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ORIGINAL CONTRIBUTION

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Isoelectric state and stability of foam films, bubbles and foams from PEO–PPO–PEO triblock copolymer (P85)

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Abstract Influence of pH of P85 copolymer solutions on stability of microscopic foam films (static conditions), lifetime of single bubbles at solution surface (quasi-static conditions), volume of the foam formed (dynamic conditions) and time of rupture of the foam column was investigated. Variations of the film equilibrium thickness as a function of pH were determined for different ionic strengths of the solutions using microinferometric method, while the combined pneumatic–mechanical method was applied in experiments on foams. It was found that lowering the pH reduced stability of the foam films, and at lower ionic strength the films ruptured at pH 2.9 (isoelectric point). Simultaneously, the lifetime of single bubbles was much shorter at lower pH of the P85 solutions. The average life, $t_{av,}$ was 11.1 s at pH 5.8, while at pH 3.0, only 3.1 s. Under dynamic conditions the pH lowering did not significantly influence the solution foamability.

Keywords Foam · Foam film · Single bubble · “pH-isoelectric” · P85 triblock copolymer

Introduction

The knowledge of the properties of the microheterogenous components of foam systems, mainly of thin liquid films formed between foam bubbles offers a better understanding of the physicochemical factors determining the stability of foam systems [1–3]. At the same time thin liquid films are well understood and there are models, widely investigated, to study the forces of interaction in colloidal systems. It is rather well established [4–6] that specific forces of interactions in thin layers (van der Waals, electrostatic, steric, structural, etc.) are responsible for the stability of foam films under static conditions. It has been well illustrated [7–9] that at constant ionic strength a lowering of the solution pH leads to a decrease in the potential of the diffuse electric layer ϕ_0 in foam films. Then, the pH value is reached at which only rupturing films of critical thickness are observed, i.e., there is a transition from an equilibrium to a non-equilibrium state. At this point (called the *isoelectric points* pH* [4, 7, 8]) the ϕ_0 decreases steeply, reaching almost zero. If the films are not ruptured but a transition from one type of the film to the other is observed, then this pH is denoted pH_{CR} [10, 11]. Values of the pH* and pH_{CR} depend on the surfactant type and concentration, ionic strength of the solution, temperature, etc.

Water soluble amphiphilic copolymers have been applied in many different areas such as foamers, defoamers emulsifiers, dispersants, thickeners, rinse aids, solubilizers, dispersion stabilizers, for drug delivery, in biosystems, for metal nanoparticles synthesis and stabilization, etc. [12–17]. Their ability to adsorb and modify the interfacial properties can be easily tailored as they have blocks with different affinity for solvent and interfaces. Blocks which interact favorably with the interface undergo adsorption, while other blocks having higher affinity towards the solvent extend into the bulk solution [18].

The paper presents the results of investigations on the influence of the isoelectric state at the solution/air interface on the stability of foam films under different conditions (static, quasi static and dynamic). ABA triblock copolymer Synperonic P85 was used as it has a low molecular weight and shows properties similar to typical non-ionic surfactants, i.e., sterical forces of interactions are small in this case, as shown in [6]. To find the pH of the isoelectric state of the interface, the dependence of the thickness of the microscopic foam films on the pH of the P85 copolymer solutions was determined. The thickness of single foam films, lifetime of single bubbles, volume of the steady state foam column and time of rupture of the foam column formed, were measured to evaluate the importance of the isoelectric state of the interface for the stability of foam films formed from the same P85 solutions but existing under very different conditions.

