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Review

Polyelectrolyte/Surfactant Mixtures: A Pathway to Smart Foams

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Cite This: https://doi.org/10.1021/acsomega.2c05739

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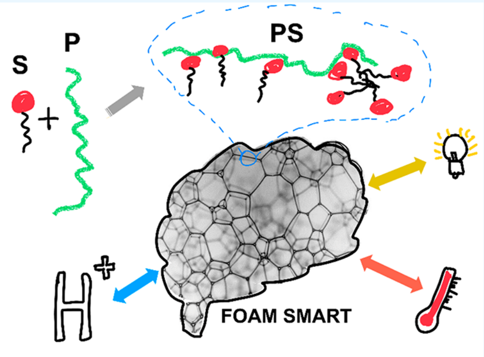
ABSTRACT: This review deals with liquid foams stabilized by polyelectrolyte/surfactant (PS) complexes in aqueous solution. It briefly reviews all the important aspects of foam physics at several scales, from interfaces to macroscopic foams, needed to understand the basics of these complex systems, focusing on those particular aspects of foams stabilized by PS mixtures. The final section includes a few examples of smart foams based on PS complexes that have been reported recently in the literature. These PS complexes open an opportunity to develop new intelligent dispersed materials with potential in many fields, such as oil industry, environmental remediation, and pharmaceutical industry, among others. However, there is much work to be done to understand the mechanism involved in the stabilization of foams with PS complexes. Understanding those underlying mechanisms is vital to successfully formulate smart systems. This review is written in the hope of stimulating further work in the physics of PS foams and, particularly, in the search for responsive foams based on polymer-surfactant mixtures.



1. INTRODUCTION

The search for responsive materials capable of reacting via some external stimulus is a very active area of research in soft matter physics and technology.[1] These kind of systems are extensively produced and studied in the field of drug delivery and nanomedicine to encapsulate and release chemical agents. The possibility of triggering release by an external stimulus, for example by applying light or electric or magnetic fields in a remote way, is of fundamental importance for the successful targeting of the active drug at the right place. Polyelectrolyte/surfactant (PS) mixtures exhibit such a rich variety of behavior[2−7] that their use is being investigated in a large number of new technological applications. Today they are present, or being considered, in technologies used for the oil, paint, and personal care industries, in wastewater treatment, as gene carriers in gene therapy, and in encapsulation in drug delivery systems, to name but a few.[8,9] PS mixtures can also be used to stabilize aqueous foams, with applications in cosmetics,[10] shampoo formulation,[11,12] medicine, pharmaceutics, and oil and food industries.[13] Here, these systems will be considered to formulate smart foams. These are chemical systems whose foamability, that is, the ability to produce foams, and the stability of the foam they produce can be modulated when the foam is subjected to an external stimulus. The stimuli can be a magnetic or electric field, temperature, pH, and light, among others.[14−17] Foam responsiveness is attained via foam stabilizers, chemical systems that can respond to external stimuli in different ways. A paradigmatic example of this kind of system is that formulated with 12-hydroxystearic acid (12-HSA) mixed with hexanolamine,[18] whose foam responsiveness is due to a structural transition of the self-assembled aggregates of 12-HSA, triggered when the temperature exceeds 60 °C. Another example, in this case a light-responsive foam, is the one formulated with a photoswitchable surfactant published by Chevallier et al.[19] They used AzoTab, a surfactant containing an azobenzene group that changes from a cis to a trans-isomer when illuminated with UV or blue light. The structural changes undergone by the surfactant molecules under illumination produce a dramatic modification of the foam stability. Fameau and Fujii[17] recently reviewed all the work done on smart foams up to the year 2020.

The complexation process between polyelectrolytes and surfactants is mainly driven by physical interactions among species, being the shape, size, and physicochemical features of the complexes, the result of an intricate balance between the attractive and repulsive forces between polyelectrolyte and surfactant molecules. Since the interactions are mainly of physical origin, the complexation process and the features of the complexes depend on physical conditions, such as pH, temperature, or ionic strength.[4,20−22] The reason why polymer-surfactant mixtures are good candidates for the formulation of smart systems lies on their dependence on these physical conditions, since by changing them it is possible,

