAm + SDS solutions. At longer times, when surfactant−polymer complexes are formed on solution surface, both systems give stable foams.

The results for the surface tension of 0.3 mM $C_{12}TAB$, with and without polymer, are compared in Figure 7 with those of the polymer solutions. Notably, at this $C_{12}TAB$ concentration, we observed a significant increase in the defoaming time for $C_{12}TAB$ + polymer foams, as compared to $C_{12}TAB$ foams (see Figure 5). However, the surface tensions of the $C_{12}TAB$ and $C_{12}TAB$ + polymer solution are the same in the frame of our experimental accuracy. They are lower than the surface tension of the polymer solution (without surfactant), which indicates that $C_{12}TAB$ is governing the surface tension of the mixed solutions. Measurements were performed at the other $C_{12}TAB$ concentrations studied (data not shown), and for all of them we did not observe significant difference between the surface tensions of $C_{12}TAB$ and $C_{12}TAB$ + polymer solutions with the same surfactant concentration. Therefore, the studied $C_{12}TAB$ + polymer systems behave as noninteracting systems with respect to the surface tension measurements, while the polymers have still significant impact on the foaminess and foam stability for $C_{12}TAB$ solutions (see Figures 1 and 3).
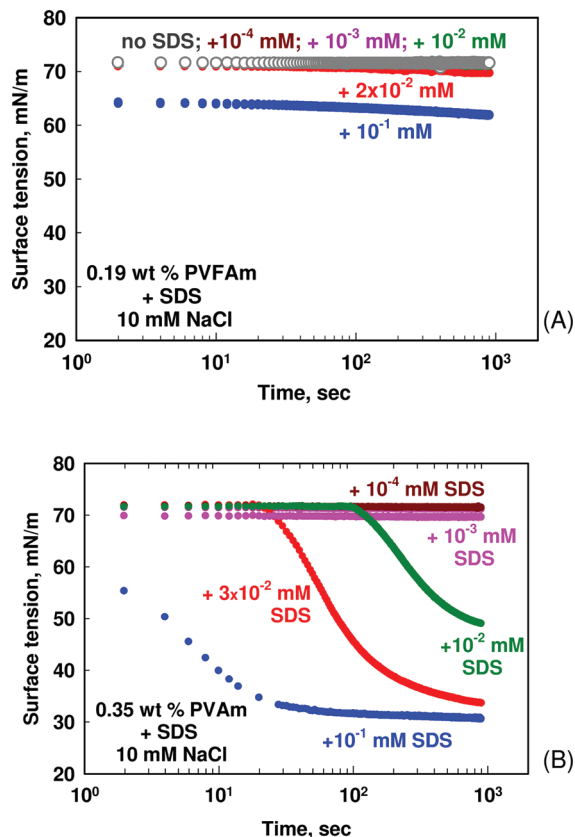
Figure 6. Surface tension as a function of time for (A) PVFAm + SDS and (B) PVAm + SDS solutions at different concentrations of SDS as indicated in the figures. All solutions contain 10 mM NaCl, and polymer concentration is 0.35 wt % for PVAm and 0.19 wt % for PVFAm.
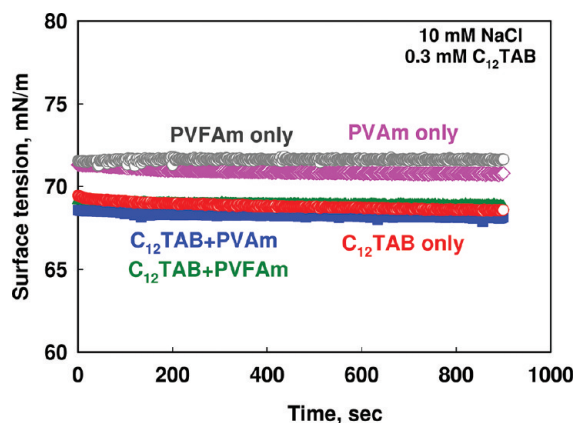
Figure 7. Surface tension as a function of time for 0.19 wt % PVFAm (gray circles), 0.35 wt % PVAm (pink diamonds), 0.3 mM C_{12}TAB (red circles), 0.3 mM C_{12}TAB + 0.35 wt % PVAm (blue squares), and 0.3 mM C_{12}TAB + 0.19 wt % PVFAm (green triangles). All solutions contain 10 mM NaCl.

A similar series of experiments was performed with $C_{12}EO_{23}$ nonionic surfactant (see Figure 8). At the lowest $C_{12}EO_{23}$
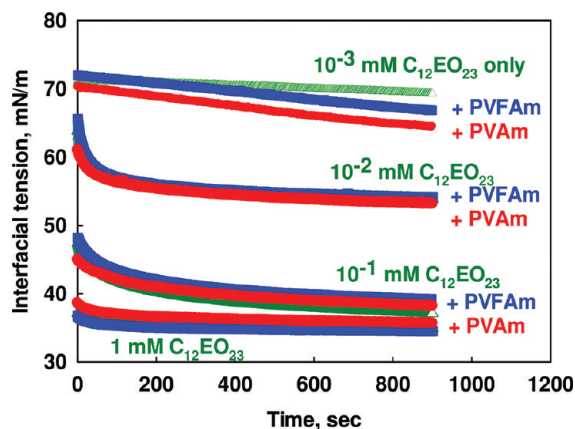

Figure 8. Surface tension as a function of time for $C_{12}EO_{23}$ (green symbols), PVFAm + $C_{12}EO_{23}$ (blue symbols), and PVAm + $C_{12}EO_{23}$ (red symbols) at different concentrations of $C_{12}EO_{23}$ as indicated in the figures. All solutions contain 10 mM NaCl and polymer concentration is 0.35 wt % for PVAm and 0.19 wt % for PVFAm.

concentration (0.001 mM), small but noticeable decrease of the surface tension for PVAm + $C_{12}EO_{23}$ solution is observed, compared to $C_{12}EO_{23}$ alone, which is probably due to formation of surface active complex at this very low surfactant concentration. However, the formation of this complex is rather slow, and it cannot affect the foamability and foam stability of the respective foams. The surface tension of the polymer-containing solutions at $C_S \geq 0.01$ mM coincides with the surface tension of the respective $C_{12}EO_{23}$ solution, which indicates that $C_{12}EO_{23}$ dominates the adsorption layer at these concentrations. However, one sees from Figure 8 that the surface tension of these solutions is well below 60 mN/m for 0.01 mM $C_{12}EO_{23}$ and even below 40 mN/m for 0.1 mM surfactant. Thus, we see that this specific surfactant is able to form dense adsorption layer at rather low concentrations (10^{-2} mM) due to its low CMC (see also the results from the foam film observations, described in section 3.3).