Methods

Microinterferometric method

The microinterferometric method of Scheludko and Exerowa [19–21] in its latest improvements [22] was applied in the foam film experiments. The method enables us to measure directly the surface forces acting in foam films; to study both equilibrium and non-equilibrium films of various kinds—foam and emulsion films, and films on a liquid or solid substratum. The critical thickness of rupture of unstable films can also be studied by this method. The cell with a glass film holder used in the present study is displayed in Fig. 1. Film thickness (h) is measured at constant capillary pressure. The cell was enclosed in an all-glass chamber (not shown) saturated with solution vapor. A microscopic foam film ($d=100$ μm) was formed in the middle of a biconcave drop hanging in the glass film holder ($d=3.8$ mm). A small portion of the liquid was sucked out of the drop through the capillary and ultimately a thin liquid film was created. The film thinned out and finally one of the several possible final states, i.e., an equilibrium thickness, critical thickness, black spot and black film formation or rupture was observed.

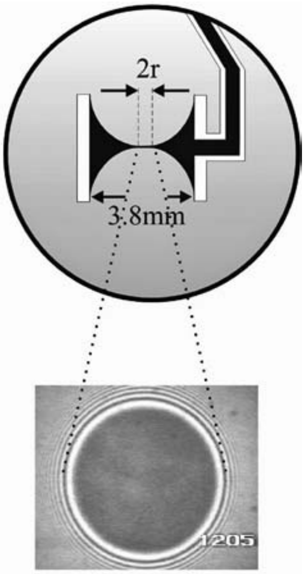

Fig. 1 Film holder of the Scheludko–Exerowa cell and a picture of the microscopic thin liquid film formed there

The capillary pressure

The capillary pressure, P_c was measured in a separate experiment. A tube, identical to that in which the biconcave drop was created, was immersed vertically into the solution. The liquid column height was measured with a cathetometer and P_c = hydrostatic pressure was calculated.

Single bubble experiments

Single bubble experiments were carried out using the experimental setup described in detail elsewhere [23]. The setup consisted of: (1) glass column ($\phi=50$ mm) with capillary of inner diameter 0.18 mm at the bottom of column, (2) gas supply system and (3) CCD camera connected to the recording and analyzing systems. The bubble formation frequency at the capillary orifice was carefully controlled by applying a precise infusion/withdrawal syringe pump (Cole–Parmer Instruments) with gas-tight glass syringes. It assured that the time of formation of every single bubble at the capillary orifice was similar and the intervals between subsequent bubbles were long enough (ca 40–60 s) to exclude all disturbances caused by the previous bubble rupturing at the solution surface. When the buoyancy force overcame the capillary force, the bubble detached and then reached the solution surface located at a distance of 6.4 cm from the capillary orifice (Fig. 2). The lifetime of the single bubble at the solution surface was measured automatically as a time interval between the bubble appearance and its rupture at the solution surface. A CCD camera coupled with a JVC BR-800E professional video recorder, and a PC with an appropriate software was used to determine the lifetime of the bubbles. The lifetimes of ca 150 separate bubbles were measured for every set of the conditions studied.

The combined pneumatic–mechanical method

The combined pneumatic–mechanical method was used to measure the foamability of the copolymers solutions under dynamic steady-state conditions. The steady-state volume of the foam was measured as a function of the gas flow rate and the rotational speed of the mixer, using the glass cylindrical vessel with a sintered glass disk at the bottom [24]. A glass mixer with four frames connected at the bottom to a ring was located just above the solution level, i.e., the glass ring of the mixer was touching the solution surface.

Time of rupture (lifetime) of the foam column

Time of rupture (lifetime) of the foam column was determined as the time between the cutting-off of the gas supply and switching-off of the mixer and the moment of appearance of a solution mirror. Every measurement was repeated at least three times and the mean values were determined.