Received: September 4, 2022
Accepted: September 26, 2022

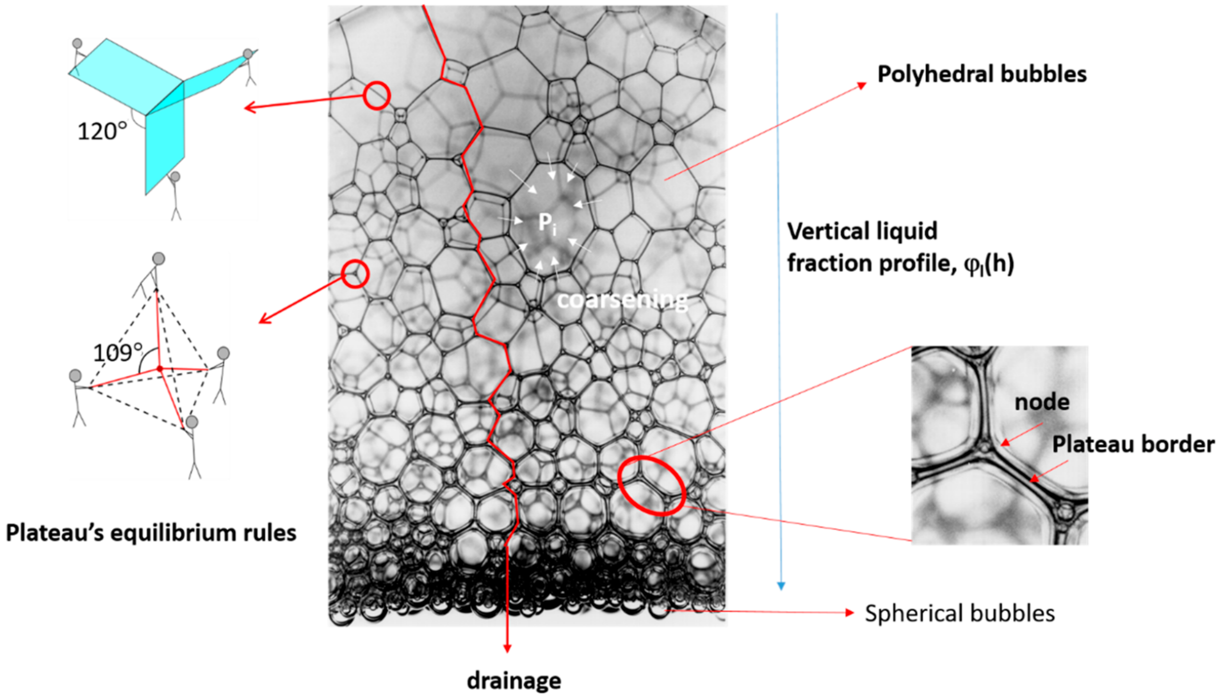


Figure 1. Foam in the gravity field. Liquid drains out of the foam through the PB and nodes. A vertical liquid profile develops; at the bottom, where the liquid fraction is high, bubbles are spherical, and at the top, they are polyhedral. For dry foams, at the top, plateau local equilibrium rules are maintained. Due to pressure differences between neighboring bubbles (Laplace, $\Delta P \sim 1/r$), they coarsen and gas flows from small bubbles into large ones. Reprinted with permission from ref 41. Copyright 2020 Elsevier.

in principle, to modulate their properties. If polymer-surfactant complexes adsorb onto the air−water interface, they could be used for creating responsive foams.[17]

This paper will shortly review the main aspects of aqueous foams stabilized with polymer-surfactant mixtures. It will also examine the equilibrium and dynamics of air−water interfaces covered with polymer-surfactant complexes, mainly with mixtures of synthetic polyelectrolytes and oppositely charged surfactants in relation to foam formation and stability. Special cases of PS mixtures with biopolymers, particularly with proteins, will not be discussed and are beyond the scope of this review. At the end of this paper, work done on smart foams designed using polymer-surfactant mixtures as stabilizers will be highlighted, and the origin and mechanisms of response to external stimulus for these particular PS systems will be discussed.

This review is not intended to be exhaustive and cover all that has been done on these systems but rather highlights the works that the author, with personal bias, considers relevant, especially those necessary to address responsive foam systems and understand the challenges that the area faces.

2. LIQUID FOAMS: A BRIEF OVERVIEW OF BASICS

Liquid foams are formed by the dispersion of a gas in a liquid matrix.[23−25] The physics of foams has been reviewed from different points of view in many review articles and books,[23−27] the last of which was published by Dominique Langevin in the year 2020.[28] Foams are ubiquitous systems found in human industries and daily life but also in nature.[26] They are metastable systems with a limited lifetime that depends on many factors. Foams, being out of equilibrium system, continuously evolve toward their true thermodynamic equilibrium state, which is the complete phase separation. Metastability is attained by slowing down or arresting the three main processes that drive liquid foams to their final end, namely drainage, coarsening, and coalescence.[24,29,30] This is achieved by adding foam stabilizers that are surface-active agents, which confer certain properties to the interfaces between liquid and gas. The most commonly used foam stabilizers are surfactants; however, polymers, proteins, and particles, as well as their mixtures among others, can also be used.[31−38] Mixtures of polymers and surfactants[13] present some advantages as foam stabilizers, the main ones being the enhanced stability and the low surfactant and polymer concentrations needed to produce and stabilize foams. In general, the improvement in foam stabilization when using PS complexes is due to the presence of polymers at the interfaces, to which they confer an increased viscoelasticity when compared to simple surfactants.[39]

