

# Role of polymer–surfactant interactions in foams: Effects of pH and surfactant head group for cationic polyvinylamine and anionic surfactants

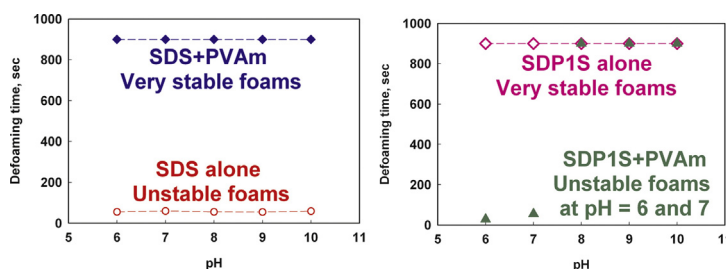
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## HIGHLIGHTS

- Effect of cationic polymer on foaming properties of SDS and SDP1S is studied.
- Effect of polymer depends significantly on the head group of anionic surfactant.
- The stability of SDS + polymer foams is much higher than the stability of SDS foams.
- The stability of SDP1S + polymer foams is lower, compared to SDP1S foams.
- Stronger complex SDP1S + polymer is formed in the bulk, as compared to SDS + polymer.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In a previous study (Langmuir, 28 (2012) 4996) we showed that the foamability of mixed solutions of the cationic polymer polyvinylamine (PVAm) and the anionic surfactant sodium dodecyl sulphate (SDS) is strongly reduced, whereas the stability of the formed foams is strongly enhanced, as compared to the solutions of SDS alone. Here we study in more detail the foaming properties of mixed solutions of PVAm with anionic surfactants. The effect of surfactant head group is studied by comparing SDS with another anionic surfactant (sodium dodecyl oxyethylene sulphate, SDP1S) which contains an additional ethoxy fragment in the charged head-group. For changing the electrostatic polymer–surfactant interactions, we varied pH between 6 and 10, thus crossing the polymer  $pK_a \approx 8.6$ . The foam tests showed that the foamability of all mixed solutions is strongly reduced in the entire range of pH values studied. The negative effect of PVAm on solution foamability is highest at low pH, where the polymer charge density is the highest. Model experiments revealed that the reduced foamability is due to prolonged lag-time for formation of mixed adsorption layer on bubble surfaces. Surprisingly, we found that the stability of SDP1S foams is also reduced strongly by PVAm at pH 6 (contrary to SDS and to conventional understanding). The obtained results indicate that the ethoxy group in SDP1S enhances the surfactant association with the polymer molecules, thus decreasing the concentration of free surfactant monomers, necessary to adsorb on the solution surface for foam stabilization during foaming and immediately after it. These results clearly demonstrate that excessively strong polymer–surfactant interactions could be a problem in the formation and stabilization of foams from mixed solutions. Moreover, the effect of cationic polymers on the foaming properties of anionic surfactants could depend significantly on the specific head group of the surfactant.

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## 1. Introduction

Polymer–surfactant mixtures are widely used for controlling the colloid stability and rheological properties of complex disperse systems in many practical applications, such as the paper industry, and in food, pharmaceutical, home and personal care products [1,2]. Due to their wide-spread usage and complex physico-chemical properties, these systems have attracted the attention of researchers and they are subject of numerous studies, aimed at revealing the role of the surfactant–polymer interactions, both in the bulk and on the solution surface, for the overall system behavior [1–38].

In the course of these studies, the researcher have distinguished between strongly interacting systems (surfactants and polymers with opposite charges) and weakly interacting systems (usually comprising neutral polymer and charged surfactant) [12]. Numerous studies have focused on the structure and composition of the mixed adsorption layers [7–8,10,12–15,22–31] and the thinning behavior of the respective foam films [9,17–18,21,32–36]. It was demonstrated that surface active polymer–surfactant complexes are able to stabilize the foam films at relatively large film thickness, even at very low surfactant and polymer concentrations (where each of the individual components is unable to stabilize the foam films). Therefore, the common understanding is that the strong surfactant–polymer interactions are important to obtain stable foams from the mixed solutions. The specific mechanisms of foam films stabilization are still under debate in literature [9]. The stability of the foam films was shown to have no direct correlation with the surface tension or surface elasticity of the solutions (as claimed in some earlier studies) [32]. Therefore, combined electrostatic-steric repulsion is usually considered as governing the stability of such mixed systems [32]. At high surfactant concentrations, polymer–surfactant aggregates are often trapped in the foam films, which might additionally stabilize the films [33]. The main results about the behaviour and stability of foam films are summarized in Refs. [4,9].

Despite the practical importance of the foams formed from such mixed solutions, there are a very limited number of studies focused on the foamability and foam stability with these systems. In our recent study [39] we combined foam tests and model experiments (optical observations of foam films, ellipsometry, and surface tension measurements) to evaluate the foamability and foam stability for several polymer–surfactant mixtures, and to explain the observed trends. Different types of surfactants (cationic, anionic and nonionic) and polymers (nonionic and cationic) were studied to clarify the factors governing the foamability and foam stability of the mixed systems. Highly hydrophilic cationic and nonionic polymers, polyvinylamine (PVAm) and polyvinylformamide (PVFam) were used.

Our experiments [39] revealed two rather unexpected trends which could not be predicted from foam film studies only. First, the experiments showed that most of the mixed solutions, including those of cationic polymer and cationic surfactant, and nonionic polymer and anionic or cationic surfactant, may show enhanced foamability and foam stability under appropriate conditions. Therefore, no strong surfactant–polymer interactions are needed for observing synergistic effects in such mixtures. Furthermore, the foam tests showed clearly that the foamability of the solutions was strongly reduced when the oppositely charged anionic surfactant SDS and cationic polymer PVAm were mixed, whereas the foam stability was enhanced, as compared to the individual components. The reduced foamability was explained with the slower formation of the adsorption layers on the bubble surface, due to the strong association of the two components in the bulk solution (thus reducing the adsorption rate).

The major aim of the current study is to clarify in more detail the role of the electrostatic interactions, and the mechanisms behind the observed trends, in such strongly interacting polymer–surfactant mixtures. The effects of surfactant head group and of polymer charge density on the foamability and foam stability were studied. Two anionic surfactants were studied – sodium dodecyl sulphate (SDS) and sodium dodecyloxyethylene sulphate (SDP1S). The same cationic polymer PVAm was used, and pH was varied between 6 and 10 to modify the charge density of the polymer molecules. Along with the foam tests, we studied the thickness and the stability of the respective foam films. The surface tension was measured and, for the most interesting systems, the surface rheological properties were determined.

The paper is organized as follows. The used methods and materials are described in Section 2. Section 3.1 presents experimental results from the foam tests. The results from the model experiments are described in Sections 3.2–3.3. The mechanisms of foam stabilization are discussed in Section 3.4. The main conclusions are summarized in Section 4.

## 2. Materials and methods

### 2.1. Materials

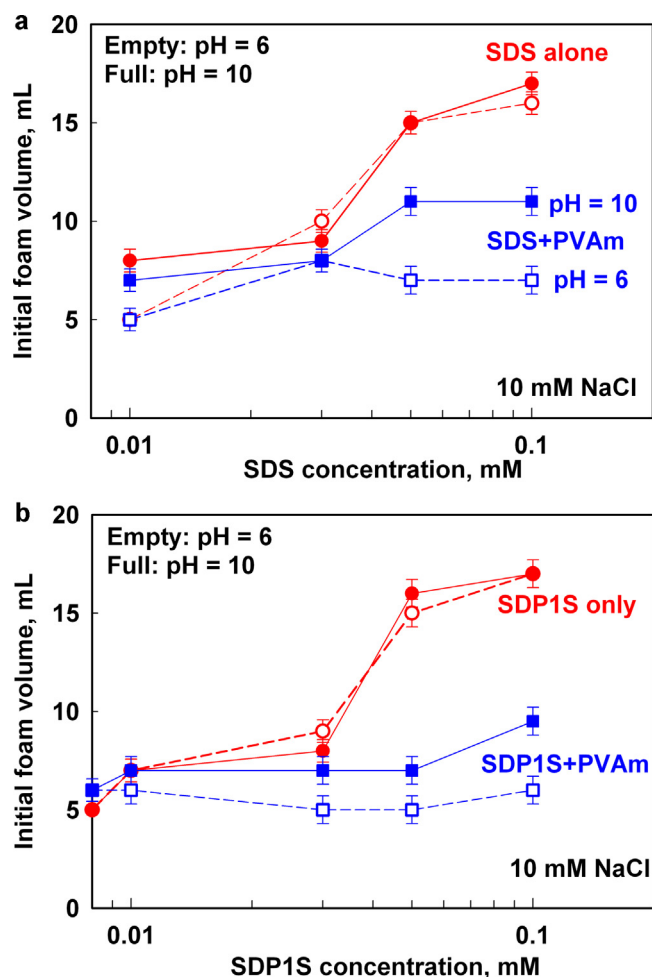
The cationic polyvinylamine (PVAm) was product of BASF. According to its producer, the used PVAm consists of 95 % vinylamine and 5 % vinylformamide. The pKa value for the polyvinylamine is around 8.6 [37,38], which means that this is a highly charged polymer at pH 6. The molecular mass of PVAm was determined by static light scattering to be around  $4.5 \times 10^4$ .