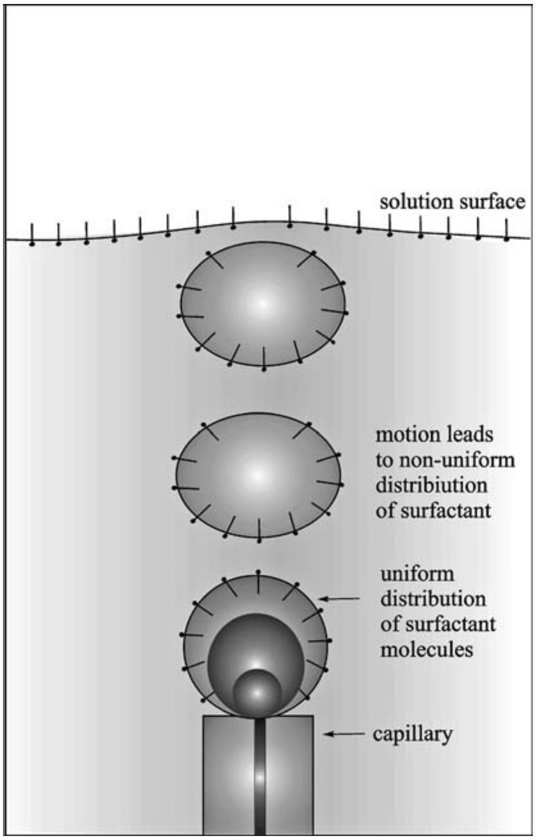

Fig. 2 Schematic of single bubbles formation, motion in the bulk and foam film formation at solution surface

Materials

The PEO–PPO–PEO triblock copolymer of polyethylene oxide (PEO) and polypropylene oxide (PPO) Synperonic P85 ($EO_{27}PO_{39}EO_{27}$, $M=4.600$) were received from ICI surfactants. Sodium chloride (NaCl) was always added to maintain a constant ionic strength of the solution. NaCl was heated to 550°C prior to use in order to eliminate any surfactant contamination. The solution pH was adjusted by addition of hydrochloric acid (HCl).

Results and discussion

The effect of pH on the thickness, *h*, of single foam films formed from 3×10^{-6} M aqueous solutions of the P85 copolymer is depicted in Fig. 3, which shows the $h=f(\mathrm{pH})$ dependences at two different values of the ionic strength I (for 1–1 electrolyte; $I=C_{\mathrm{el}}$). Constant ionic strength of the solutions was ensured by keeping the total concentration (NaCl + HCl) constant while varying the NaCl/HCl ratio. Figure 3 shows that the overall trend is very similar for both ionic strengths (3×10^{-4} and 1×10^{-3}). Within the pH range 5.6–4 a plateau is observed. Further pH lowering led to a continuous decrease of the film thickness. It is seen that at higher ionic strength (Fig. 3, curve 1), within the pH range 5.6–3.8, either thick films or black films were obtained at identical pH, i.e., this is a metastable zone [6, 9] (dotted lines

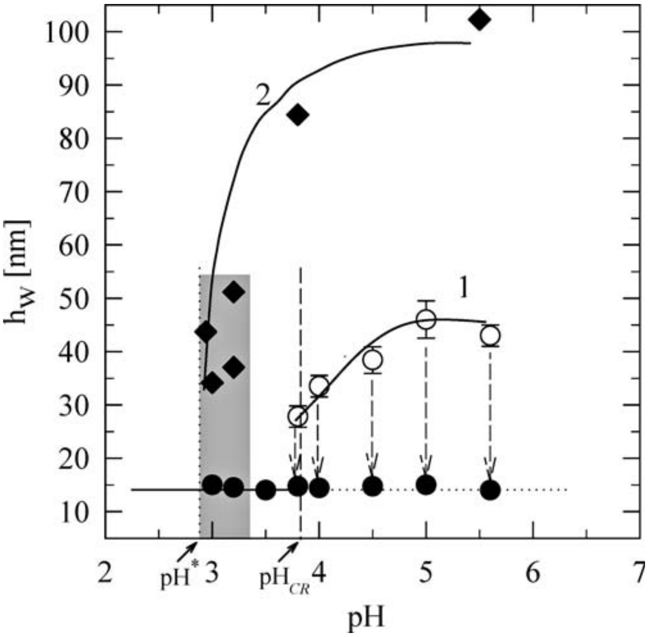

Fig. 3 Film thickness h_w vs pH for single foam films from P85 solution of concentration 3×10^{-6} M, *curve 1* ionic strength $I=1\times10^{-3}$ and *curve 2* ionic strength $I=3\times10^{-4}$ (except points below pH 3.8)