Both the structure and the shape of bubbles in foams depend on the relative contents of gas and liquid.[40] This is commonly represented by the liquid volume fraction, $\varphi_l = V_l/V_f$, with V_l and V_f being the volumes of liquid and foam, respectively. For large liquid fractions, bubbles are spherical as the result of minimizing interfacial energy, but as φ_l is reduced, bubbles pack together and compress against each other as liquid drains and films get thinner (see Figure 1) and deform adopting shapes of polyhedra. When $\varphi_l < 0.05$ (dry foams), liquid films separating bubbles smoothly meet three at a time at 120° angles. This is known as the first Plateau equilibrium rule.[24] The intersection of these films forms liquid channels between adjacent bubbles; these channels are called Plateau borders (PB). They meet four at a time in a vertex or node at approximately 109° angles; this is the second Plateau equilibrium rule.[24] PB and nodes form a network through which liquid can flow by gravity and capillarity (see Figure 1).

To create foams, some work[42] (e.g., to shake them) is required to deliver the energy needed to create the interfaces, which is given by the product of the surface tension, γ, and the total area created, A. Surface-active agents help to reduce the surface tension and thus the energy needed to create the bubble interfaces. Once created, foams are trapped in one of many metastable states; the selected state depends on the system history, but for a given liquid fraction, the geometry of both the bubbles and the foam structure is determined by the minimization (local minimum) of the interfacial area[40] (i.e., the interfacial energy). Surface active agents reduce surface tension but also confer surface viscoelasticity[39] to the interfaces, enhancing the ability of liquid films to resist thermal fluctuations and increasing their stability by arresting all or some of the processes mentioned above: coalescence, drainage, and coarsening.

Drainage refers to liquid flow through the PB network. This flow is driven by gravity and capillarity. Immediately after freshly forming, liquid begins to drain out of the foam due to gravity; the top of the foam becomes dry while the bottom, in contact with the liquid, remains wet (Figure 1). A vertical profile of liquid content develops along the height of the foam until it reaches a stationary state, in which the force of gravity is balanced by the vertical pressure gradient.[43] There are some theoretical models for the drainage dynamics in foams.[27,29] The problem is very complex, but it has been solved for dry foams and for the case of forced drainage in which, once the foam reaches the stationary liquid fraction profile, liquid is added at the top of the foam column. In this case, a liquid front travels down the foam at a constant velocity (v). In the model, the PB network is replaced by randomly oriented cylinders where the velocity profile can be plug-like or Poiseuille-like, depending on whether the interfaces are mobile (low shear surface viscosity) or rigid (high shear surface viscosity), respectively. In both cases, the expression for the front velocity reads,[29]

$$v = K\frac{\rho g L^2}{\eta}\phi_L^{\alpha} \tag{1}$$

where ρ is the liquid density, g is the gravity constant, η is the liquid viscosity, K is a dimensionless number describing the foam permeability (an analog to the permeability in Darcy's law for flows in porous media), L is the PB length, and α is an exponent that varies between 1 for rigid interfaces and 0.5 for mobile surfaces.

The continuous change in bubble size as foam ages is known as coarsening or disproportionation, and it is due to gas diffusion among adjacent bubbles with different gas pressures. Larger bubbles grow at the expense of smaller bubbles that shrink. The Young−Laplace equation[44] states that the internal bubble pressure varies as the inverse of its radius, thus gas tends to diffuse from small bubbles to large ones.

$$\Delta P = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)\gamma \tag{2}$$

where ΔP is the pressure difference inside and outside the bubble and r_1 and r_2 are the main curvature radii. Given that in order to transfer from one bubble to another the gas must dissolve in the liquid films separating the bubbles, coarsening is not possible for perfectly insoluble gases. Coarsening is slowed down if bubbles are all exactly the same shape and size (monodisperse). In that case, the Young−Laplace equation, eq 2, dictates that they all have the same internal pressure, and there is no driving force for gas diffusion. However, even for perfectly monodisperse foams, coarsening is not completely arrested due to thermal fluctuation that produces the transient defects that initiate the coarsening process. The rate of disproportionation also depends on the kind of surface-active agent used. Gas has to pass through the interface covered by surface−active molecules (surfactants, polymer, particles, etc.) that can act as barriers.[35] Coarsening is also arrested when the interfacial compression modulus reaches a value equal to approximately half the surface tension, a result predicted by Gibbs.[45] There are well-established theoretical models for coarsening in 2D foams,[24,27] but the situation is different for 3D foams.[46,47] For future reference, a useful expression for the coarsening rate is[48]

$$\frac{dL^2}{dt} = 2\frac{8\delta_A}{3\delta_V\beta}\frac{\gamma D_m H_e V_m}{h}f(\phi_L) \tag{3}$$

where δ_A, δ_V, and β are geometrical variables that depend on bubble area and volume, L is the average length of the Plateau borders,[48] H_e is the Henry constant (a measure of gas solubility in the liquid), D_m is the gas diffusion constant through the film, $f(\varphi_L)$ is a function that tends to 1 for very dry foams,[49] V_m is the ideal gas molar volume, and h is the thickness of the film separating bubbles. Note that coarsening dynamics is proportional to the gas solubility (H_e) and diffusivity (D_m) through the film, which includes any barrier due to the complex surface layers, and inversely proportional to the film thickness (h).