From these series of experiments we can conclude that the SDS + PVFAm mixture behaves as weakly interacting system

with respect to surface tension. In contrast, strong interaction is observed in SDS + PVAm solutions. No significant effect of the studied polymers on the surface tension of $C_{12}EO_{23}$ and C_{12}TAB solutions is detected for all surfactant concentrations studied. Important qualitative difference between these two surfactants is that, due to their very different CMC values, the surface tension of $C_{12}EO_{23}$ containing solutions is much lower than that of the polymer solutions (indicating that $C_{12}EO_{23}$ dominates the adsorption layers in the mixed systems), whereas the surface tension remains high in the presence of C_{12}TAB, thus indicating that the surface activity of C_{12}TAB and the polymers is comparable in these systems.

Another important conclusion from all data is that no any direct obvious correlation is observed between the surface tension, on one side, and the foamability and foam stability of the foaming solutions, on the other side.

3.2.2. Adsorption on the Solution Surface. In this series of experiments we measured by ellipsometry the adsorbed amount on the solution surface for the solutions of individual polymers, 0.1 mM SDS, and their mixture.

One sees from Figure 9 that PVFAm does not adsorb on the air−water interface in detectable quantity, in the absence of
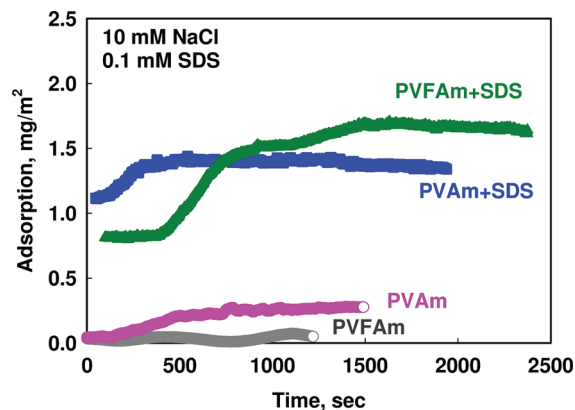

Figure 9. Adsorption as a function of time for 0.19 wt % PVFAm (gray circles), 0.35 wt % PVAm (pink diamonds), 0.1 mM SDS + 0.35 wt % PVAm (blue squares), and 0.1 mM SDS + 0.19 wt % PVFAm (green triangles). All solutions contain 10 mM NaCl.

surfactants. Slow accumulation of PVAm is observed with time and after 500 s this amount is estimated to be ≈0.2 mg/m², which corresponds to a very loose adsorption layer. These measurements confirm the claim that the studied polymers are very hydrophilic and do not adsorb strongly on solution surface. Note that the foam film observations (section 3.3) do indicate the presence of adsorbed polymer molecules, forming adsorption layers with thickness around 70 nm for PVAm and around 60 nm for PVFAm, respectively. However, these loose adsorption layers are unable to stabilize the foam films formed in the real foam tests.

The experiments with 0.1 mM SDS solutions (no polymer) also indicated no significant amount of adsorbed SDS molecules, due to the very low surfactant concentration which is around 35 times below the CMC. This result is in agreement with the surface tension measurements and with the calculated adsorption of SDS.[48] As shown in ref 48, the SDS adsorption is below 0.2 mg/m² at such low surfactant concentrations, which is in the frame of our experimental accuracy.

Experiments with PVAm + SDS and PVFAm + SDS mixed solutions showed the formation of significant adsorption layers for both systems. The measured adsorbed amounts by ellipsometry are ≈1.5 mg/m^2 for SDS + PVAm solution and ≈2.0 mg/m^2 for SDS + PVFAm solution. Experiments with foam films (section 3.3) evidence that the adsorption layers are with thickness of around 60−70 nm for both types of mixed systems. Assuming a homogeneous distribution of the adsorbed material in the adsorption layer, we would estimate a density of around 0.03 g/cm^3 average density of the adsorbed molecules, which corresponds to a very dilute layers—the respective space filling by the adsorbed molecules would be around 3 vol % (on average). One should note, however, that the surface tension decreases down to 30 mN/m for the SDS + PVAm system, whereas it remains around 65 mN/m for SDS + PVFAm. Thus, we see no simple correlation between the amount of adsorbed material and the value of the surface tension for such complex surfactant−polymer mixtures.[12]

We can conclude from these measurements that a significant amount of polymer−surfactant complexes is adsorbed on the solution surface for both SDS + PVAm and SDS + PVFAm solutions, even at low SDS concentration of 0.1 mM. However, the equilibrium surface tensions are rather different for these two mixtures, a result which indicates very different structures of the respective adsorption layers (see section 3.4 for further discussion of this point).

3.3. Foam Films Studies. In this section we describe results from the optical observations of submillimeter sized foam films, formed in a capillary cell.[40]

In the first series of experiments we studied foam films, stabilized by polymers only. In these experiments the capillary pressure, $P_C \approx 140$ Pa, was estimated using the equation[49]

$$P_C = \frac{2\sigma R_C}{R_C^2 - r_f^2 \cos \psi}$$

where R_C denotes the radius of the capillary cell, r_f is the film radius, σ is the surface tension, and ψ is the three phase contact angle film-meniscus. In our experiments, we used a capillary cell with radius $R_C = 1$ mm. The radius of the studied films was ≈150 μm. The contact angle ψ was measured to be below 0.5°. Therefore, the capillary pressure for the polymer solutions with high surface tension, $\sigma \approx 70$ mN/m, was estimated to be around 140 Pa.

At this pressure the films thinned down to their equilibrium thickness for more than 100 s, which clearly indicated the presence of adsorbed polymer molecules on the foam film surface—otherwise, the film thinning would be 2 orders of magnitude faster. An equilibrium film thickness was observed at ≈115 nm for PVFAm and ≈140 nm for PVAm (see Figure 10). The equilibrium films stabilized by PVFAm were very homogeneous in thickness, whereas the films stabilized by PVAm contained also thinner regions, appearing slightly brighter in Figure 10B. Note that the equilibrium film thickness in both polymer systems is much larger than the Debye screening length, $\kappa^{-1} \approx 3$ nm, which evidence that these films are stabilized predominantly by steric repulsion, created by loosely adsorbed polymer molecules. These foam films, stabilized by polymer molecules only, were stable for more than 10 min if their diameter was rather small, below ca. 200 μm. The larger foam films spontaneously ruptured, and the film lifetime decreased with the increase of the film diameter and/or the capillary pressure which drives the film thinning. The film
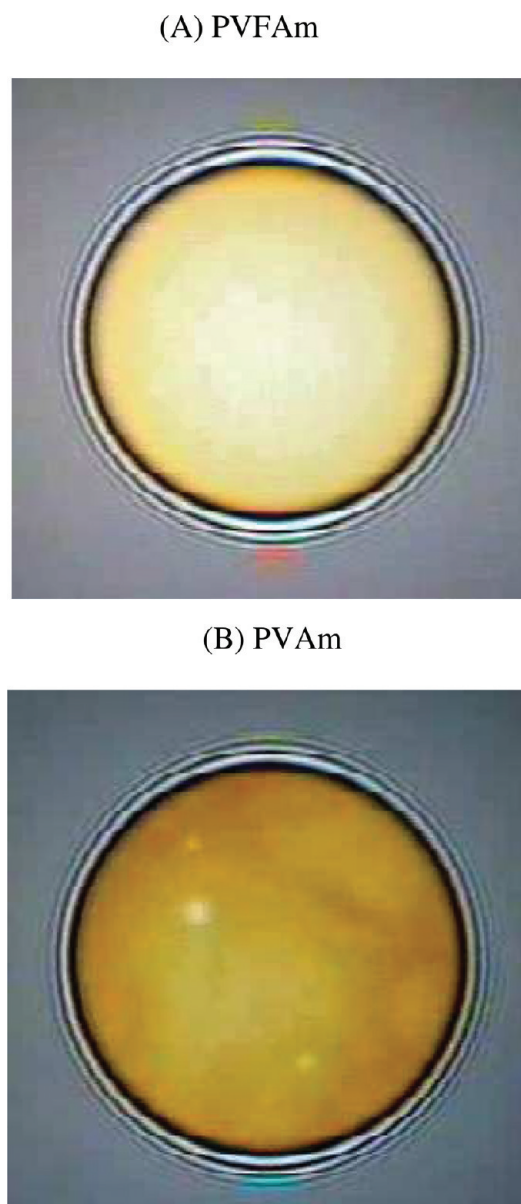
(A) PVFAm