in Fig. 3). Below pH$_{CR}$ 3.8 only the black films were formed and their thickness (15 nm) was pH independent. At lower ionic strength (Fig. 3, curve 2) the equilibrium thick films were formed in the pH range 5.6–3.8 and there was no transition to black films. However, when the pH was decreased to 2.9–3.2, then either equilibrium or rupturing films were observed. This pH range is a zone of metastable films and is marked gray color in Fig. 3. When the pH reached the isoelectric point, pH* (pH 2.9, vertical dotted line in Fig. 3), then every film ruptured. Similar results for non-ionic surfactants have been reported earlier [4, 6, 8, 9, 24, 25].

When the solution pH decreases the bulk concentration of H^+ ions increases and consequently their adsorption at the solution/air interface increases. Here, they recombine with an excess of the potential-forming OH^- ions and the negative charge is neutralized. Thus, the ϕ_0 potential decreases and eventually vanishes at the pH* and therefore every microscopic foam film ruptured at this pH. Values of the potential of the diffuse electric layer ϕ_0 can be determined by the equilibrium foam film method [4, 7] using the DLVO theory [26, 27]. The potential of the diffuse electric layer ϕ_0 can be estimated from experimental data of the film thickness h and capillary pressure P_c. At known electrolyte concentration, C_{el}, of the solution forming the microscopic foam film, the ϕ_0 potential value, was calculated from the theory of electrostatic disjoining pressure. As seen in Fig. 3 , at low electrolyte concentration (3×10^{-4} M) and for pH > 3.8, the equilibrium CTFs (common thin films) with $h\geq80$ nm were formed. It is well known that for such film thickness none other than electrostatic and van der Waals forces act. The van der Waals component of disjoining pressure can be neglected here, because the films are thick ($h > 80$ nm). Thus, the ϕ_0 values were calculated using a software enabling solving the full equation of Poisson–Boltzman [28] for the electrostatic component of the disjoining pressure. For film thickness 84 ± 1 nm, $\phi_0 = 26 \pm 0.8$ mV was obtained, while for the thickness 90 ± 1 nm the $\phi_0 = 31 \pm 1.5$ mV. Similar values of ϕ_0 for non-ionic surfactants have been reported earlier [4, 9].

The results of measurements of the lifetime of single bubbles at the free surface of P85 solutions are shown in Fig. 4a, b for pH 5.5 and 3.0, respectively. The lifetime is shown as a function of the "bubble number", i.e., of successive bubbles reaching the solution surface. As seen, the lifetimes of single bubbles are randomly scattered and no dependence of the lifetime on the bubble number can be noticed. In other words, no time dependent effect was observed, because the higher the "bubble number", the longer the time from the start of the experiment. Lack of any time dependent effect indicates that we always succeeded in avoiding the possible adsorption and accumulation of surface active contaminants from within the measuring system and/or from the laboratory atmosphere. Comparing data of Fig. 4a, b it is clearly seen that for the lower pH (3.0), the bubble's lifetime is significantly shorter ($t_{av} = 3.1 \pm 1.8$ s) than for pH 5.5 ($t_{av} = 11.1 \pm 3.9$ s). When the bubble reaches the solution surface, the top of the bubble forms the bottom interface of the film and a local area of the solution surface constitutes the top interface. The state of the adsorption layers at both interfaces of the foam film formed determines the bubble lifetime. Shorter lifetime of the bubbles at the surface of the P85 solution of pH 3.0 shows straightforwardly that the foam film stability is lower at this pH. Thus, these results are in good agreement with the results obtained for microscopic foam films (Fig. 3).