The process of foam coalescence[30] refers to the rupture of the liquid films separating bubbles in a foam. Today there are two models in vogue, both considering different types of thermal fluctuations. The first model, proposed by Sheludko and extended by Vrij,[50] is based on the assumption that a film ruptures because of thermal fluctuations in the film thickness. For certain fluctuations, an instability occurs that cannot be damped and grows leading to film rupture. This process is controlled by surface tension and disjoining pressure.[25] Disjoining pressure plays a fundamental role in the stabilization of liquid films in foams and is defined as,

$$\Pi_d(h) = -\left(\frac{\partial U}{\partial h}\right)_{S,V,\mu_i,A} = \Pi_d^{(\mathrm{elec})} + \Pi_d^{(\mathrm{vdw})} + \Pi_d^{(\mathrm{non-DLVO})}\ldots \tag{4}$$

Π_d is the interaction force per unit area between the two facing interfaces of the liquid film separated by a distance h. From the thermodynamic formalism it is defined as the derivative of the internal energy, U, with respect to the film thickness, h, at constant entropy, volume, chemical potential, and area. The disjoining pressure contains contributions from attractive van der Waals forces ($\Pi_d^{(\mathrm{vdw})}$), repulsive electrostatics ($\Pi_d^{(\mathrm{elec})}$), which are called DLVO (Derjaguin−Landau−Verwey−Overbeek) forces,[51,52] as well as short-range non-DLVO contributions, such as hydration (forces originated from ordering of dipoles under confinement or hydrogen bonding), steric, hydrophobic forces, etc.[25,28,53]

Exerowa et al.[54] and de Gennes[55] proposed that fluctuations in the interfacial surfactant concentration are responsible for film ruptures instead of fluctuations in film thickness. De Gennes gave an expression for the nucleation characteristic time, τ_c, for holes (regions without surfactant), which should vary exponentially with the interfacial compression elastic modulus, E_0, as,[30,55]

$$\tau_c \sim \exp\left(\frac{E_0 a}{k_B T}\right) \tag{5}$$

where a is the area occupied by surfactant molecules at the interface. These fluctuations can produce regions or holes without surfactant molecules at the interfaces. If the size of these regions is greater than a certain critical value (typically on the order of half the film thickness), the hole grows and the film breaks. As stated above, in this case the rupture is controlled by compression surface elasticity. Both Scheludko-Vrij and Exerowa-de Gennes models have been developed for single isolated films; however, the coalescence dynamics of a macroscopic 3D foam is much more complicated.[41,56−62] Drainage, coarsening, and coalescence, when considered separately, act on different time scales. The stationary vertical profile of the liquid fraction is established by drainage in a few minutes; coarsening might last from minutes to days, but the rupture of a single film occurs in a fraction of seconds. Despite this separation of time scales, in macroscopic foams, the three processes affect each other and cannot be separated easily, thus they need to be considered simultaneously in modeling foam dynamics.[63] In this respect, experiments in microgravity are very useful to study the foam dynamics in the absence of drainage and better understand the coarsening and coalescence mechanisms and the behavior of wet foams.[64] They also permit one to perform force drainage experiments to study the effect of surface shear rheology (see eq 1), simplifying the modeling of the experimental data.[65]

3. POLYMER/SURFACTANT COMPLEXES AT EQUILIBRIUM IN BULK, AT INTERFACES, AND CONFINED WITHIN LIQUID FILMS

The first step in the search for understanding PS systems as foam stabilizers is to study them in bulk and at interfaces under stationary or equilibrium conditions. The distinction between true equilibrium states and stationary metastable states is necessary because PS complexes frequently remain kinetically trapped in nonequilibrium metastable states, both in bulk and at interfaces, whose features depend on the history of the systems, for example, on mixing protocols or the time elapsed before preparation.[6,66−70]

The complexation of polymer and surfactants, both in bulk and at interfaces, has been the subject of work for decades;[9,20] this work has been reviewed over the years many times and from different points of view.[2,3,6,7,22,31,71−76] Here, the intention is not to provide a detailed overview of all the work done but to highlight the main aspects necessary to understand polymer-surfactant systems as foam stabilizers. First, the phase behavior of PS mixtures must be briefly discussed. For a more exhaustive review on the phase behavior, see the review by Piculell[4] referring specifically to oppositely charged PS mixtures, which are the most common systems found in foams, or the more general one by Guzmán et al.[3]