As low-molecular-mass surfactants we used two anionic surfactants, which have similar chain length and differ in their head groups – sodium dodecylsulfate (SDS, product of Acros) and sodium dodecyloxyethylenesulfate with one ethoxy group, SDP1S (product of STEPAN Co., with commercial name STEOL CS-170). According to its producer, SDP1S contains 68–72 wt% sodium alkyl (C10–16) ether sulfate, 24–32 wt% water and less than 2.5 wt% C12–14 ethoxylated alcohols. The CMC values of these surfactants are  $\approx 3.5$  mM for SDS and  $\approx 0.25$  mM for SDP1S (determined from surface tension isotherms at 10 mM NaCl). The used SDS sample did not show minimum in the surface tension isotherm – therefore, it does not contain dodecanol as a contaminant.

The two surfactants and the polymer were used as received. The aqueous solutions were prepared with deionized water, purified by Milli-Q Organex system (Millipore). All solutions contained 10 mM NaCl as background electrolyte.

To prepare mixed surfactant–polymer solutions we first prepared separate stock solutions with doubled concentrations of surfactant and polymer. Afterwards, by mixing these stock solutions (1:1 by weight) we obtained the final working solutions with the desired concentrations of the two components. The stock solution of the polymer was prepared by the following procedure: 0.7 wt% of PVAm was added to 10 mM NaCl solution and stirred at 35 °C for 1 h with a magnetic stirrer.

Therefore, the PVAm concentration in the solutions used for the actual experiments was fixed at 0.35 wt %, corresponding to 0.078 mM polymer molecules and to approx. 80 mM of monomer units, included in these polymer molecules. The surfactant concentration was varied between 0.01 and 0.1 mM, because this is the range where the foam becomes stable in these mixed systems. The polymer concentration was chosen to be well in excess to the used surfactant, in order to avoid the possible replacement of the polymer molecules on the solution surface by competitively adsorbing surfactant (an effect which is beyond the scope of the current study). pH of the mixed solutions was adjusted just before the



**Fig. 1.** Initial foam volume,  $V_0$ , as a function of surfactant concentration for (A) SDS and (B) SDP1S-containing foams, formed from solutions of surfactant alone (red circles) or surfactant + PVAm (blue squares), at pH 6 (empty symbols) and pH 10 (full symbols). All solutions contain 10 mM NaCl and 0.35 wt% PVAm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

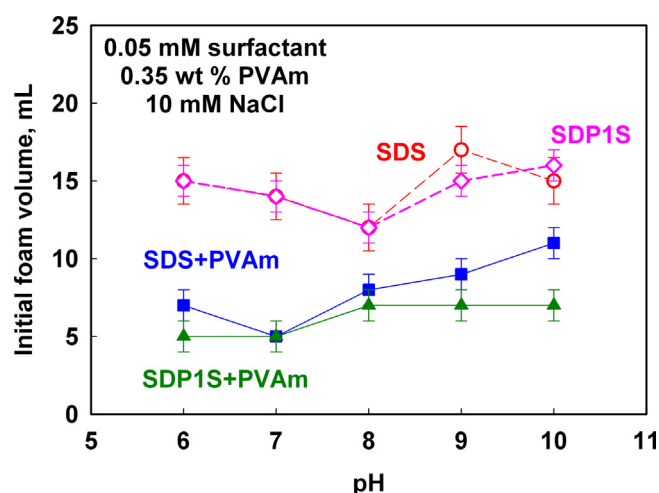
actual experiments with 0.06 or 0.25 M HCl solution (Merck, Cat.N 1.00318), or with 3 M NaOH (Sigma, Cat.N 82730). As explained in Section 3.4 below, the positively charged polymer groups were in a large excess to the anionic surfactants in the entire range of surfactant concentrations and pH values studied.

## 2.2. Experimental methods

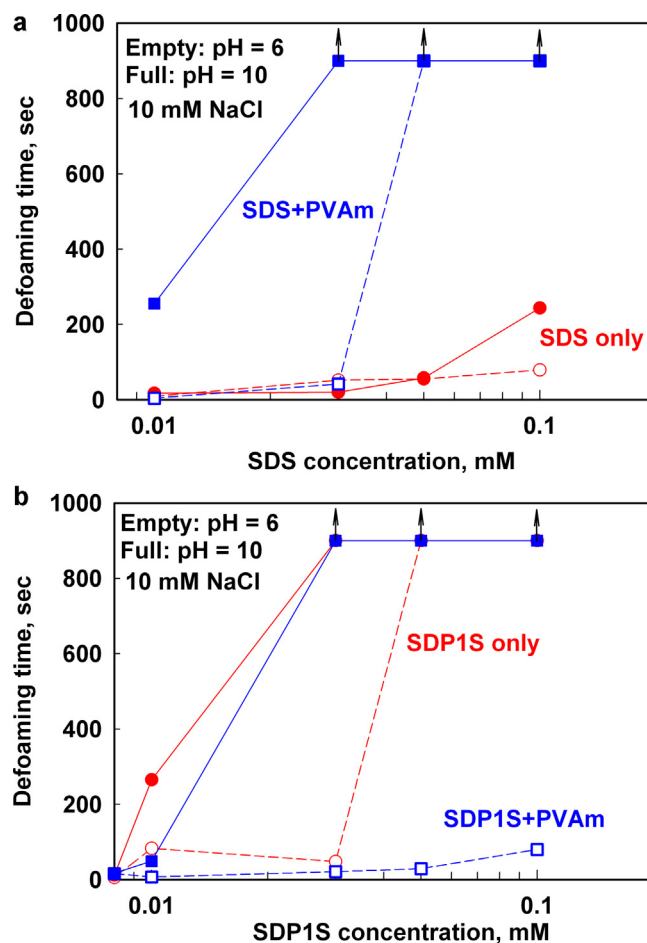
### 2.2.1. Foam test

To compare the foamability and foam stability of the studied solutions, 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, ten standard hand-shakes of the cylinder were applied. The initial foam volume and the subsequent foam decay were monitored during the following 15 min.

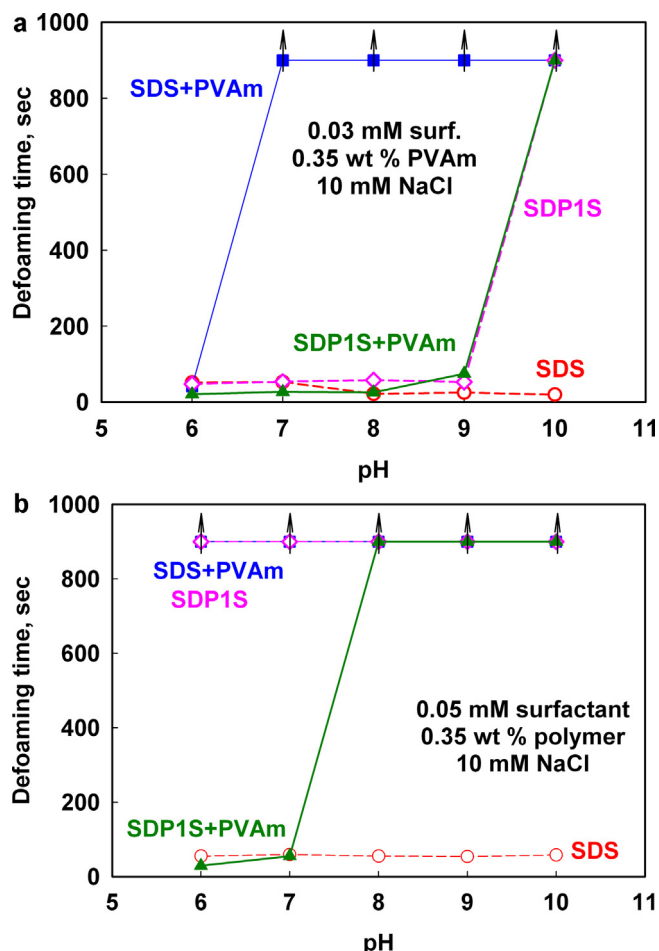
The solution foamability was characterized by the volume of trapped air,  $V_0$ , immediately after shaking (at  $t = 0$ ), while the foam stability was characterized by the defoaming time,  $t_{DEF}$ , which is defined as a time required for obtaining half of the solution surface free of bubbles. The experimental results for  $V_0$  and  $t_{DEF}$  were determined from (at least) three consecutive measurements. The symbols shown in Fig. 1–4 represent the average values from these measurements and the error bars in Figs. 1 and 2 represent the



**Fig. 2.** Initial volume,  $V_0$ , as a function of pH for foams, formed from 0.05 mM SDS (red empty circles); 0.05 mM SDP1S (pink empty diamonds); 0.05 mM SDS + 0.35 wt% PVAm (blue squares) or 0.05 mM SDP1S + 0.35 wt% PVAm (green triangles). All solutions contain 10 mM NaCl, 0.35 wt% PVAm and 0.05 mM surfactant. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



**Fig. 3.** Defoaming time,  $t_{DEF}$ , as a function of surfactant concentration for (A) SDS and (B) SDP1S-containing foams, formed from solutions of surfactant alone (red circles) or surfactant + PVAm (blue squares), at pH 6 (empty symbols) and pH 10 (full symbols). All solutions contain 10 mM NaCl and 0.35 wt% PVAm. The arrows show that the defoaming time is longer than 15 min. The experimental data are average from three experiments – the scattering of the data is represented by the symbol size. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



**Fig. 4.** Defoaming time,  $t_{\text{DEF}}$ , as a function of pH for (A) 0.03 mM surfactant or (B) 0.05 mM surfactant. The empty red circles represent data obtained with SDS alone, the blue squares represent data for SDS + 0.35 wt% PVAm, the empty pink diamonds represent data for SDP1S alone, and green triangles are for SDP1S + 0.35 wt% PVAm foams. All solutions contain 10 mM NaCl and 0.35 wt% PVAm. The arrows show that the defoaming time is longer than 15 min. The experimental data are average from three experiments – the scattering of the data is represented by the symbol size. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

respective standard deviations. For the defoaming times shown in Figs. 3–4, the scattering of the data is less than the symbol size.