Figures 5 and 6 present the volume of the foam formed under steady state conditions from 3×10^{-6} M solutions of P85 as a function of the gas flow rate and the mixer speed. Steady state means that the foam is under dynamic conditions and identical numbers of the foam elements are formed and ruptured at a given

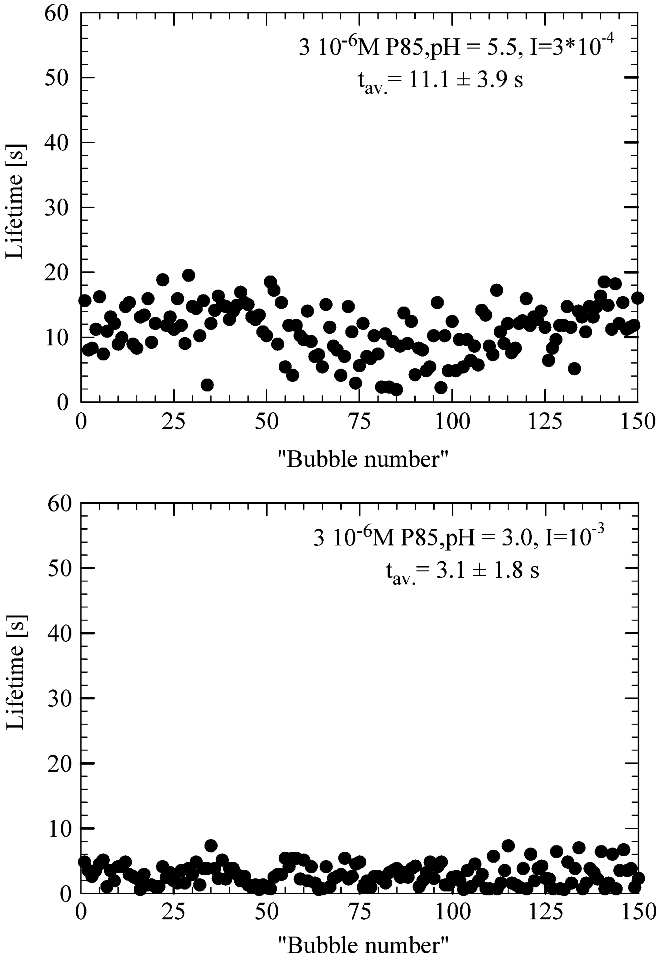

Fig. 4 Lifetimes of single bubbles at the free surface of P85 copolymer solutions of pH 5.5 (*top part*) and pH 3 (*bottom part*)

period of time. Dynamic condition means that there is a lot of both internal and external disturbances (there is a permanent motion and rupture of foam bubbles, drainage of liquid from the foam films and Gibbs–Plateau borders, falling droplets from rupturing top foam films, pressure shocks—rupture of a foam cell causes a pressure shock for the neighboring cells, etc). Moreover, the foam column is under centrifugal force exerted by the mixer and the foam elements are constantly "hit" by frames of the mixer. As a result the foam films of the dynamic foam (even the thinnest ones, which are at the foam top layer) have rather low chances to reach the equilibrium thickness observed in the case of the microscopic films under static conditions. As seen in Fig. 5 there are minor differences in the volume of the foam formed from solutions of pH 3 and 5.5—they are noticeable only at higher gas flow rates. Nevertheless, we can see that the trend is similar—at lower pH the volume of the foam formed under steady state conditions is smaller. A similar picture can be noticed in Fig. 6, but the effect of the mixer rotation on the volume of the foam formed is more complicated. This kind of dependence of the foam volume on the mixer speed, *n*, is discussed in detail elsewhere [24].