3.1. PS Complexation in Bulk and Phase Diagrams. The phase behavior of PS mixtures is very complex, and the structures of the complexes they can produce are very rich.[6,77,78] This richness stems from the multitude of variables that come into play in the association process between polymers and surfactants, which modulate their interaction and complexation mechanisms.[9,79] The formation of PS aggregates can lead to a stable colloidal dispersion of micelle-like aggregates or soluble complexes, or to precipitates, gels, and even coacervates. Phase separation occurs via associative or segregated phase separation.[4,9] The phase diagrams as well as the structure of the aggregates depend, as mentioned, on a large number of parameters. These include the charge density on the polymer, the rigidity or flexibility of the polymer chain, the molecular weight and degree of branching, the charge ratio between polymer chains and surfactant molecules, the type of counterions carried by polymer and surfactant molecules, the hydrophobic/hydrophilic balance of surfactant molecules and the chemical groups on the polymer chain, the presence of other components in the mixture such as salt, physical conditions such as temperature or pH, and polymer and surfactant concentrations. Because of the large number of variables to be taken into account, the search for generalities in the features and phase behavior of these systems is a very difficult task. Figure 2a shows schematically a phase diagram for PS mixtures, which are the most common mixtures used as foam stabilizers, as mentioned above. In Figure 2a, Z = [P]/[S] is the ratio of charged monomers on the polymer chain, [P], to surfactant concentration, [S], both expressed in monomers, and C is the total concentration. The particular ratio Z = [P]/[S] = 1 = 1/Z is often referred to as the equivalence point (EP) in mixtures of oppositely charged polymers and surfactants, and it is commonly associated with the onset of phase transitions. These type of phase diagrams is generally obtained from a turbidity plot. Figure 2b shows an example of such a plot. In that figure, the light intensity transmitted through the PS solution was measured as a function of concentration, typically the surfactant concentration at a constant polymer concentration and temperature. From this type of plot, phase diagrams of PS mixtures (Figure 2a) can be constructed.[80]

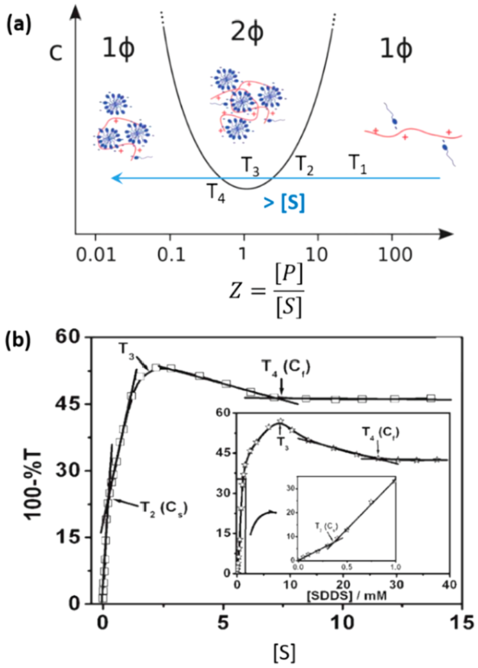


Figure 2. (a) Schematic phase diagram for PS mixtures, indicating the one- and two-phase regions. Adapted with permission from ref 72. Copyright 2013 RSC. (b) Turbidity plot for a PDADMAC-SDBS mixture, transmittance (T) is plotted as a function of surfactant concentration [S]. Adapted from ref 80. Copyright 2011 American Chemical Society.

In the following, a general but oversimplified picture of the association process and its correlation with phase behavior will be presented. It should be noted that, depending on the chemical systems and their particular interactions and on physical conditions such as pH or temperature, this picture might deviate from a particular real system. That said, when we add a surfactant in steps to an aqueous solution of a polyelectrolyte, no physical change is observed if the surfactant concentration remains very low ($Z \gg 1$). This region falls into the molecular solution region, where single surfactant molecules attach to the polymer chain, as depicted in Figure 2a for large *Z* values (low surfactant concentrations). This is mainly driven by the entropic gain due to the release of polymer and surfactant small counterions. As the surfactant concentration increases, a first evidence of PS complexation is observed at a characteristic surfactant concentration. This concentration is the critical aggregation concentration, cac, also called T1 concentration (see Figure 2a). The T1 point, which is not seen in the turbidity plot in Figure 2b but it is clearly seen in surface tension measurements in Figure 3 and will be discussed later, indicates the onset of the cooperative aggregation process. T1 (or cac) occurs at concentrations 1 to 3 orders of magnitude lower than cmc, the surfactant critical micelle concentration, and it is driven mainly by hydrophobic interactions among surfactant molecules, for which polymer chain sites act as nuclei. The aggregate structure in this region is typically of the micellar type, forming either a pearl-necklace structure[81] or a dense pack of micelles linked by the polymer chain.[72,82−86] Further addition of the surfactant continues the PS aggregation process until a second characteristic concentration point, T2, is reached. This concentration can be identified by an inflection point on the turbidity plot (see Figure 2b). T2 often indicates the entrance into a two-phase region and frequently coincides with a *Z* value close to 1 (see Figure 2a). Neutralization of the colloidal charge and an increased hydrophobicity of the aggregates result in precipitation of the complexes (associative phase transition). For some PS systems under certain conditions, multichain aggregates, coacervates, and gels can form in this concentration region.[3,4,6,67,72,73] If the surfactant concentration is further increased, $Z \ll 1$ precipitates can redissolve giving rise to soluble complexes. This occurs at another characteristic concentration, generally called T3, and is often associated with a charge inversion of the colloidal dispersion[87] and a change in aggregate structures.[72] This process is accompanied by a turbidity decrease (see Figure 2b) until a T4 concentration is reached. At $[S] > \mathrm{T4}$, free surfactant micelles form and turbidity remains constant. For some PS systems, T3 and T4 closely coincide and cannot be distinguished.