(B) PVAm

Figure 10. Illustrative pictures of equilibrium foam films formed from (A) 0.19 wt % PVFAm and (B) 0.35 wt % PVAm at $P_C = 140$ Pa. All solutions contain 10 mM NaCl.

rupture occurred through a thinning of the central film region down to around 90 nm, when thinner dark spots with 30−40 nm thickness were suddenly formed, followed by a rapid film rupture.

The observed stability of the small foam films in the capillary cell is certainly ensured by weakly attached polymer molecules, which are not expelled from the film area during the gentle film formation in this specific experimental method. These weakly attached molecules create steric repulsion between the film surfaces (combined with electrostatic repulsion for PVAm) which is sufficient to stop the film thinning at relatively large film thickness, around 2 times larger than the thickness of the polymer adsorption layers when the capillary pressure is low. Similar observations and explanation were reported by Jean et al.[36] with foam films, formed from poly(N-isopropylacrylamide) solutions. Because the adsorption layers in our systems are very dilute (as evidenced by ellipsometry) and the polymer

adsorption is relatively slow, these polymer adsorption layers cannot stabilize the real foams in the used foam test.

The second series of experiments was performed with SDS only (no polymer), at four concentrations varied between 3×10^{-3} and 0.1 mM. This concentration range was chosen to include the transition between unstable and stable foams in the Bartsch test (see Figure 3A). The experiments showed that the foam films, formed at $C_S = 3 \times 10^{-3}$ mM, were very unstable. They thinned down to 100 nm for 5 s; afterward, a dark spot with thickness of ≈35 nm was formed inside the film, and the film ruptured around 2 s later. At $C_S = 0.01$ mM the films were also unstable—they ruptured typically around 35 s after their formation, at $h \approx 25$ nm. The increased lifetime of these films was related to the fact that the films survived the expansion of the formed dark spots and the film ruptured only when the entire film area acquired a thickness of ≈25 nm. Similar behavior was observed with the films formed from 0.03 mM SDS solution and the film lifetime was around 40 s. When 0.1 mM SDS solution was used, the films remained stable for more than 10 min at $P_C = 140$ Pa, with equilibrium thickness $h \approx 25$ nm (electrostatic stabilization). Therefore, the transition in film stability at capillary pressure of 140 Pa was in a good agreement with the transition of the foam stability for SDS solutions. Note however that the surface tension of all these solutions (including 0.1 mM SDS) was ≥69 mN/m. The latter result indicates the presence of very dilute surfactant adsorption layers on bubble surface which are still able to stabilize the foams and foam films (see section 3.4). Our results for the formation of stable foam films from very dilute SDS solutions are in agreement with results of other authors.[50]

Experiments with SDS + PVFAm solutions at 0.19 wt % polymer and four different SDS concentrations (between 0.003 and 0.1 mM SDS) were also performed. All films had relatively large thickness which increased from around 120 nm up to 140 nm (at 140 Pa capillary pressure) with the increase of SDS concentration. This large film thickness evidence that SDS does not displace PVFAm in the studied concentration range, but rather consolidates the polymer layer on the film surfaces. No significant effect of SDS on the film thinning behavior was observed—the films from SDS + PVFAm solutions behaved as films formed from solutions of PVFAm without surfactants. At higher capillary pressure, the films thinned down to 25−30 nm and ruptured.

The experiments with SDS + PVAm solutions showed that the corresponding foam films behaved rather differently from those stabilized by SDS or PVAm alone. During the initial film thinning at $P_C = 140$ Pa, the films had uneven film thickness, with the main fraction of the film area being with $h \approx 120$ nm. These films trapped surfactant−polymer aggregates, as illustrated in Figure 11. Similar phenomena were reported in the literature with cationic surfactant and anionic polymers.[33] All studied films of PVAm + SDS were stable at $P_C = 140$ Pa. The increase of capillary pressure led to further film thinning down to 30 nm, and the film stability depended on SDS concentration. The films formed at $C_{SDS} \leq 0.01$ mM were unstable when they reached the thickness of 30 nm, whereas the films formed at 0.03 and 0.1 mM SDS remained stable. Therefore, we have good agreement between the foam film stability at higher capillary pressure and the foam stability for SDS + PVAm solutions (see Figure 3A).

Experiments with 3×10^{-3} and 0.01 mM $C_{12}EO_{23}$-containing solutions were also performed. The films formed from $C_{12}EO_{23}$ solutions (without polymers) thinned very rapidly to 100 nm
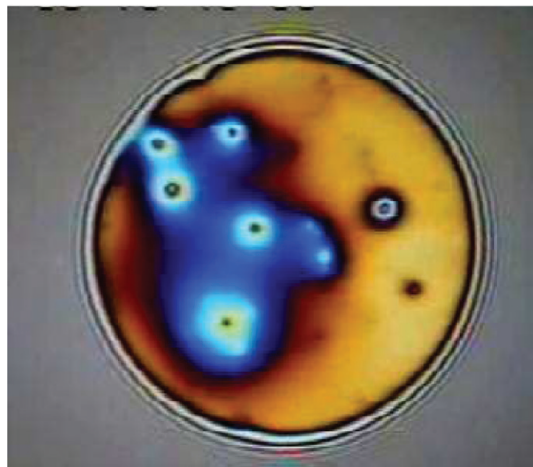
PVAm + 0.03 mM SDS

Figure 11. Illustrative picture of film formed from 0.35 wt % PVAm + 0.3 mM SDS at $P_C = 140$ Pa. All solutions contain 10 mM NaCl.