There are two opposite effects exerted on the foam column by the mixer rotation as shown in [24]: (1) effect of the centrifugal motion generated and (2) mechanical impact of the mixer's frames on the foam films. The first slows down the gravitational drainage of solution from the foam column and therefore is advantageous for foam stability. The second one is destructive—foam films are ruptured due to the impact of the glass frames of the rotating mixer. The relative importance of the two effects varies with the speed of the mixer. At lower speed the centrifugal force effect is the more important with the result that the foam volume increases with increasing mixer speed. At higher speeds, the destructive mechanical impact of the mixer's frames prevails and the volume of the foam formed diminishes. Mechanical rupture of the foam films by rotating frames of the mixer occur most probably at greater thickness and it seems reasonable to assume that with increasing speed the thickness of rupturing films increases leading to a reduction of the volume of the foam formed. Moreover, when the thickness of the foam films at rupture exceeds the distances of the repulsive interactions of the adsorption layers (electrostatic component of the disjoining pressure) then the pH cannot influence the volume of the foam formed under steady state conditions. As seen in Fig. 6 this was observed for mixer speeds above 600 rpm. Thus, the data of Figs. 5 and 6 clearly illustrate that under dynamic conditions the foam films

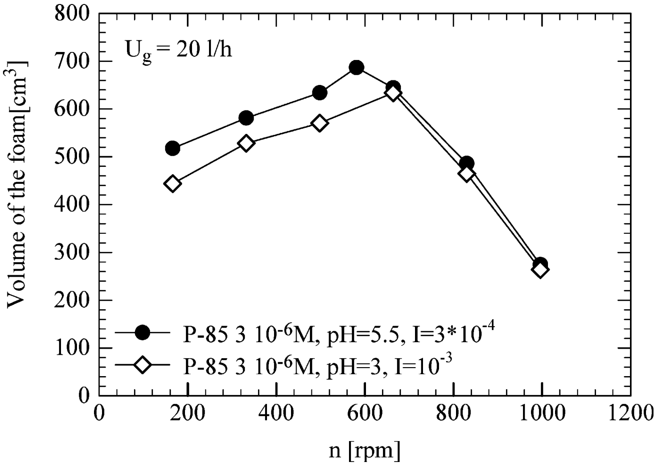

Fig. 6 Volume of the foam formed from P85 solutions of different pH as a function of mixer speed at constant gas flow rate (20 l/h)

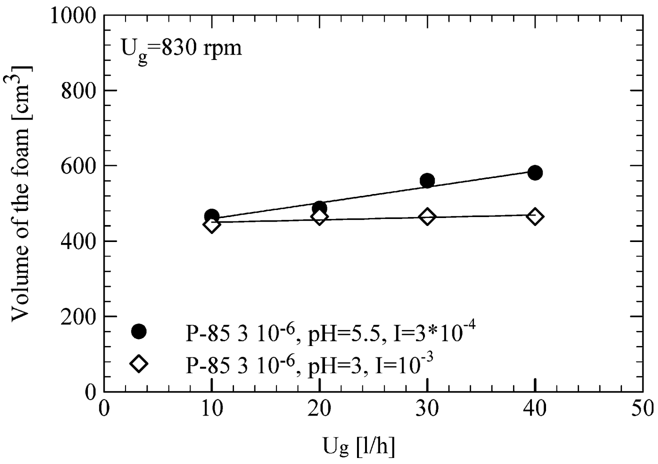

Fig. 5 Volume of the foam formed from P85 solutions of different pH as a function of gas flow rate at constant mixer speed (830 rpm)

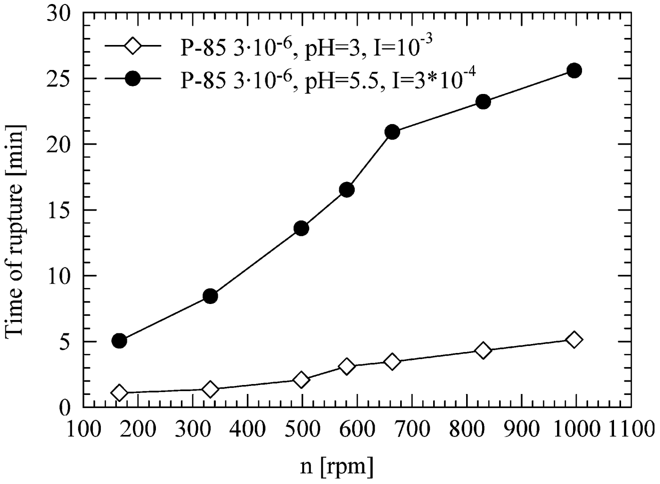

Fig. 7 Time of rupture of the foam column formed from P85 solutions of different pH

ruptured at thickness larger than the distance of electrostatic double layer repulsions.