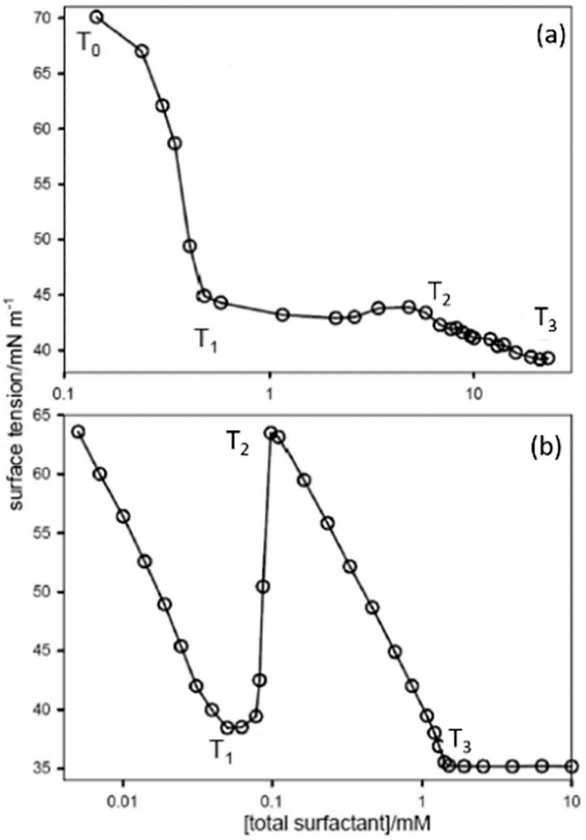


Figure 3. (a) Type 1 surface tension isotherm showing a plateau between T1 and T2; system: PSS(100 ppm)/DTAB. The concentration T0 is defined as the concentration at which the surface tension begins to fall. (b) Type 2 surface tension isotherm exhibiting a peak; system: PDADMAC(10 ppm)/SDS + 100 mM NaCl. Adapted from ref 103. Copyright 2018 American Chemical Society.

The presence of solid precipitates, gels, or even droplets of coacervates has an impact on the formation and stability of foams; for example, those soft particles can clog the Plateau border channels, effectively reducing the foam permeability constant (*K* in eq 1), stopping or slowing down the drainage velocity, and helping to increase the stability of foams.[88,89] They can also produce the opposite effect on foam stability, destabilizing the liquid films: some PS particles, particularly if they are hydrophobic, can help to break the films between bubbles by the bridging effect.[23,90,91]

3.2. Surface Tension Isotherms. The features of PS complexes at interfaces under stationary or equilibrium conditions will be discussed below. Air−liquid interfaces covered with PS complexes have been studied for decades, starting with the work of Goddard and co-workers in the 1970s.[92,93] In the late 1990s, Langevin and co-workers studied the correlation between the features observed in PS surface tension isotherms and the features of polyelectrolytes such as flexibility or rigidity.[94−97] Closer in time, many reviews have been published dealing with PS complexes at interfaces.[3,6,75,98] The features of surface tension isotherms cannot be fully understood without considering the behavior of PS complexes in bulk. Bulk and interfacial behavior of PS complexes are coupled through thermodynamics due to the condition of equality of the chemical potentials in all present phases, including the water−air interface. In the 2000s, Thomas and co-workers, using neutron reflectometry (NR), correlated the structure of oppositely charged PS mixtures at interfaces with surface tension isotherms measured on the same systems.[99−101] They found two types of behavior: a "type 1" PS mixture for which the surface tension isotherm showed a surface tension plateau characterized by interfaces that were covered with thick layers (multilayers)[102] and a "type 2" mixture that exhibited abrupt peaks in the surface tension isotherms and more compact layers (monolayers). Prototypical examples of PS mixtures for these two representative limiting behaviors would be poly(sodium styrenesulfonate)/dodecyltrimethylammonium bromide (PSS/DTAB) for type 1 and poly(diallyldimethylammonium chloride)/sodium dodecyl sulfate (PDADMAC/SDS) for type 2.[103]