### 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  $25.0 \pm 0.5^\circ\text{C}$ . The kinetics of the surface tension decrease, after a pendant drop has been formed rapidly on the capillary tip, was monitored for 15 min. The dynamic surface tension of the solutions was measured by the maximum bubble pressure method (MBPM) on tensiometer BP2 (Krüss GmbH, Germany).

### 2.2.3. Surface rheological properties

The surface dilatational rheological properties of the foaming solutions was measured by the oscillating drop method (ODM) [40]. In this method, the surface of surfactant solution is perturbed sinusoidally,  $a(t) = a_0 \sin(\omega t)$ , where  $a(t) = [A(t) - A_0]/A_0$  is the normalized change of the drop surface area around the mean area,  $A_0$ , while  $a_0$  is the relative amplitude of oscillations. The

resulting variation of the surface tension is measured and (for small deformations) is presented as:

$$\sigma(t) = E_{\text{SD}} a_0 \sin(\omega t) + E_{\text{LD}} a_0 \cos(\omega t) \quad (1)$$

where  $E_{\text{SD}}$  is the surface storage modulus (related to surface elasticity) and  $E_{\text{LD}}$  is the surface loss modulus, which is related to surface dilatational viscosity,  $\mu_{\text{SD}} = E_{\text{LD}}/\omega$ . The total surface dilatational modulus is

$$E_{\text{D}} = (E_{\text{SD}}^2 + E_{\text{LD}}^2)^{1/2} \quad (2)$$

Measurements were performed at 5 s oscillation period and the amplitude of deformation was varied between 1 and 7 %, at temperature  $T = 25^\circ\text{C}$ .

### 2.2.4. 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 film-thinning pattern. The observations were made in reflected light, by using the method of Scheludko [41]. The films were formed from a biconcave drop, placed in a short capillary (i.d. 2.5 mm, height 3 mm), by sucking out liquid through a side orifice. The observations were performed in reflected light by means of a microscope Axioplan (Zeiss, Germany), equipped with a long-distance objective Zeiss Epiplan  $20\times/0.40$ , CCD camera (Sony SSC-C370P), video-recorder and monitor. The film thickness was determined by light interferometry, using the method of Scheludko–Exerowa [41]. The relation between the instantaneous values of the intensity of the reflected light  $I(t)$  and film thickness  $h(t)$  can be expressed by the equation:

$$h = \frac{\lambda}{2\pi n_0} (k\pi + \arcsin \sqrt{\frac{I - I_{\min}}{I_{\max} - I_{\min}}})$$

where  $I_{\max}$  and  $I_{\min}$  denote the maximal and minimal intensity of the reflected light, respectively,  $k = 0, 1, \dots$  is the order of the interference maximum,  $\lambda$  is the wavelength of the incident light and  $n_0$  is the refractive index of the liquid forming the film.

## 3. Results and discussion

### 3.1. Foamability and foam stability

#### 3.1.1. PVAm solutions (no surfactant added)

Experiments at five different pH values, varied between 6 and 10, were performed with polymer solutions without surfactant added. The polymer concentration is fixed in all experiments at 0.35 wt%. Under all conditions studied, the foamability of the polymer solutions was low – the initial foam volume was  $\approx 5 \pm 1$  mL. The generated foams contained relatively large bubbles, with diameter  $\approx 1$ –2 cm, and were very unstable – with defoaming time shorter than 10 s. No significant effect of pH was found on the foamability and foam stability for these polymer systems.

Concluding, PVAm alone is unable to stabilize the foams, under all conditions studied, due to its hydrophilic character (see also the experimental data in Ref. [39]).

#### 3.1.2. Surfactant–polymer solutions

In our previous study [39] we demonstrated a strong synergy between SDS and PVAm with respect to foam stability, and antagonistic effect with respect to the foamability of the mixed solutions. The experiments in the previous study were performed at the natural pH, obtained after dissolution of the components (without adjustment) which was measured to be  $\text{pH} \approx 9.2$  for all PVAm-containing solutions.

In the current study we performed experiments at different pH values for SDS and SDS + PVAm solutions. The experimental results



for the initial foam volume, at pH 6 and pH 10, are shown in Fig. 1A, as functions of SDS concentration. One sees that there is no significant effect of SDS on the foamability of the polymer solution at very low surfactant concentrations,  $C_S < 0.03$  mM. The volume of the initially formed foam is  $V_0 \approx 6 \pm 2$  mL, which is similar to the initial foam volume in the absence of surfactant. At higher SDS concentrations,  $C_S \geq 0.05$  mM, the foam volume produced with SDS solutions (without polymer) approaches 10 mL. However, the addition of PVAm to these SDS solutions reduces the foam volume rather significantly (compared to SDS alone), especially at higher SDS concentrations and low pH. Thus we see that the cationic polymer PVAm acts as pronounced foam inhibitor for the anionic surfactant SDS, in the entire range of pH values studied.

To investigate in detail the effect of pH on the foamability of the mixed solutions, we present in Fig. 2 the experimental results for the initial volume  $V_0$  (pH) of the foams, produced from 0.05 mM SDS + 0.35 wt% PVAm solutions. No significant effect of pH on the foamability of 0.05 mM SDS solution (without polymer) is seen – the volume of the generated foam is  $\approx 14 \pm 3$  mL for all pH values studied. There is a weak minimum in  $V_0$  around pH 8, but this effect is relatively small, compared to the other effects studied.

On the other hand, the increase of pH from 6 to 10 leads to a gradual increase in  $V_0$  for SDS + PVAm solutions (from 5 to 6 to 10 mL, see the blue squares in Fig. 2) which evidences that the foam inhibition effect of PVAm is stronger at lower pH. The latter trend is related to the higher charge density of the polymer molecules at low pH. Note that  $pK_a$  for PVAm is  $\approx 8.6$ , which means that the polymer molecules are highly charged at pH  $\approx 6$  and 7, whereas only  $\approx 10\%$  of the amine groups are charged at pH 10 [39]. As a consequence, the fraction of bound SDS molecules to the polymer molecules is expected to increase strongly with the decrease of pH below the  $pK_a$  of the polymer.

The results for the foamability of SDP1S-containing solutions are presented in Fig. 1B. Similarly to SDS, no detectable effect of SDP1S on the foamability of the polymer solution is observed at  $C_S \leq 0.03$  mM, while PVAm acts as foam inhibitor at  $C_S \geq 0.05$  mM, with the effect being bigger at higher surfactant concentrations. The effect of pH on the initial foam volume for 0.05 mM SDP1S and 0.05 mM SDP1S + 0.35 wt% PVAm solutions is illustrated in Fig. 2. One sees that the foamability of SDP1S solutions (with and without polymer) is not affected significantly by the pH variation. Shallow minimum at pH 8 is observed for the system without polymer and slight increase is observed for the system with polymer, but both effects are relatively small. As in the case of SDS, the polymer is a strong foam inhibitor in the whole range of pH values studied.

As explained in our previous study [39], the initial foam volume for all three surfactants studied there (SDS, DTAB,  $C_{12}EO_{23}$ ) were found to be very similar in the absence of polymers. This unexpected result was explained with the prevailing effect of the kinetics of surfactant adsorption at such low surfactant concentrations on the solution foamability – this adsorption kinetics is expected to be similar for given molar concentration of the various surfactants, in the case of diffusion-limited control of adsorption. In the current study we see that SDP1S also gives very similar initial foam volume to SDS (cf. the curves for SDS and SDP1S in Figs. 1 and 2) and, hence, to the other two surfactants studied in Ref. [39] (DTAB and  $C_{12}EO_{23}$ ).

In contrast, when comparing the mixed polymer–surfactant solutions, we see that the foamability of SDP1S + PVAm solutions is somewhat lower than the foamability of SDS + PVAm solutions, especially at high pH, see Fig. 2. This comparison suggests that a stronger attraction between SDP1S + PVAm (compared to SDS + PVAm) leads to more pronounced binding of the SDP1S molecules to the polymer backbone in the bulk, which decreases the adsorption rate and the foamability of the mixed PVAm–SDP1S solutions. This explanation is supported by the measurements of

the adsorption kinetics, which is slower for SDP1S + PVAm, compared to SDS + PVAm (see Fig. 9A).