(for around 5 s); afterward, the films thinned slower for the next 30 s down to $h \approx 30$ nm and ruptured. Therefore, the films stabilized by $C_{12}EO_{23}$ were unstable at these low surfactant concentrations. The behavior of the films formed from $C_{12}EO_{23}$−PVFAm and $C_{12}EO_{23}$−PVAm solutions was different. The foam films from these mixed polymer−surfactant solutions rapidly thinned down to $h \approx 150−180$ nm and remained at this large thickness for ≈30 s. During this period, several darker spots were observed to form spontaneously in the foam films and the films ruptured soon afterward (see Figure 12A). The main qualitative difference between the mixed solutions containing PVFAm and PVAm was that the films stabilized by $C_{12}EO_{23}$−PVFAm solutions were rather homogeneous in thickness until the thin dark spots were formed (Figure 12A) while the films from $C_{12}EO_{23}$ + PVAm solution contained some aggregates and were inhomogeneous in thickness (Figure 12B).

Films formed from 0.01 or 0.1 mM $C_{12}TAB$ were also very unstable. They thinned rapidly down to 100 nm for 5 s, then to 30 nm for the next 30 s, and ruptured. These results are in a good agreement with the low stability of the respective foams, which disappeared for less than 30 s (see Figure 5). The films formed from 0.01 mM $C_{12}TAB$ + PVFAm behaved as films formed from pure polymer solution—the film drainage time and film thickness were practically the same. These films were stable at $P_C = 140$ Pa with $h \approx 120$ nm, while at higher pressure they thinned down to 30 nm and ruptured. Therefore, under these conditions, the foam film properties were controlled by the polymer while $C_{12}TAB$ had no noticeable effect on film behavior. With the increase of $C_{12}TAB$ concentration (0.1 mM), however, the situation became different—the behavior of the $C_{12}TAB$ + PVFAm stabilized films became closer to that of $C_{12}TAB$ stabilized films. The major difference was that the polymer-containing films thinned more slowly and were more stable.

The foam films, formed from $C_{12}TAB$ + PVAm, initially thinned rapidly to a thickness of around 100 nm. In the process of film thinning, dark spots were formed inside the film (see Figure 13). At 0.01 mM $C_{12}TAB$, these spots rapidly thinned down to 30 nm and the films ruptured. At the higher $C_{12}TAB$ concentration of 0.1 mM, however, these spots remained stable. At higher capillary pressure, the fraction of dark spots in the
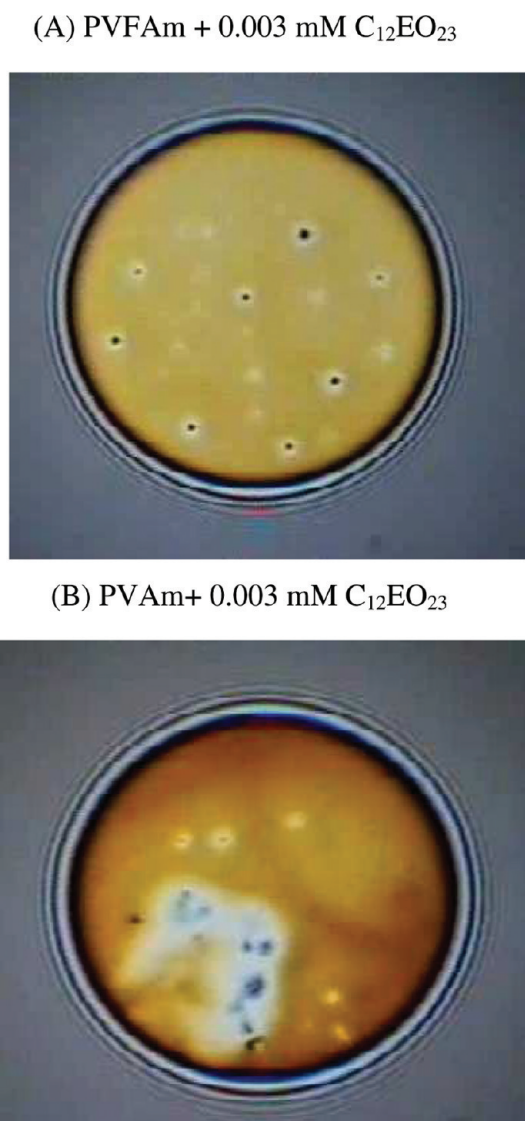
(A) PVFAm + 0.003 mM $C_{12}EO_{23}$

(B) PVAm + 0.003 mM $C_{12}EO_{23}$

Figure 12. Illustrative pictures of films formed from (A) 0.19 wt % PVFAm + 0.003 mM $C_{12}EO_{23}$ and (B) 0.35 wt % PVAm + 0.003 mM $C_{12}EO_{23}$ just before their rupture at P_C = 140 Pa. All solutions contain 10 mM NaCl.

films increased, but the foam films still remained stable. These observations are in agreement with the results from the foam tests and demonstrate a synergy between the cationic surfactant $C_{12}TAB$ and the cationic polymer PVAm. The exact molecular mechanism by which a coadsorption layer of polymer and surfactant is formed in this specific system is unclear—obviously, the strong electrostatic repulsion between the positive charges on the surfactant and polymer molecules is insufficient to prevent the formation of mixed adsorption layer, able to stabilize the foams and foam films. On the basis of the available data, we can speculate that the surfactant adsorption layer is rather dilute, so that fragments of the polymer molecules can still adsorb on the surface between the surfactant molecules, thus creating additional steric repulsion between the foam film surfaces. Alternatively, nonionized surfactant molecules in the adsorption layer could interact with nonionized monomer units in the polymer chain (the degree of ionization is below 100% in both cases), thus ensuring a weak polymer–surfactant interaction on the solution surface.

Further more detailed studies are needed to distinguish between these two possibilities.

From these experiments one can conclude the following:

Foam films with thickness >100 nm are formed from PVAm and PVFAm solutions, despite the fact that the surface tension of the respective solutions is almost the same as that of pure water. These thick films evidence for the presence of weakly adsorbed polymer molecules, forming a very dilute adsorption layer on solution surface.

At very low surfactant concentrations, the foam film behavior is dominated by the polymers, as expected. In the intermediate range of surfactant concentrations (around 10 times below the CMC) a subtle interplay between the surfactant and polymer molecules is observed, with possible formation of surfactant–polymer complexes on solution surface. The surfactants and polymers compete for participation in the adsorption layer in a complex manner—there is no direct correlation between the surface tension, adsorbed amount, film thickness, foaminess, and foam stability. One needs a combination of various methods to find the explanations of the main trends observed in the foam tests. With the further increase of surfactant concentration and approaching the CMC, the surfactant may displace the polymer molecules from the adsorption layer and dominate the surface properties.

3.4. Explanations of the Main Effects Observed in the Foam Tests. First we discuss briefly the polymer solutions (without surfactants), next we discuss the foam stabilization by SDS without polymer (below the CMC of SDS), and finally we discuss the polymer–surfactant mixtures.