They revisited these two PS systems[103] and related the shape of the surface tension isotherms, the one with a peak and the one with a plateau, to the PS binding process in bulk. They correlated the binding isotherms, measured by potentiometry using surfactant-selective electrodes, with the surface layer structure, studied by NR, and with the surface tension isotherms. The appearance of peaks in the surface tension in the type 2 system is attributed to the formation, at a certain threshold of the total surfactant concentration close to the phase boundary, of nonsurface-active, poor soluble complexes in the region with $Z > 1$. In this case, surface tension values could be explained by nonassociated surfactant molecules that adsorb at the interface giving rise to a monolayer with a high surface tension (due to a depleted free $[S]$). Hence, if the surfactant concentration is increased above the concentration for which the nonsoluble aggregates redissolve due to a charge inversion and a structural change of the aggregates (between T3 and T4 in the turbidity plot in Figure 2b), this can lead to complexes that become surface active again, producing a drop in surface tension. This process results in the surface tension peak observed in the isotherms. Authors thus explain the shape of the surface tension isotherms by the different degrees of cooperativity observed in the binding isotherms. For PDADMAC/SDS (type 2), the weak direct interaction of the surfactant with the polyelectrolyte binding sites results in a complexation process driven mainly by the surfactant–surfactant interaction in previously bound surfactant molecules (i.e., a cooperative binding process) that occurs close and above T1. For $[S] <$ T1, the PS complexes are surface active and the surface tension is low, but for $[S] >$ T1, the cooperative binding produces high stoichiometric aggregates that are not surface active, and a surface tension peak is observed. On the contrary, for type 1 mixtures such as PSS/DTAB, the direct interaction between individual surfactant molecules and polyelectrolyte binding sites are stronger than for PDADMAC/SDS. This leads to a more gradual complexation process dominated by noncooperative binding, resulting in a variety of complexes with different surface activities depending on their stoichiometry. Because of this progressive noncooperative binding process, there is no reason for a surface tension peak at the onset of the phase transition for this system, and a plateau is observed instead.[103] However, this interpretation was a matter of controversy because of possible nonequilibrium effects.[73] Varga and Campbell, for the same PS mixtures, have convincingly demonstrated experimentally that the features of type 1 surface tension isotherms are a consequence of the presence of kinetically trapped (i.e., out of equilibrium) PS complexes in bulk and at interfaces,[87] due to very slow complexation dynamics in bulk. The aggregates formed in PSS/DTAB mixtures take weeks, even a month, to equilibrate (see Figure 4); in the meantime, there are kinetically trapped aggregates that can adsorb and dissociate onto the water–air interface lowering the surface tension, this being responsible for the plateau observed in these mixtures. If enough time is given to PSS/DTAB systems to reach equilibrium, the plateau becomes a peak as it does for PDADMAC/SDS mixtures, as can be clearly seen in Figure 4. Thus, Vargas and Campbell claim that peaks are characteristic of true equilibrium (type 2), whereas plateaus indicate kinetically trapped complexes in a nonequilibrium near-stationary state (type 1). This certainly seems correct for the two particular systems studied: PSS/DTAB and PDADMAC/SDS; however, it does not necessarily apply to all possible PS mixtures,[94] particularly if no phase separation occurs after the equivalence point of charges ($Z \sim 1$) is reached.[94,97,104,105] In this regard, Li et al.[102] have recently reviewed the formation of multilayers, a feature of type 1 PS systems, at the air–water interface, providing arguments and examples that seem to indicate that some PS surfaces are at equilibrium, even if in bulk they are not fully equilibrated. Further work is clearly needed, particularly on systems for which surface tension plateaus have been reported in short-term experiments that should be revisited.

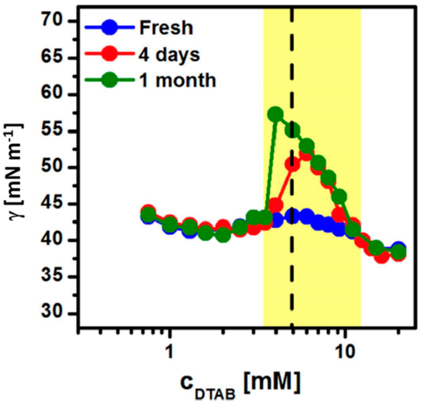


Figure 4. Surface tension isotherms for PSS/DTAB mixtures as a function of equilibration time. Note how the peak develops with time, showing that type 1 isotherms become type 2 if enough time to equilibrate is given. Adapted from ref 87. Copyright 2017 ACS.