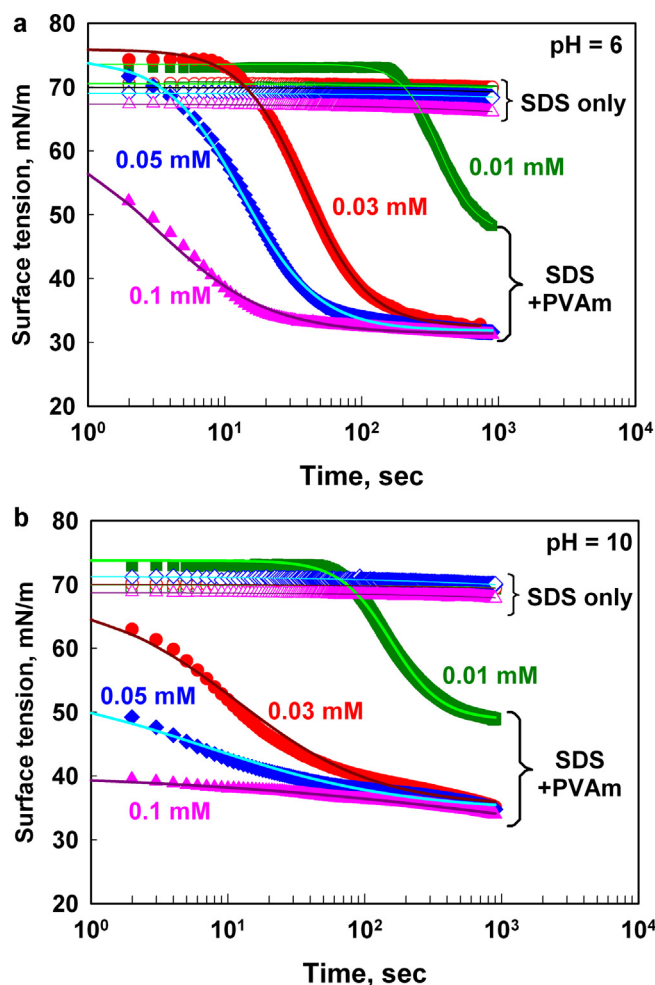
We studied also the stability of the generated foams, as a function of pH and surfactant concentration. As mentioned already, the foams formed from the polymer solutions (without surfactants) were very unstable and disappeared for less than 10 s. The effects of SDS and SDP1S concentration on the defoaming time at pH 6 and 10 are compared in Fig. 3. One sees a qualitative difference between the trends for SDS-containing foams and SDP1S-containing foams. First, the foams generated from solution of SDS (without polymer) are unstable at both pH values (6 and 10) in the entire range of SDS concentrations studied,  $C_S \leq 0.1$  mM, see the red circles in Fig. 3A. In contrast, the SDP1S foams (without polymer) are stable for more than 900 s at  $C_S \geq 0.05$  mM for pH 6 and at  $C_S \geq 0.03$  mM when pH 10, see Fig. 3B. We recall that the initial volumes of the foam, formed from SDS and SDP1S solutions, are very similar (cf. Figs. 1 and 2 above) which means that these two surfactants stabilize the bubbles with similar efficiency under dynamic conditions (during foam generation). However, as seen from Fig. 3, the SDS foams are much less stable under static conditions.

The effect of PVAm on the stability of SDS and SDP1S foams depends significantly on the pH, especially around the threshold surfactant concentration which separates the stable from unstable foams. As seen from Fig. 3, this concentration is between 0.03 mM and 0.05 mM for both SDS and SDP1S solutions. To clarify better the effect of pH on the stability of surfactant + PVAm foams, we performed additional experiments at these two surfactant concentrations, varying pH between 6 and 10 – see Fig. 4.

Let us discuss first the foam stability in the absence of polymer. The stability of foams, formed from 0.03 mM and 0.05 mM SDS does not depend on pH – the defoaming time for all these foams was less than 60 s. Even at the highest concentration studied, 0.1 mM SDS, the defoaming time was  $< 100$  s. On the other hand, for 0.03 mM SDP1S solution, the defoaming time increased from 50 s up to 900 s with the increase of pH from 9 to 10. Similarly,  $t_{DEF}$  increased from 50 to 265 s upon increase of pH from 9 to 10 for 0.01 mM SDP1S solution (data not shown). The defoaming time  $t_{DEF}$  for 0.05 mM SDP1S solutions was longer than 900 s in the entire range of pH values studied. These results demonstrate once again that SDP1S foams are significantly more stable than the SDS foams in the transitional range of concentrations (in the absence of polymer).

The effect of PVAm on the stability of SDS and SDP1S foams is qualitatively different. The addition of 0.35 wt% PVAm to 0.05 mM SDS leads to very stable foams,  $t_{DEF} > 900$  s, for all pH values studied, see Fig. 4B, despite the very low stability of SDS foams at this surfactant concentration. In contrast, the addition of 0.35 wt% PVAm at the same surfactant concentration of SDP1S, leads to unstable foams with  $t_{DEF} < 50$  s at pH 6 and 7, despite the high foam stability in the absence of polymer, see Fig. 4B. At the lower surfactant concentration (0.03 mM) the foams formed from SDS and PVAm are all stable at pH  $\geq 7$ , whereas the addition of PVAm to the SDP1S solutions does not affect noticeably the foam stability. Therefore, there is a significant difference in the interactions of the anionic surfactants SDS and SDP1S with the cationic PVAm polymer, which deserves more detailed analysis.

The main results from all these experiments can be summarized as follows: (1) Under all conditions studied, PVAm solutions produce unstable foams with initial volume of 3–5 mL, defoaming time  $< 10$  s, and relatively large bubbles. (2) The addition of PVAm to SDS and SDP1S solutions decreases the foamability for both surfactants. This effect is strongest at lower pH where the polymer is highly charged. (3) The stability of SDS foams is strongly enhanced in the presence of PVAm at  $C_S \geq 0.03$  mM. (4) The stability of SDP1S foams is strongly reduced after addition of PVAm at pH between 6 and 8. The most intriguing results here are the observed synergy for SDS + PVAm foams and the opposite antagonistic effect



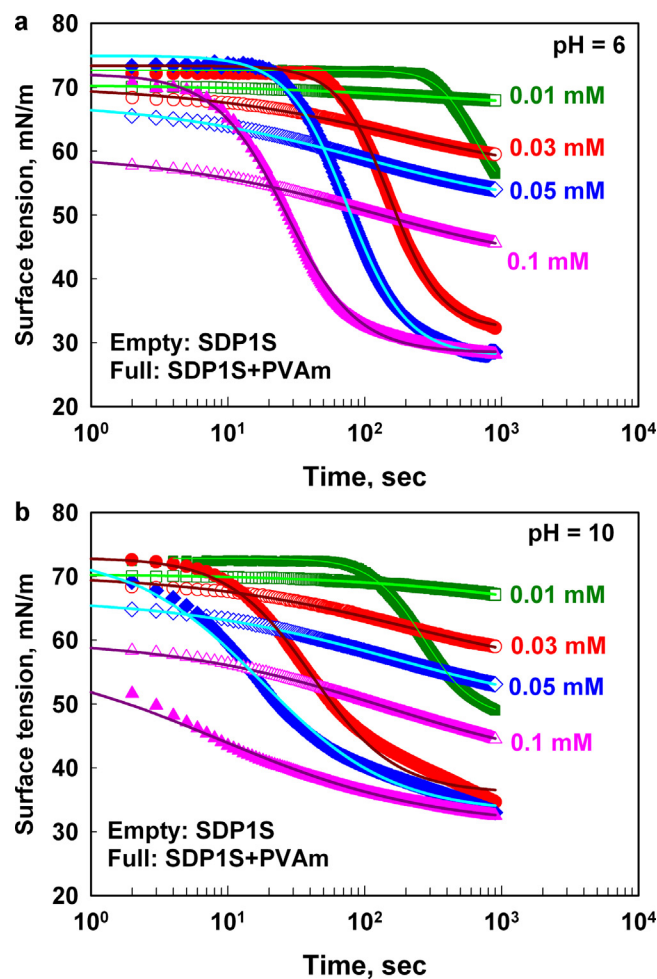
**Fig. 5.** Surface tension as a function of time for 0.01 mM SDS (green squares); 0.03 mM SDS (red circles); 0.05 mM SDS (blue diamonds) and 0.1 mM SDS (pink triangles) without (empty symbols) and with 0.35 wt% PVAm (full symbols), at (A) pH 6 and (B) pH 10. All solutions contain 10 mM NaCl. The symbols are experimental data, obtained by drop shape analysis of pendant drops, whereas the curves are best fits according Eq. (3) for SDS solutions and Eq. (4) for SDS + PVAm solutions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

for SDP1S + PVAm foams, as well as the fact that these effects are more pronounced in the region of pH where the polymer is highly charged.

### 3.2. Surface properties

The surface properties of SDS and SDP1S-containing solutions were characterized by measuring their dynamic surface tension by MBPM, their surface tension at long surface age by drop shape analysis, and their surface rheological properties by oscillating drop method.

Experiments with the mixed PVAm + SDS and SDP1S + PVAm solutions, at pH 6 and 10, were performed. The complete set of results, obtained by drop shape analysis of pendant drops from the studied solutions, is shown in Figs. 5 and 6. The experimental results for PVAm alone at pH 6 and 10 are presented in Figure S1 in supporting information. One sees that the shape of the curve  $\sigma(t)$  for SDP1S + PVAm solution is similar to that of SDS + PVAm solutions and the surface tension at long adsorption times is rather low (<30 mN/m). Therefore, similarly to SDS + PVAm, the mixture SDP1S + PVAm behaves as strongly interacting system with respect



**Fig. 6.** Surface tension as a function of time for 0.01 mM SDP1S (green squares); 0.03 mM SDP1S (red circles); 0.05 mM SDP1S (blue diamonds) and 0.1 mM SDP1S (pink triangles) without (empty symbols) and with 0.35 wt% PVAm (full symbols), at (A) pH 6 and (B) pH 10. All solutions contain 10 mM NaCl. The symbols are experimental data, obtained by drop shape analysis of pendant drops, whereas the curves are best fits according Eq. (3) for SDP1S solutions and Eq. (4) for SDP1S + PVAm solutions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

to surface tension. Thus we conclude that the reduced foam stability for SDP1S + PVAm mixture requires deeper analysis to clarify the mechanisms and the factors, which lead to such qualitatively different behavior, when compared to SDS + PVAm.