Foams formed from the polymer solutions (PVFAm or PVAm) are very unstable (t_{DEF} < 10 s), which is explained with the very hydrophilic nature of these specific polymers—their molecules are weakly attached to the bubble surface, and as a consequence, their adsorption is very low (see Figures 7 and 9). Small in diameter foam films, formed in the capillary cell, could be stable under low compressing capillary pressure (100–200 Pa). Therefore, these weakly adsorbed polymer molecules are able to create steric repulsion, sufficiently strong to stabilize the foam films when the latter are gently formed in a capillary cell. However, during the rapid process of foam generation in the actual foam tests, there is no enough time for adsorption of the large polymer molecules, and as a consequence, the generated foams collapse within 10 s.

Foams formed from SDS solutions (alone) become stable at relatively low surfactant concentration, $C_S \approx 0.1$ mM, when the measured surface tension is still rather high, ≈ 69 mN/m. Using the adsorption model for ionic surfactants from ref 48, we calculated the dimensionless surface coverage by the adsorbed SDS molecules, $\theta = \Gamma / \Gamma_\infty$, to be only $\theta \approx 0.3$ for $C_S = 0.1$ mM. Thus, we see that even dilute adsorption layer of SDS is sufficient to ensure foam stability for more than 900 s in the foam tests. This appreciable foam stability is explained by a significant electrostatic repulsion between the foam film surfaces. From the adsorption model for SDS,[48] we can estimate the electric surface potential of the adsorption layer, $\Psi_S \approx 110$ mV, and the related DLVO barrier in the disjoining pressure stabilizing the foam films, $\Pi_{MAX} \approx 3$ MPa. Note that similar quantitative estimates were used in ref 51 to explain the formation of emulsions at very low SDS concentrations. At the highest SDS concentration used in the current study, 1 mM, the calculated surface coverage is ≈ 0.6 and the electrostatic surface potential is ≈ 150 mV, which ensures very good electrostatic stabilization of the formed foams, $\Pi_{MAX} \approx 4.3$ MPa. Therefore,

the observed stability of the SDS foams is explained well (semiquantitatively) by the electrostatic repulsion between the film surfaces. The other two surfactants can also stabilize the foams and foam films when their concentration is about an order of magnitude lower than CMC—C_{12}TAB via electrostatic repulsion, whereas $C_{12}EO_{23}$ via steric repulsion between the film surfaces, created by the bulky ethoxy chains of the surfactant headgroups.

The experimental results allow us to distinguish three types of surfactant–polymer mixtures (see Figure 1): The weakly interacting mixtures of SDS + PVFAm, C_{12}TAB + PVAm, and C_{12}TAB + PVFAm demonstrated both increased foaminess and enhanced foam stability. In contrast, the mixture of the strongly interacting SDS and PVAm showed a significant decrease in foaming (decreased volume of the generated foam) at increased foam stability, as compared to the solutions of SDS without polymer. The mixtures of $C_{12}EO_{23}$ with either of the studied polymers showed no any significant synergistic or antagonistic effect—the foam properties were dominated by $C_{12}EO_{23}$. These types of behavior are briefly explained below, by combining the results from the various experiments.

The observed synergy between the surfactant and polymer in the weakly interacting systems can be explained with the combination of the faster surfactant adsorption on the solution surface (which facilitates foaming) and strong steric repulsion by the surface active surfactant–polymer complex, formed in the static foams. During foaming, the surfactant molecules adsorb rapidly and, due to the Marangoni effect, decelerate the foam film thinning, thus providing longer time for polymer adsorption and foam film stabilization (see Figure 14). As evidenced with the measurements of the SDS + PVFAm solutions, the adsorption in the mixed systems could be much bigger, as compared to the adsorption from the solutions of the individual components, which shows the formation of surface active surfactant–polymer complex. The latter is particularly efficient in stabilizing the foam films. Note that the formation of such a complex does not require a significant reduction of the surface tension of the mixed solutions—the most sensitive method to visualize the presence of polymers on the solution surface was the foam film observation.

The behavior of the PVAm + SDS solutions is different with respect to foaming, due to the strong electrostatic attraction between these oppositely charged molecules in the bulk solution. The formation of bulk surfactant–polymer complexes reduces the concentration of free SDS monomers in the mixed solutions and thus leads to lower foamability of the mixed PVAm + SDS solutions (compared to SDS or SDS + PVFAm solutions) (see Figure 14C). Under static conditions, however, the formed foams remain very stable, due to the formation of surface active complexes which create strong steric repulsion between the foam film surfaces (Figure 14D). Thus, the strongly interacting system of oppositely charged surfactant and polymer increases the foam stability due to formation of surface complexes between surfactant and polymer molecules (evidenced by the low surface tension) but decreases the solution foaminess due to the formation of strong bulk complexes of the same molecules.

The nonionic surfactant $C_{12}EO_{23}$ behaved differently from the ionic once—no significant effect of the polymers was observed for the solutions of this surfactant. The obtained results allow us to conclude that this difference in the behavior is due mostly to the much lower CMC of this surfactant. Even at very low bulk concentration of 10^{-2} mM, this surfactant
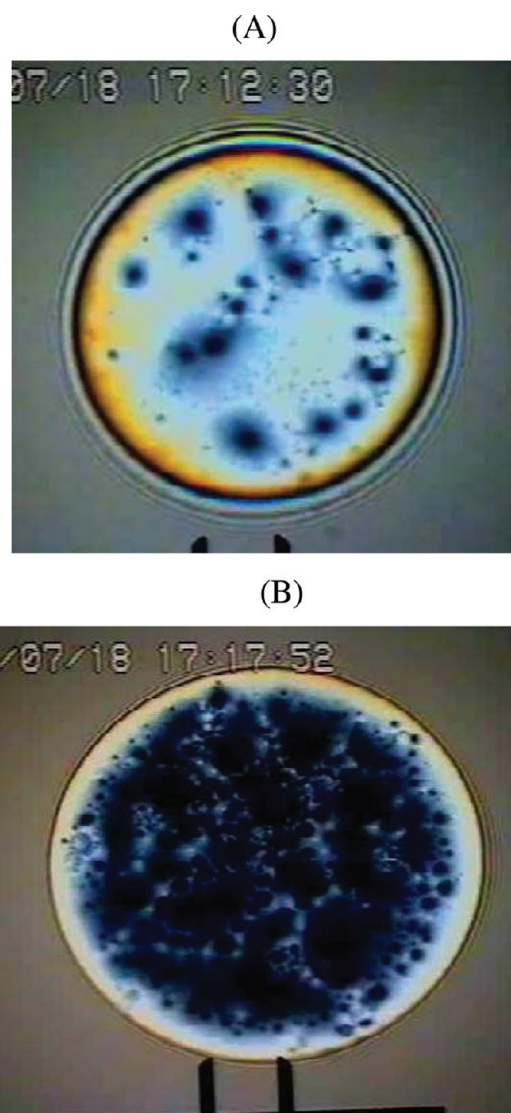
(A)

(B)

Figure 13. Illustrative pictures of film formed from 0.35 wt % PVAm + 0.1 mM C_{12}TAB solution at (A) P_C = 140 Pa and (B) $P_C \approx 10^5$ Pa. Solution contains 10 mM NaCl.

dominates the surface adsorption layer, and the polymer is weakly attached to the surfactant monolayer (Figure 15). As a result, the foam film behavior, foaming, and foam stability are dominated by the adsorbed surfactant molecules.