The results presented in Fig. 7 are, in our opinion, additional, illustrative evidence showing the importance of external conditions on the stability of the foams formed from P85 solutions. These results also clearly show the increasing importance of the electrostatic state of the film interface for foam stability when the system "moves" towards more and more static conditions. The values of the time of rupture of the foam column formed from 3×10^{-6} M P85 solutions of pH 3.0 and 5.5 at gas flow rate 20 l/h and mixer speeds in the range 150–1,000 rpm are compared. In both series of experiments the foam columns were formed under identical conditions and when a steady state foam volume was obtained the mixer and gas supply to the measuring cell were switched off. Then the time of rupture, i.e., the time from the moment of switching-off the gas supply and mixer rotation until the appearance of the solution mirror was measured. At the beginning of the measurements the foam columns were under identical dynamic conditions. With elapsing time the conditions under which the foam columns existed were shifting from very dynamic towards more and more quasi-static. Thus, after the mixer switching-off, the chances that the foam films could approach their equilibrium thickness were increased and therefore the effect of pH was very clearly noted there. As seen in Fig. 7, at pH 5.5, the time of rupture of the foam column was significantly longer. For example, at $n=660$, the time of rupture was 21 min for pH 5.5, while only 4 min for solution pH 3.0. Thus, when the conditions of the foam existence were shifted towards quasi-static, the importance of the isoelectric point (pH*) was clearly manifested again. At lower pH, the stability of foam films was lower and therefore the times of rupture of the foam column were much shorter.

Quasi-static conditions mean that there was a smaller number of various kinds of external disturbances and therefore the foam films had higher chances to reach their equilibrium thickness and/or distances of the electrostatic interactions. This is the reason why the time of rupture of the foam column formed from P85 solutions was significantly lower for pH 3.0 than for pH 5.5. Under static conditions, as shown above (see Fig. 3), every foam film ruptured at the isoelectric point (pH^*). These results also indicate that under dynamic conditions the films in the top layer of the steady-state foam ruptured at a thickness larger than the distance of interactions of the electrical double layer of both film interfaces. Therefore, as shown above (Figs. 5 and 6), there was practically no influence of pH on the volume of the foam formed under dynamic steady-state conditions. These data show how important are the conditions under which foam properties are evaluated, because different factors can be of major importance under different conditions of the foam formation and existence.

Concluding remarks

The stability of single foam films and lifetime of single bubbles formed from P85 copolymer solutions diminish at the isoelectric point of the interface, while the volume of the foam formed under dynamic conditions is almost unaffected. However, the time of rupture of the foam column formed was much shorter at the isoelectric point.

Depending on the ionic strength of the solutions, either rupture of the common thin films at the isoelectric point (pH* 2.9) or transition to CBFs ($h=15$ nm) at pH_{CR} 3.8 was observed. Using the measured thickness h of the film and capillary pressure values, the potential of the diffuse electric layer ϕ_0 was determined from the DLVO theory.

The external conditions under which the foam films of P85 solutions were formed and existed were of high importance for their stability. Under quasi-static conditions the stability of single bubbles and foams was affected by the isoelectric state of the interface in a manner similar to the stability of the microscopic foam films under static conditions. The lifetime of single bubbles at the surface of a P85 copolymer and the time of rupture of the foam column were significantly shorter at pH 3.0 than at pH 5.5. Under steady state conditions, the volume of the foam was practically unaffected by the pH changes. This shows that the foam films here were ruptured prior to reaching the thicknesses at which the electrostatic component of the disjoining pressure started to operate.

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