To compare quantitatively the kinetics of adsorption for SDS and SDP1S containing solutions (with and without PVAm) we tried to fit the kinetic data for  $\sigma(t)$  by appropriate equations and to extract values for the characteristic parameters, such as the characteristic adsorption time.

For the data obtained with SDS and SDP1S solutions (no polymer) we used the kinetic equations for diffusion-limited control of adsorption [42]:

$$\sigma(t) = \sigma_{EQ} + (\sigma_0 - \sigma_{EQ}) \exp\left(-\frac{t}{t_D}\right) \operatorname{erfc}\left(\sqrt{\frac{t}{t_D}}\right) \quad (3)$$

Here  $t_D$  is the characteristic diffusion time,  $\sigma_{EQ}$  is the equilibrium surface tension, and  $\sigma_0$  is the initial surface tension after drop formation which might be much lower than the surface tension of the clean solution surface, if rapidly adsorbing components are present. The characteristic adsorption time  $t_D$  in Eq. (3) is the time

required for the total surface stress,  $\sigma_0 - \sigma_{EQ}$ , to decrease by 1.74 times. The long time asymptotics of Eq. (3) reads [42]:

$$\sigma(t) = \sigma_{EQ} + (\sigma_0 - \sigma_{EQ}) \sqrt{\frac{t_D}{\pi t}} + O\left[\frac{1}{t}\right]^{3/2} t \rightarrow \infty \quad (3a)$$

which indicates a  $t^{-1/2}$  relaxation of the surface tension at long times. Eq. (3) was found to describe rather well all experimental curves for the surfactant solutions, in the absence of polymer, see Figs. 5 and 6 (note that all these solutions are below the critical micelle concentration of SDS and SDP1S). The best fits to experimental data with Eq. (3) are shown as continuous curves in Figs. 5 and 6 (for the data without PVAm).

However, we found that Eq. (3) does not describe the experimental data for the polymer–surfactant solutions, because it cannot represent the two well defined regions, observed in the experimental curves  $\sigma(t)$ . Noting that the shape of the curves for surfactant + PVAm solutions resembles (visually) that for the bulk viscosity of solutions of worm-like micelles versus shear rate [43–48], we modified the equation for the viscosity of micellar solutions, to define the following empirical equation for the surface tension of the mixed polymer–surfactant solutions:

$$\sigma(t) = \sigma_{EQ} + \frac{(\sigma_0 - \sigma_{EQ})}{1 + (t/t_{ADS})^n} \quad (4)$$

Here  $\sigma_0$  and  $\sigma_{EQ}$  have the same physical meaning as those in Eq. (3). The characteristic adsorption time,  $t_{ADS}$ , here is the time required for the total surface stress,  $\sigma_0 - \sigma_{EQ}$ , to decrease twice. The specific value of the power-law index  $n$  is related to the slope of the curve  $\sigma(t)$  in the intermediate time period. The fits of the experimental data by Eq. (4) are also shown in Figs. 5 and 6 – one sees that Eq. (4) describes very well the data for all studied polymer–surfactant mixtures at pH 6 and reasonably well the data at pH 10 (though some non-negligible deviations are seen at the latter pH). It is worth mentioning that, at not-very-short times, Eq. (3) predicts similar kinetics as Eq. (4) with  $n = 0.5$  and it was successfully applied in Ref. [49] to describe experimental data for the dynamic surface tension for solutions of several low-molecular-mass surfactants (incl. SDS). In other words, we can describe the experimental data for SDS and SDP1S solutions by eq. (4) as well, with  $n = 0.5$ . The data for the surfactant–polymer mixtures were described by Eq. (4) when considering the power law index  $n$  as adjustable parameter and it varied between 0.5 and 1, depending on the specific solution composition. For comparison of the adsorption kinetics of the different polymer–surfactant mixtures, we used the values of  $t_{ADS}$ ,  $\sigma_0$  and  $\sigma_{EQ}$  which do not depend on the specific value of  $n$ .

The obtained values of  $\sigma_0$  and  $\sigma_{EQ}$  are compared in Fig. S1 and Fig. 7, respectively, as functions of surfactant concentration, at pH 6 and 10. One sees that the initial surface tension is very close to that of pure water,  $\sigma_0 \approx 72$  mN/m, for most of the solutions studied. Significantly lower values of  $\sigma_0$  (indicating fast surfactant adsorption) are determined only for SDS + PVAm solutions, at  $C_S \geq 0.05$  mM and pH 10. It should be noted that the initial surface tension for SDS solutions (without polymer) is lower than the initial surface tension for SDS + PVAm solution at  $C_S \leq 0.05$  mM and pH 6. This comparison demonstrates clearly that PVAm is slowing the SDS adsorption from the solution at pH 6 (when the polymer molecules are strongly charged). Only at the highest SDS concentration of 0.1 mM, the initial surface tension of SDS + PVAm solution is lower than that of the SDS solution, indicating fast adsorption of SDS–PVAm complex. The slowing of the adsorption rate by PVAm is even more pronounced for SDP1S solutions – the initial surface tension of the surfactant solutions (without polymer) is lower than the initial surface tension of the mixed SDP1S + PVAm solutions, for all surfactant concentrations studied. The most probable explanation for the slower kinetics of adsorption from PVAm–surfactant solutions is the decreased

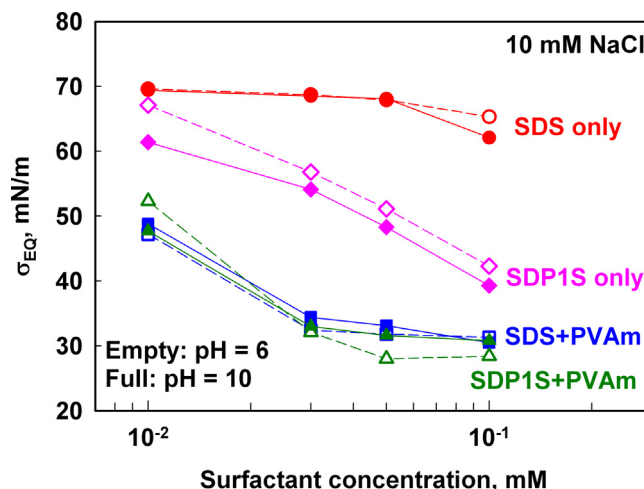


Fig. 7. Equilibrium surface tension,  $\sigma_{EQ}$ , as determined from the best fit of  $\sigma(t)$  by Eq. (3) for SDS (red circles) and SDP1S (pink diamonds) solutions, and by Eq. (4) for SDS + PVAm (blue squares) and SDP1S + PVAm (green triangles) solutions, as a function of surfactant concentration. The empty symbols are for pH 6 and the full symbols are for pH 10. All solutions contain 10 mM NaCl. The concentration of PVAm in surfactant–polymer solutions is 0.35 wt%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

concentration of free surfactant monomers in the solution, due to their strong binding to the polymer molecules.

To check for a direct correlation between the initial surface tension and the initial foam volume, we plot in Fig. 8 the experimental data for  $V_0$  versus  $\sigma_0$ . One sees that the experimental data for the surfactant solutions (without polymer) and for the surfactant–polymer solutions group around two distinct separate curves. These experimental data show that, for the surfactant solutions, an initial surface tension of 69.5 mN/m (the vertical dashed line in Fig. 8) is sufficient for generating noticeable amount of foam – when  $\sigma_0$  is higher than this threshold value, the generated foam is of negligible volume. The further decrease of  $\sigma_0$  does not affect significantly the initial foam volume which indicates that, once the dynamic foam films are stabilized by the surfactant, the foam volume is governed by the mechanical energy in the foaming process

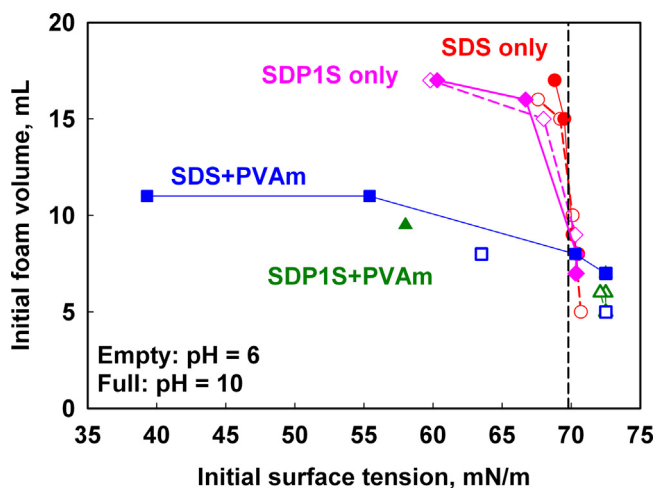


Fig. 8. Initial foam volume, as a function of initial surface tension,  $\sigma_0$ , for SDS (red circles); SDP1S (pink diamonds); SDS + PVAm (blue squares); and SDP1S + PVAm (green triangles). Empty symbols represent data obtained at pH 6, whereas the full symbols represents data obtained at pH 10. All solutions contain 10 mM NaCl. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



(similar relations have been studied in detail and explained with emulsions – see Refs. [50–51] for detailed discussion).