Let us compare the different studied surfactants at concentration of 0.1 mM, where strong synergy between SDS and the studied polymers is observed (see Figures 1A and 3B), no synergy was detected for $C_{12}EO_{23}$ (see Figures 1B and 4), and noticeable synergy for DTAB and the polymers was seen (Figures 1C and 5).

The absence of any synergy between $C_{12}EO_{23}$ and the studied polymers is in agreement with the measured surface tensions, which were the same for $C_{12}EO_{23}$ and $C_{12}EO_{23}$ + polymer solutions (see Figure 8). At this surfactant concentration, the surface tension of $C_{12}EO_{23}$ solution is $\sigma \approx$ 39 mN/m, which indicates that an almost complete adsorption layer is formed (for the complete adsorption layer we measured $\sigma \approx$ 37 mN/m at CMC). Therefore, even without polymer, this surfactant is able to form almost complete adsorption layer at this low concentration, due to its very low CMC. On the other hand, the other studied surfactants, SDS and DTAB, gave
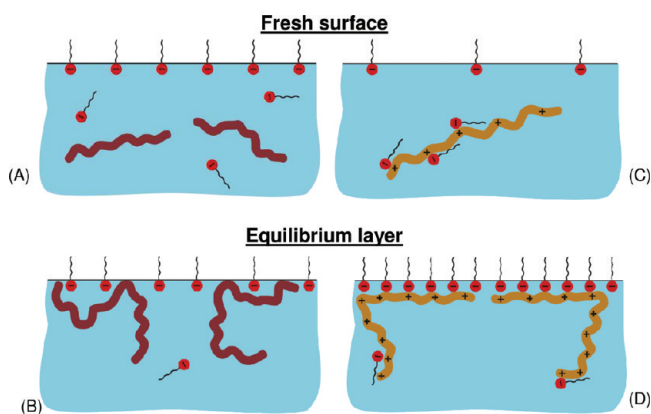
Figure 14. Schematic presentation of the adsorption layers formed in the process of foam formation in the cases of (A, B) weakly interacting surfactant and polymer and (C, D) oppositely charged, strongly interacting surfactant and polymer. (A) and (C) show the adsorption layers soon after surface formation—less surfactant is adsorbed on the surface in (C) because the surfactant molecules are bound to the polymer chains in the bulk solution. (B) and (D) illustrate schematically the different structures of the equilibrium adsorption layers—denser adsorption layer is formed in the strongly interacting system, as evidenced by the lower surface tension of the solution.

surface tensions of 66 and 68 mN/m, respectively, at 0.1 mM concentration. These surface tensions are well above the surface tensions of complete adsorption layers for these surfactants, which are $\sigma \approx 37$ mN/m. This means that DTAB and SDS form loose adsorption layers at 0.1 mM, which cannot stabilize the foam films between the bubbles in the foam. As a consequence, the polymer adsorption over the surfactant layer or the formation of mixed adsorption layers leads to significant effect of the polymers on the foamability and foam stability of SDS and DTAB containing solutions.

4. SUMMARY OF THE MAIN RESULTS AND CONCLUSIONS

Systematic series of experiments with three surfactants (anionic SDS, nonionic $C_{12}EO_{23}$, and cationic $C_{12}TAB$) and two polymers (cationic PVAm and nonionic PVFAm) were performed, with the aim to compare and explain the foamability and foam stability for the various mixed systems. The surfactant concentration was varied between 10^{-4} and 1 mM, at fixed polymer concentration of 0.35 wt % PVAm and 0.19 wt % PVFAm.

The main conclusions from the obtained results can be summarized as follows:

- With respect to foaming and foam stability, three types of surfactant−polymer mixtures were distinguished (Figure 1). The mixture of strongly interacting anionic surfactant SDS and cationic polymer PVAm showed a significant decrease in foaming at increased foam stability (as compared to the solutions of SDS without polymer). The weakly interacting mixtures (SDS + PVFAm, $C_{12}TAB$ + PVAm, and $C_{12}TAB$ + PVFAm) showed both increased foaminess and enhanced foam stability. The mixtures of $C_{12}EO_{23}$ with any of the studied polymers showed no any significant synergistic or antagonistic effect—the foam properties were dominated by $C_{12}EO_{23}$, despite its lower weight concentration in the solutions.
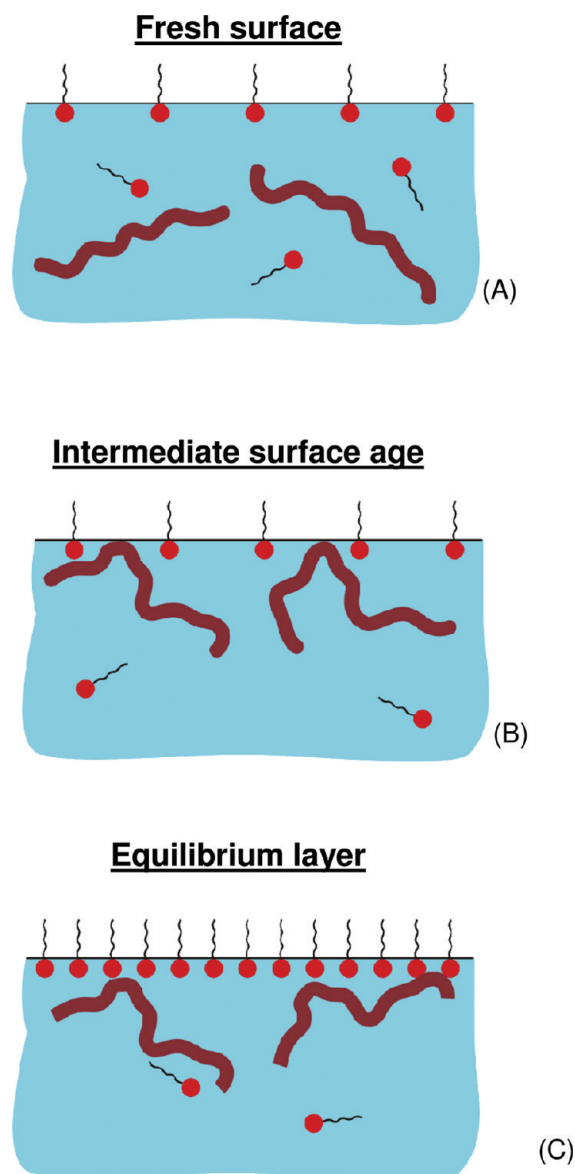- The lower foamability in the strongly interacting system SDS + PVAm is explained with the decreased

Figure 15. Schematic presentation of the adsorption layers formed in the case of weakly interacting surfactant with low CMC ($C_{12}EO_{23}$). Although the polymer could coadsorb at intermediate surface age, as shown in (B), the equilibrium adsorption layer contains surfactant mostly and the polymer is weakly attached to the surfactant monolayer.

concentration of free SDS monomers (due to their binding to the polymer chains). The higher foam stability is due to the formation of dense surfactant−polymer layer on the solution surface, as evidenced by ellipsometry and the strongly reduced surface tension (Figure 6B).