On the other hand, the experimental data for the foam volume of the surfactant + polymer mixtures lay much lower than the data for the single surfactants. This comparison shows that the molecular mechanism of foam film stabilization, during foam generation, is different for the low molecular mass surfactants and for the surfactant–polymer mixtures. As discussed in our previous study, the surfactants can ensure rapid stabilization of the foam films by Marangoni effect, due to their ability to rapidly adsorb and spread on the solution surface. This explanation is supported by the fact that both the initial surface tensions and the initial foam volumes are very similar for the SDS and SDP1S solutions (see Figs. 1 and 2), as one may expect for dynamic foams, stabilized by Marangoni effect. This dynamic stabilization of the foam films is less efficient in strongly interacting polymer–surfactant mixtures, due to the association of the surfactant molecules with the big and slowly diffusing polymer molecules.

The results for the equilibrium surface tension of these solutions,  $\sigma_{EQ}$ , are compared in Fig. 7. We note first that, as seen in Figs. 5 and 6, for most of the systems studied, the surface tension continues to decrease slowly even after 15 min of surface age. Because we were primarily interested in the foam stability up to 15 min of foam lifetime, we did not measure the surface tension at longer times. Therefore, the values of  $\sigma_{EQ}$  shown in Fig. 7 and discussed below, are obtained by fitting the experimental data with Eqs. (3) or (4), and present extrapolated values at long adsorption times. The second important notice is that the values of  $\sigma_{EQ}$  for SDS and SDP1S solutions are very different, contrary to their initial surface tensions. The equilibrium surface tension of the SDS solutions is very close to  $\sigma_0$  (the difference is  $<2$  mN/m), whereas  $\sigma_{EQ}$  for SDP1S solutions is reduced by more than 15 mN/m, as compared to the initial one (except for the lowest SDP1S concentration). The third important notice is that no significant effect of pH is seen for SDS solutions (except for the highest SDS concentration, where we observe also an increase in the defoaming time, cf. Fig. 3A), whereas the increase of pH from 6 to 10 leads to a significant decrease of  $\sigma_{EQ}$  for the SDP1S solutions. Note that no such effect was observed for  $\sigma_0$ . On the other hand, the large difference in  $\sigma_{EQ}$  of the SDS and SDP1S solutions practically disappears when 0.35 wt% PVAm is added to the solutions. Interestingly we see that  $\sigma_{EQ}$  for SDP1S + PVAm solutions at pH 6 is the lowest, while the stability of the respective foams is also very low, cf. with Fig. 3B. Also, there is no significant effect of pH on  $\sigma_{EQ}$ , whereas we observe large effect of pH on the foam stability for these solutions, cf. with Fig. 4. Concluding, no any correlation between the equilibrium surface tension and the stability of the formed foams is observed for the mixed polymer–surfactant systems (same conclusion was drawn in Ref. [39] with the other surfactants studied there).

Let us clarify that the observed low surface tensions in surfactant–polymer mixtures (Fig. 7) indicate the formation of denser adsorption layers in the presence of PVAm. Indeed, the variations in the surface tension upon changes of the solution composition are described by Gibbs adsorption isotherm [42]:

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \quad (5)$$

where index 1 refers to the surfactant and index 2 – to the polymer. Eq. (5) shows that the decrease of the surface tension is related to increase of the surfactant (polymer) chemical potential and/or to increase of surfactant (polymer) adsorption. The attraction of the surfactant and the polymer in the bulk solution certainly reduces the chemical potential of the surfactant. Therefore, we could explain the observed lower surface tension in the surfactant–polymer mixtures ( $\sigma_{EQ} \approx 30$  mN/m) only by formation of denser adsorption layer in these mixtures – the increase of  $\Gamma_1$  (and possibly of  $\Gamma_2$ ) compensates for the decrease of  $\mu_1$  which (alone) would

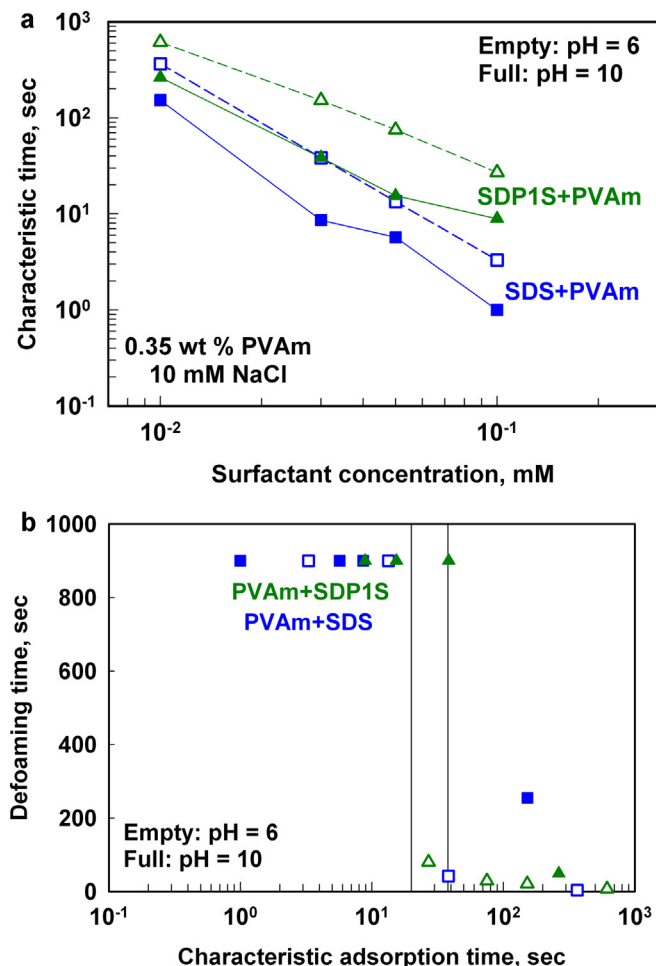
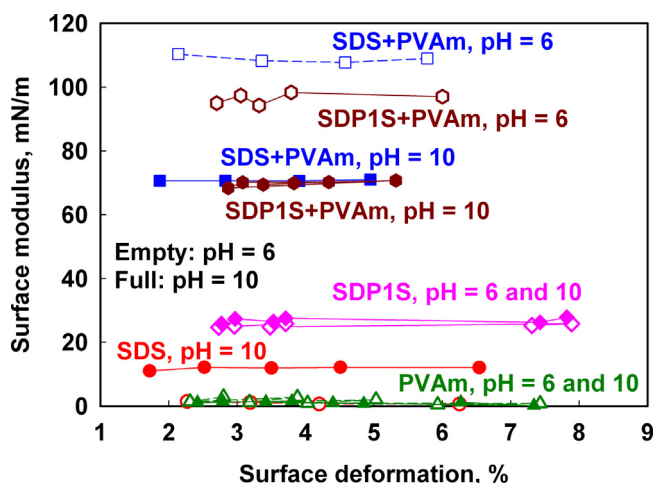


Fig. 9. (A) Characteristic time for SDS+PVAm (blue squares) and SDP1S+PVAm (green triangles), as a function of surfactant concentration, at pH 6 (empty symbols) and pH 10 (full symbols). (B) Defoaming time, as a function of characteristic adsorption time, for PVAm + SDS (blue squares) and PVAm + SDP1S (green triangles) solutions, containing 0.35 wt% PVAm and 10 mM NaCl. The two vertical lines indicate the range of adsorption times, in which a sharp decrease of the defoaming time is observed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

lead to increase of  $\sigma$ . The latter explanation is in a good agreement with the experimental results obtained by direct methods for measuring the adsorption in Ref. [12]. It was shown for SDS/PDMAAC mixtures that dense surfactant adsorption layer was formed on the air–water interface when the surface tension was low,  $\approx 35$  mN/m, even at very low surfactant concentrations (see Fig. 15 in Ref. [12]).

To check how important is the kinetics of adsorption for the foam stability in such slowly-adsorbing polymer–surfactant mixtures, we determined the characteristic adsorption time for the various solutions using Eq. (4), see Fig. 9A. The characteristic times,  $t_{ADS}$ , were found to decrease rapidly with surfactant concentration, following a power-law function, for both mixtures studied. The power-law index is  $\approx -2$  for SDS–PVAm mixtures and  $\approx -1.5$  for SDP1S–PVAm mixtures, which is in a reasonably good agreement with the theoretical prediction [42] for diffusion limited adsorption,  $t_{ADS} \propto C^{-2}$ . The characteristic adsorption times are about 3–5 times shorter for SDS + PVAm (corresponding to faster adsorption), as compared to SDP1S + PVAm solutions. Note also that the characteristic adsorption times vary between ca. 5 and 200 s in the intermediate range of surfactant concentrations (between 0.03 and 0.05 mM), which illustrates rather well the excessively slow adsorption in these systems.





**Fig. 10.** Surface modulus, as a function of surface deformation, for 0.03 mM SDS (red circles); 0.03 mM SDP1S (pink diamonds); 0.35 wt% PVAm (green triangles); 0.03 mM SDS + 0.35 wt% PVAm (blue squares); and 0.03 mM SDP1S + 0.35 wt% PVAm (brown hexagons), at pH 6 (empty symbols) and pH 10 (full symbols). All solutions contain 10 mM NaCl. Measurements made by the oscillating drop method, 15 min after surface formation, at oscillation period of 5 s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The characteristic adsorption times depend also significantly on pH of the solution – compare the empty and full symbols in Fig. 9A. The increase of pH leads to faster formation of dense adsorption layer. This effect can be explained by considering the fact that the PVAm molecules are less charged at higher pH, which means that they bind less surfactant – therefore, there are more free surfactant monomers, able to adsorb rapidly on the surface and to start building the mixed adsorption layer.