- The observed synergy between the surfactant and polymer in the weakly interacting systems is explained with the combination of fast surfactant adsorption on the solution surface (which facilitates foaming) and strong steric repulsion by the surface active surfactant−polymer complex, formed in the static foams.
- The lack of any significant effect of the polymers in the $C_{12}EO_{23}$ solutions is explained by the low CMC of this surfactant. Even at very low bulk concentration of 10^{-2} mM, this surfactant dominates the surface adsorption

layer and the polymer is weakly attached to the surfactant monolayer.

- The studied polymers are rather hydrophilic, and in the absence of surfactant, they adsorb very weakly on the solution surface and do not affect significantly the solution surface tension ($\sigma \approx 71$ mN/m). These features lead to poor foaminess and very low foam stability for the solutions containing polymers only (defoaming time <10 s).

- With respect to the individual surfactants, the transitional concentrations, above which the foams become stable, were found to be 10−30 times below the CMC, which is explained by a significant electrostatic repulsion in the foam films stabilized by the ionic surfactants, such as SDS (despite the very high surface tension $\sigma \approx 69$ mN/m and low surface coverage $\theta \approx 0.3$ at the transitional concentration) and by steric repulsion for $C_{12}EO_{23}$ stabilized foams.

Several nontrivial effects of the surfactant−polymer interactions on the foaminess and foam stability deserve to be emphasized. For example, the increased foaminess and foam stability of the mixture of cationic surfactant and cationic polymer ($C_{12}TAB$ + PVAm) and the strongly reduced foaminess of the mixture of anionic surfactant with cationic polymer are effects which were clearly demonstrated. Neither of these effects could be predicted on the basis of simply considering the changes in the surface tension (dynamic or equilibrium) or in the total amount of adsorbed species on the solution surface. Therefore, a combination of several complementary methods was needed to explain the observed foam behavior, while the simple correlations, often used in the studies of surfactant−polymer mixtures, were found to be insufficient.

■ AUTHOR INFORMATION

Corresponding Author
*Ph: (+359-2) 962 5310; Fax: (+359-2) 962 5643; e-mail: sc@lcpe.uni-sofia.bg.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; *Application of Surfactants with Polymers and Proteins*; CRC Press: Boca Raton, FL, 1993.

(2) Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; *Application of Polymer-Surfactant Systems*; Surfactant Science Series Vol. 77; Marcel Dekker: New York, 1998.

(3) Hansson, P. Interaction between polyelectrolyte gels and surfactants of opposite charge. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 351.

(4) Langevin, D. Complexation of oppositely charged polyelectrolytes and surfactants in aqueous solutions. A review. *Adv. Colloid Interface Sci.* **2009**, *147−148*, 170.

(5) Hansson, P.; Almgren, M. Interaction of Alkyltrimethylammonium Surfactants with Polyacrylate and Poly(styrenesulfonate) in Aqueous Solution: Phase Behavior and Surfactant Aggregation Numbers. *Langmuir* **1994**, *10*, 2115.

(6) Anthony, O.; Zana, R. Interactions between Water-Soluble Polymers and Surfactants: Effect of the Polymer Hydrophobicity. 1. Hydrophilic Polyelectrolytes. *Langmuir* **1996**, *12*, 1967.

(7) Mezei, A.; Meszaros, R. Novel Method for the Estimation of the Binding Isotherms of Ionic Surfactants on Oppositely Charged Polyelectrolytes. *Langmuir* **2006**, *22*, 7148.

(8) Bain, C. D.; Claesson, P. M.; Langevin, D.; Meszaros, R.; Nylander, T.; Stubenrauch, C.; Titmuss, S. Complexes of surfactants with oppositely charged polymers at surfaces and in bulk. *Adv. Colloid Interface Sci.* **2010**, *155*, 32.

(9) Üzüm, C.; Kristen, N.; Von Klitzing, R. Polyelectrolytes in thin liquid films. *Curr. Opin. Colloid Interface Sci.* **2010**, *15*, 303.

(10) Zhang, X. L.; Taylor, D. J. F.; Thomas, R. K; Penfold, J. Adsorption of polyelectrolyte/surfactant mixtures at the air-water interface: Modified poly(ethyleneimine) and sodium dodecyl sulfate. *Langmuir* **2011**, *27*, 2601.

(11) Langevin, D.; Monroy, F. Interfacial rheology of polyelectrolytes and polymer monolayers at the air−water interface. *Curr. Opin. Colloid Interface Sci.* **2010**, *15*, 283.

(12) Taylor, D. J. F.; Thomas, R. K.; Penfold, J. Polymer/surfactant interactions at the air/water interface. *Adv. Colloid Interface Sci.* **2007**, *132*, 69.

(13) Penfold, J.; Thomas, R. K.; Taylor, D. J. F. Polyelectrolyte/surfactant mixtures at the air-solution interface. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 337.

(14) Nylander, T.; Samoshina, Y.; Lindman, B. Formation of polyelectrolyte-surfactant complexes on surfaces. *Adv. Colloid Interface Sci.* **2006**, *123−126*, 105.

(15) Rao, A.; Kim, J.; Thomas, R. Interfacial rheological studies of gelatin-sodium doedecyl sulfate complexes adsorbed at the air-water interface. *Langmuir* **2005**, *21*, 617.

(16) Monteux, C.; Liauro, M.-F.; Baigl, D.; Williams, C. E.; Anthony, O.; Bergeron, V. Interfacial microgels formed by oppositely charged polyelectrolytes and surfactants. 1. Influence of polyelectrolyte molecular weight. *Langmuir* **2004**, *20*, 5358.

(17) Monteux, C.; Williams, C. E.; Bergeron, V. Interfacial microgels formed by oppositely charged polyelectrolytes and surfactants. 1. Influence of surfactant chain length and surfactant/polymer ratio. *Langmuir* **2004**, *20*, 5367.

(18) Monteux, C.; Fuller, G. G.; Bergeron, V. Shear and dilational surface rheology of oppositely charged polyelectrolyte/surfactant microgels adsorbed at the air-water interface. Influence on foam stability. *J. Phys. Chem. B* **2004**, *108*, 16473.

(19) Jones, M. The interaction of sodium dodecyl sulfate with polyethylene oxide. *J. Colloid Interface Sci.* **1967**, *23*, 36.

(20) Staples, E.; Tucker, I.; Penfold, J.; Warren, N.; Thomas, R. K.; Taylor, D. J. F. Organization of Polymer−Surfactant Mixtures at the Air−Water Interface: Sodium Dodecyl Sulfate and Poly(dimethyldiallylammonium chloride). *Langmuir* **2002**, *18*, 5139.

(21) Klitzing, R. Effect of interface modification on forces in foam films and wetting films. *Adv. Colloid Interface Sci.* **2005**, *114−115*, 253.

(22) Noskov, B. A.; Loglio, G.; Miller, R. Dilational surface viscoelasticity of polyelectrolyte/surfactant solutions: Formation of heterogeneous adsorption layers. *Adv. Colloid Interface Sci.* **2011**, *168*, 179.

(23) Noskov, B. A. Dilational surface rheology of polymer and polymer/surfactant solutions. *Curr. Opin. Colloid Interface Sci.* **2010**, *15*, 229.

(24) Noskov, B. A.; Grigoriev, D. O.; Lin, S.-Y.; Loglio, G.; Miller, R. Dynamic surface properties of polyelectrolyte/surfactant adsorption films at the air/water interface: Poly(diallyldimethylammonium chloride) and sodium dodecylsulfate. *Langmuir* **2007**, *23*, 9641.

(25) Klebanau, A.; Kliabanova, N.; Ortega, F.; Monroy, F.; Rubio, R. G.; Starov, V. Equilibrium behavior and dilational rheology of polyelectrolyte/insoluble surfactant adsorption films: Didodecyldimethylammonium bromide and sodium poly(styrenesulfonate). *J. Phys. Chem. B* **2005**, *109*, 18316.

(26) Díez-Pascual, A. M.; Compostizo, A.; Crespo-Colín, A.; Rubio, R. G.; Miller, R. Adsorption of water-soluble polymers with surfactant character. Adsorption kinetics and equilibrium properties. *J. Colloid Interface Sci.* **2007**, *307*, 398.

(27) Díez-Pascual, A. M.; Monroy, F.; Ortega, F.; Rubio, R. G.; Miller, R.; Noskov, B. A. Adsorption of water-soluble polymers with surfactant character. Dilational viscoelasticity. *Langmuir* **2007**, *23*, 3802.

(28) Noskov, B. A.; Loglio, G.; Miller, R. Dilational viscoelasticity of polyelectolyte/surfactant adsorption films at the air/water interface: Dodecyltrimethylammonium bromide and sodium poly (styrenesulfonate). *J. Phys. Chem. B* **2004**, *108*, 18615.

(29) Campbell, R. A.; Yanez Arteta, M.; Angus-Smyth, A.; Nylander, T.; Varga, I. Effects of bulk colloidal stability on adsorption layers of poly(diallyldimethylammonium chloride)/sodium dodecyl sulfate at the air-water interface studied by neutron reflectometry. *J. Phys. Chem. B* **2011**, *115*, 15202.

(30) Regismond, S. T. A. K.; Gracie, D.; Winnik, F. M.; Goddard, E. D. Polymer/Surfactant Complexes at the Air/Water Interface Detected by a Simple Measure of Surface Viscoelasticity. *Langmuir* **1997**, *13*, 5558.

(31) Regismond, S. T. A.; Winnik, F. M.; Goddard, E. D. Surface viscoelasticity in mixed polycation anionic surfactant systems studied by a simple test. *Colloids Surf., A* **1996**, *119*, 221.

(32) Kristen, N.; Simulescu, V.; Vullings, A.; Laschewsky, A.; Miller, R.; Klitzing, R. No Charge Reversal at Foam Film Surfaces after Addition of Oppositely Charged Polyelectrolytes? *J. Phys. Chem. B* **2009**, *113*, 7986.

(33) Bergeron, V.; Langevin, D.; Asnacios, A. Thin-Film Forces in Foam Films Containing Anionic Polyelectrolyte and Charged Surfactants. *Langmuir* **1996**, *12*, 1550.

(34) Kolaric, B.; Jaeger, W.; Hedicke, G.; Klitzing, R. Tuning of Foam Film Thickness by Different (Poly)electrolyte/Surfactant Combinations. *J. Phys. Chem. B* **2003**, *107*, 8152.

(35) Kristen, N.; Klitzing, R. Effect of polyelectrolyte/surfactant combinations on the stability of foam films. *Soft Matter* **2010**, *6*, 849.

(36) Jean, B.; Lee, L.-T.; Cabane, B.; Bergeron, V. Foam Films from Thermosensitive PNIPAM and SDS Solutions. *Langmuir* **2009**, *25*, 3966.

(37) Hong, J.; Pelton, R. The surface tension of aqueous polyvinylamine and copolymers with N-vinylformamide. *Colloid Polym. Sci.* **2002**, *280*, 203.

(38) Mezei, A.; Pojjak, K.; Meszaros, R. Nonequilibrium Features of the Association between Poly(vinylamine) and Sodium Dodecyl Sulfate: The Validity of the Colloid Dispersion Concept. *J. Phys. Chem. B* **2008**, *112*, 9693.

(39) Denkov, N. D. Mechanisms of foam destruction by oil-based antifoams. *Langmuir* **2004**, *20*, 9463.

(40) Scheludko, A. Thin liquid films. *Adv. Colloid Interface Sci.* **1967**, *1*, 391.

(41) Kralchevsky, P. A.; Nagayama, K. *Particles at Fluid Interfaces and Membranes: Attachment of Colloid Particles and Proteins to Interfaces and Formation of Two-Dimensional Arrays*; Elsevier: Amsterdam, 2001.

(42) Russev, S. C.; Argirov, T. V. Rotating analyzer-fixed analyzer ellipsometer based on null type ellipsometer. *Rev. Sci. Instrum.* **1999**, *70*, 3077.

(43) Russev, S. C.; Arguirov, Tz. V.; Gurkov., T. D. β-casein adsorption kinetics on air-water and oil-water interfaces studied by ellipsometry. *Colloids Surf., B* **2000**, *19*, 89.

(44) Gurkov, T. D.; Russev, S. C.; Danov, K. D.; Ivanov, I. B.; Campbell, B. Monolayers of globular proteins on air/water interfaces: Applicability of the Volmer equation of state. *Langmuir* **2003**, *19*, 7362.

(45) Tajima, K.; Muramatsu, M.; Sasaki, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1991.

(46) Tajima, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3063.

(47) Tajima, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1767.

(48) Kolev, V. L.; Danov, K. D.; Kralchevsky, P. A.; Broze, G.; Mehreteab, A. Comparison of the van der Waals and Frumkin adsorption isotherms for sodium dodecyl sulfate at various salt concentrations. *Langmuir* **2002**, *18*, 9106.

(49) Toshev, B. V.; Ivanov, I. B. *Colloid Polym. Sci.* **1975**, *253*, 558.

(50) Exerowa, D.; Kruglyakov, P. M. *Foams and Foam Films: Theory, Experiment, Application*; Elsevier: Amsterdam, 1998.

(51) Tcholakova, S.; Denkov, N. D.; Danner, T. Role of surfactant type and concentration for the mean drop size during emulsification in turbulent flow. *Langmuir* **2004**, *20*, 7444.