All these results and conclusions were additionally checked with MBPM measurements (see Fig. S3). The obtained results confirmed unambiguously that the adsorption time is shorter at higher pH and that the initial adsorption is significantly faster for SDS + PVAm, compared to SDP1S + PVAm. The latter result indicates that the surfactant–polymer complexes formed in SDP1S–PVAm solutions are stronger than the complexes formed in SDS–PVAm solutions – as a result, the concentration of free surfactant monomers is lower and the adsorption is slower for SDP1S–PVAm solutions. In the absence of PVAm, the kinetics of adsorption for the two surfactants is very similar, which is reflected in the similar foamability of SDS and SDP1S solutions – see Figs. 1 and 2.

To check whether the characteristic adsorption time for surfactant–polymer mixtures correlates with the defoaming time of the respective foams, we plotted in Fig. 9B the data for  $t_{\text{DEF}}$  versus  $t_{\text{ADS}}$ . One sees that for all solutions with  $t_{\text{ADS}} < 10$  s, the formed foams were stable for more than 900 s, whereas all solutions with  $t_{\text{ADS}} > 50$  s produced unstable foams. In the intermediate range of adsorption times, some of the foams were stable while others were unstable. This correlation of the foam stability with the adsorption time shows convincingly that the kinetics of formation of the adsorption layers plays a crucial role for the foam formation and stability in these slowly adsorbing, mixed polymer–surfactant systems.

An additional comparison of the adsorption layers, formed from 0.03 mM SDS, 0.03 mM SDP1S; 0.35 wt% PVAm, and mixed SDS + PVAm or SDP1S + PVAm solutions, was performed by measuring the surface dilatational modulus at pH 6 and pH 10, see Fig. 10. At pH 6, the adsorption layers from SDS and PVAm solutions had very low surface modulus ( $< 2$  mN/m). Intermediate surface modulus at pH 6 was measured for SDP1S solutions,  $\approx 25$  mN/m. In contrast, the surface moduli of the mixed SDS + PVAm

and SDP1S + PVAm solutions were rather high,  $\approx 110$  mN/m and 100 mN/m, respectively. This moduli did not depend on the amplitude of surface deformation, when the latter was varied between 0.6 and 6 %. The elastic component was much higher than the viscous one (108 versus 13 mN/m for SDS + PVAm and 94 versus 17 mN/m for SDP1S + PVAm), i.e. the mixed adsorption layer behaved as elastic body at the deformation rates applied in our experiments.

The experimental results for the surface moduli, at pH 10, are also shown in Fig. 10. One sees that the moduli for SDS + PVAm and SDP1S + PVAm solutions decrease from 110 to 70 mN/m, indicating that the adsorption layer at pH 10 is weaker compared to pH 6. The latter result could be expected, because the charge density of the PVAm molecules is much lower at high pH. The surface modulus of the SDS solutions (no polymer) showed some increase at pH 10 (from 2 to 10 mN/m), but this effect is relatively small and does not affect significantly the foam properties. No such effect was determined for SDP1S solutions.

From all these experiments we can conclude that dense adsorption layers are formed on the solution surfaces from mixed PVAm + SDP1S and PVAm + SDS solutions, at all pH values studied. The characteristic adsorption time decreases approximately with the square of surfactant concentration in the mixture, and is shorter at higher pH. At given pH and fixed surfactant concentration, the characteristic adsorption time for SDP1S + PVAm mixture is around 3–5 times longer than that for SDS + PVAm solutions. Good correlation was observed between the characteristic adsorption time and the foam stability for the mixed surfactant–polymer systems for which the adsorption is relatively slow (Fig. 9B). The mixed adsorption layers of SDS + PVAm and SDP1S + PVAm show rather high surface elasticity, whereas very low surface modulus is measured for the surface layers formed from SDS, SDP1S and PVAm, when taken separately. No any correlation is observed between the values of the surface modulus and the foamability or foam stability of the respective solutions.

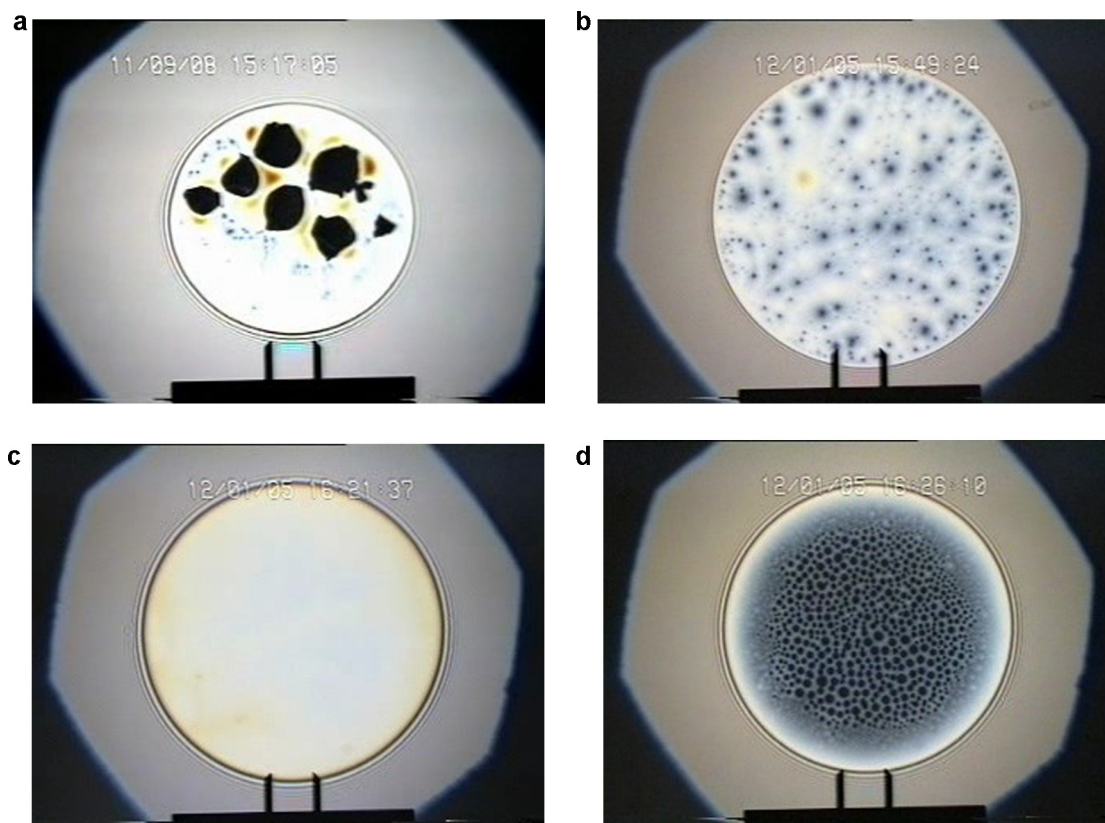
### 3.3. Foam films

Experiments with films, formed from solutions of 0.03 mM SDS, 0.03 mM SDP1S, 0.35 wt% PVAm, and the mixed solutions 0.03 mM SDS + 0.35 wt% PVAm and 0.03 mM SDP1S + 0.35 wt% PVAm were performed, at pH varied between 6 and 10. The obtained results are briefly discussed in this section.

#### 3.3.1. Films from PVAm solutions

As explained in our previous study [39], PVAm is a very hydrophilic polymer and does not affect significantly the surface tension of its solutions. Nevertheless, PVAm is able to adsorb weakly on the film surface and decelerate the film thinning process, by creating a combined electrostatic-steric repulsion in the foam films. We showed in Ref. [39] that the studied polymers are able to stabilize the foam films at equilibrium film thickness  $\approx 100$  nm, if the film radius is smaller than ca. 150  $\mu\text{m}$ . These experiments were performed at the natural pH 9.2 of the PVAm solutions. The increase of the foam film radius resulted in much larger probability for formation of thin spots in the foam films, followed by a rapid film rupture. Because the typical foam films, formed between the bubbles in the studied PVAm foams, are much larger than 200  $\mu\text{m}$ , in the current study we studied only the behavior of the large foam films with radius  $> 150$   $\mu\text{m}$ .

The increase of pH for PVAm solutions decreased significantly the lifetime of the foam films. These films were stable at pH 6 and unstable at pH 8 and 10 (the capillary pressure squeezing the foam film was  $P_c \approx 140$  Pa in these experiments). The main difference at higher pH was the formation of foam films with uneven thickness, in which thinner spots with thickness  $\approx 60$  nm spontaneously



**Fig. 11.** Illustrative images of foam films, formed from (A) 0.03 mM SDS + 0.35 wt% PVAm at pH 6; (B) 0.03 mM SDP1S + 0.35 wt% PVAm at pH 6; (C) 0.03 mM SDP1S + 0.35 wt% PVAm at pH 10 at  $P_C = 140$  Pa. (D) The foam film from (C) at higher capillary pressure.

appeared and the films ruptured soon afterwards. This observation supports our explanation that these foam films are stabilized by combined electrostatic + steric repulsion between the polymer molecules, adsorbed on the opposite film surface. At high pH, the polymer molecules loose their charge and the electrostatic component of the disjoining pressure disappears, thus decreasing the film stability.

The main conclusions from this series of experiments are: (1) The stability of PVAm foam films decreases with the increase of pH  $\geq 8$ ; (2) No direct correlation between the stability of the foam films in the capillary cell and the stability of actual foams is observed (all foams, formed from polymer solution without surfactant, were very unstable).

### 3.3.2. Films from polymer–surfactant mixtures

Opposite to the case of PVAm (without surfactants), we observed that the foam films from the mixed SDS+PVAm solutions are unstable at pH 6 and extremely stable at pH  $\geq 7$ . When the films at pH 6 are formed, they thin to 100 nm for 50 s, and dark spots with thickness  $h \approx 30$  nm are formed afterwards. These spots increase their area in the following 30 s and occupy almost the entire film, see the images in Fig. 11A. At this stage, the foam films usually break. On the other hand, at higher pH the films become very stable (both at low and high capillary pressure). At low capillary pressure, the foam films remain relatively thick,  $h_{EQ} \approx 100$  nm, which means that these foam films are sterically stabilized by adsorbed polymer–surfactant complexes with thickness of the adsorption layers  $\approx h_{EQ}/2 \approx 50$  nm. When we increase the capillary pressure, the films thin down to 10 nm, with trapped polymer–surfactant complexes remaining inside the film (see Fig. 11D), but do not break.

The behaviour of the films formed from SDP1S + PVAm solutions was very similar to that from SDS + PVAm solutions. At low

pH, films with uneven thickness were formed, see Fig. 11B. These films ruptured after the formation of dark spots. The time for film thinning increased with the increase of pH. At pH 10, the films remained at equilibrium film thickness  $\approx 100$  nm at low capillary pressure. After increasing the capillary pressure, darker spots were formed in the films, but they remained very stable. Upon decrease of the film diameter we observed strong adhesion between the film surfaces (evidenced by a significant increase of the contact angle film–meniscus) which indicated that the polymer molecules had bridged the opposite film surfaces. Similar effect was observed in our previous study with other cationic polymers and was linked to the significant increase of the yield stress of the respective foams [52].

The comparison of the SDS+PVAm and SDP1S + PVAm foam films, shows that the main difference between these two systems (at fixed surfactant concentration and pH) is in the film drainage time (down to 100 nm thickness). The films from SDP1S + PVAm solutions thinned faster than the films formed from SDS + PVAm solutions.

### 3.4. Discussion

The obtained results clearly show that some of the concepts, which are widely discussed in literature for surfactant–polymer mixtures, cannot be applied directly to the systems studied. For example, our results show that strong surfactant–polymer interactions could have a negative effect on both the foamability and foam stability of these mixtures. Also, the formation of thick adsorption layers does not necessarily lead to formation of stable foams [39]. A specific feature of these systems seems to be the relatively slow formation of the adsorption layers, due to the strong binding of the surfactant molecules to the polymer in the bulk solution (enhanced by the low surfactant concentration and the excess of polymer).

Therefore, the obtained results call for different mechanistic explanations of the observed trends.

One of the key observations is that the foamability of the mixed polymer–surfactant solutions is lower than the foamability of the respective surfactant solutions, even when the initial surface tension of the polymer–surfactant solution is lower than that of the respective surfactant solution, see Fig. 8. This result clearly indicates that the intimate mechanisms of foam film stabilization during foaming are different for these two types of systems. Let us clarify first the reasons for this difference.

The initial stabilization of the foams, containing surfactants only, is related to the surfactant ability to adsorb rapidly on the solution surface and to prevent the bubble–bubble coalescence by increasing the film drainage time (due to Marangoni effect) and by creating electrostatic repulsion between the film surfaces.

The behavior of the PVAm + SDS and PVAm + SDP1S solutions is different with respect to foaming, due to the strong electrostatic attraction between the oppositely charged molecules in the bulk solution. From the weight concentration of the polymer (0.35 wt%) and the monomer mass (44 a.u.), one can calculate the monomer molar concentration in the studied solutions. According to Refs. [37–38] around 90 % of the PVAm units are charged at pH around 6. Thus we estimate around 70 mM positive charges in the polymer-containing solutions, viz. these charged monomers are in a large excess to the anionic surfactants used in our study (the maximal surfactant concentration was 0.1 mM). Upon increase of pH, the concentration of the positively charged monomers decreases down 35 mM (50 % ionization) at pH  $\approx$  pK  $\approx$  8.6 and further to  $\approx$  7.7 mM at pH 10 (10 % ionization [38]), still remaining around 80 times higher than the concentration of the surfactant molecules. Therefore, in the entire range of surfactant concentrations and pH values studied, the positively charged polymer groups were in a large excess to the anionic surfactants.

Based on the above estimates, we can speculate that during foaming (especially at pH 6), there are almost no free surfactant molecules and that the positively charged polymer molecules are only weakly attached to the bubble surfaces. As a consequence, the bubbles are stabilized during foaming mainly by the polymer molecules (with attached surfactant molecules to them). This hypothesis is supported by the optical observations of the foam films – indeed we observed initially the formation of relatively thick foam films, with behavior resembling that of the polymer solutions without surfactants, thus supporting the role of the polymer in the initial film stabilization for the mixed systems.

The experimental data from the surface tension measurements also support these explanations. When the surfactant concentration increases and pH increases, the initial surface tension of PVAm + SDS solutions becomes lower than that of the SDS solutions, while the foamability of the mixed solutions still remains very low. These trends could be explained taking into account that the initial SDS foams are stabilized mainly by the efficient Marangoni effect (plus electrostatic repulsion), whereas the PVAm + surfactant foams are stabilized by polymer molecules which are not very efficient stabilizers during foaming, because the films rupture when thin spots are formed inside them. These results evidence that the low-molecular–mass surfactants are more efficient during foaming than the strongly associated surfactant–polymer complexes.

The stronger interactions in the bulk, which are achieved in our study by decreasing pH or by the presence of ethoxy fragment in the surfactant head-group, leads to even slower formation of the adsorption layer on the solution surface (see Figs. 9A and S3), which in turn leads to lower foamability and lower film stability at pH 6. To verify this explanation, we measured by dynamic light scattering the size of the polymer–surfactant aggregates in SDS–PVAm and SDP1S–PVAm solutions, at pH 6 and pH 10 (instrument Zetasizer Nano ZS, Malvern, UK). In agreement with the observed

effects of pH on the kinetics of adsorption and foamability, we found that the aggregates are much smaller at pH 10, where the surfactant–polymer interactions are weaker. Indeed, the hydrodynamic diameter of the aggregates was 15 nm for SDS–PVAm and 20 nm for SDP1S–PVAm at pH 10 (averaged by volume of the aggregates) versus 650 nm for SDS–PVAm and 550 nm for SDP1S–PVAm at pH 6.

It is important to emphasize that the discussion presented above refers only to the strongly interacting surfactant–polymer mixtures, in excess of the polymer, as those studied in the current paper. As shown in Ref. [39], strong synergistic effects with respect to both foaming and foam stability were observed with weakly interacting surfactant–polymer mixtures.

#### 4. Conclusions

The effect of the cationic polymer polyvinylamine (PVAm) on the foaming and surface properties of the solutions of two anionic surfactants (SDS and SDP1S) was studied. The main results and conclusions from the performed study could be summarized as follows:

1. The foamability of the solutions containing oppositely charged surfactants and polymers decreases strongly with the increase of the degree of ionization of polymer molecules (in our experiments controlled via variation of solution pH). This effect is associated with an increased lag-time in the adsorption process for building a dense adsorption layer (as evidenced by dynamic surface tension measurements) and the related lower stability of the newly formed foam films.
2. The stability of SDS + PVAm foams is much higher than the stability of SDS foams, in the entire range of surfactant concentrations (0.03 to 0.1 mM) and pH values studied (between 6 and 10).
3. Much lower stability of the SDP1S+PVAm foams was determined, especially at pH 6, as compared to SDP1S foams without polymer.
4. The different effect of PVAm on the stability of SDS and SDP1S foams is explained with the formation of stronger complex between SDP1S and PVAm in the bulk (compared to SDS and PVAm). This complex adsorb very slowly on the solution surface (as evidenced by surface tension measurements) which leads to much lower stability of the newly formed SDP1S+PVAm foam films, compared to the SDS + PVAm system. Similar kinetic effects explain the fact that the stability of the polymer–surfactant foams increases with the increase of pH, which is related to a shorter characteristic adsorption time for formation of dense adsorption layer on the bubble surfaces.

The main conclusion from the study is that the excessive attraction between the surfactant and polymer molecules in their mixtures could be a serious problem with respect to the foamability and foam stability of the respective solutions. Especially from the viewpoint of foam generation, the weakly interacting systems have shown obvious benefits and synergistic effects – see the results in Ref. [39]. With respect to the foam stability, the strong interactions could be beneficial or detrimental, and these effects could depend strongly on the specific surfactant and/or the specific procedure for foam generation.

From the performed comparison of SDS and SDP1S solutions, one sees that the effect of cationic polymers on the foaming properties of anionic surfactants could depend significantly on the specific head group of the surfactant. Furthermore, opposite effects could be observed with different surfactants of the same charge. Therefore, any generalization about the role of polymer–surfactant interactions in the foaming properties, which are based only on



consideration of the charge–charge interactions in these systems, should be considered with great caution.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2013.01.021>.

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