However, important and interesting it may be, both from academic and applied perspectives, the impact of the equilibrium/nonequilibrium controversy on the understanding of foam formation and stability is probably relative. As discussed above, equilibrium is reached very slowly in these systems, from hours to months, but foam formation and the dynamics involved in foam stabilization occur on much shorter time scales, from seconds to hours generally. Unfortunately, to my knowledge, nobody has ever measured surface tension directly on films of a real foam stabilized with PS mixtures. Despite this, one could be fairly certain that the liquid–air interfaces in foams are far from equilibrium. Foam production involves some kind of work, agitation, or shear through constrictions such as pores, capillaries, microfluidic devices, etc.[42] Although very stable foams can be produced,[106] foams generally disintegrate in periods of time much shorter than the days, weeks, or months needed to reach equilibrium in bulk and at interfaces in PS surfactant mixtures.

3.3. Foam Films and Disjoining Pressure Isotherms. An additional issue related to foam stability is that polymer-surfactant complexes are confined within liquid films in a foam.[107,108] The study of foam films took a major step forward with the development of the thin film pressure balance (TFPB) by Mysels[109] and Exerowa.[25,110] The TFPB technique allows the disjoining pressure (eq 4) to be measured as a function of film thickness in foam films. The film is formed in a hole made in a porous glass plate, which is placed in a pressure cell that allows changing the external pressure in steps. The film thickness is measured by interferometry while the pressure in the cell is increased against the atmospheric pressure. As the pressure increases, the film drains and thins until the repulsive interaction between both films prevents further thinning until the equilibrium thickness for the applied pressure is reached. An example of a disjoining pressure isotherm can be seen in Figure 5.

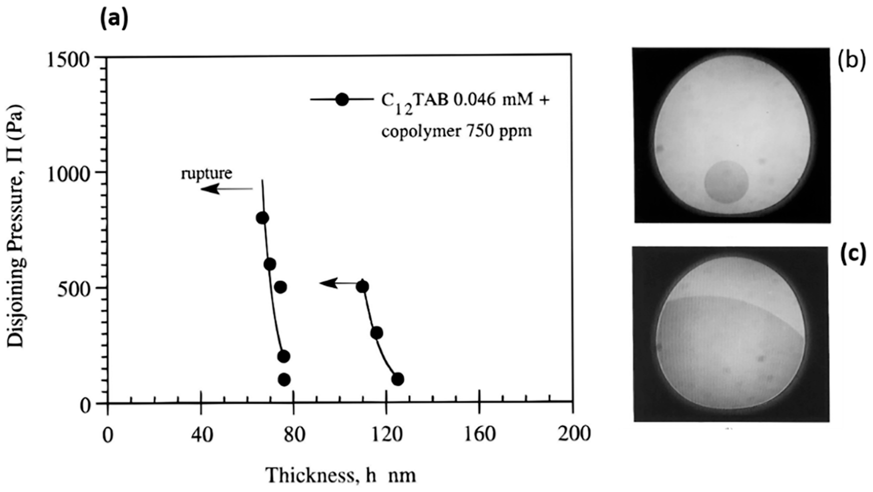


Figure 5. (a) Disjoining pressure isotherm for mixtures of PAMPS and DTAB; (b) and (c) are pictures showing the stratification process. In (b), a thin region nucleates; in (c), it propagates to the whole film. The film thickness transition ranges from 125 to 75 nm. Adapted from ref 94. Copyright 1996 American Chemical Society.

For aqueous solutions of pure surfactants at concentrations below cmc (i.e., in the absence of aggregates) Π(h) isotherms are characterized by a monotonic decrease in film thickness. The DLVO forces between both interfaces of the film eventually counterbalance the force due to the capillary suction and result in a common black film (CBF)[94] with typical thicknesses of a few tens of nanometers. Short-range forces, non-DLVO attractive forces, such as solvation forces, might enter into play and produce a transition to Newton Black Films (NBF), with thicknesses of only a few nanometers, typically ∼5 nm,[111] which eventually leads to film rupture. The situation is different when aggregates are present within the films. For simple surfactants, when $[S]$ > cmc, the film thinning dynamics by drainage is stepwise,[94,112,113] which is a consequence of structural oscillatory forces due to confinement-induced layering of aggregates.[94,112,114−116] The same behavior is encountered when films are stabilized by some polymer-surfactant mixtures.[94,117−122] PS films could thin continuously or stepwise (stratification), depending on whether the polymer overlaps or not.[94,117] The behavior and structure of PS complexes under this confinement has a direct impact on the stability of liquid films and thus, one would expect, on the stability of macroscopic foams made from them.[94] Foam film stability can increase or decrease with the addition of polymer compared to pure surfactant solutions.[117] By measuring the disjoining pressure isotherms, it was shown that the stability of foam films in mixtures of oppositely charged PS mixtures depends on the net charge of the aggregates within the films and adsorbed at the interfaces.[117] When the species adsorbed at the two approaching liquid interfaces that form the liquid films are equally charged, the charge repulsion increases the disjoining pressure stabilizing the films (positive contribution in eq 4). The net charge of the aggregates depends on the stoichiometry of the complexes, which in turn depends on PS interactions and on the relative surfactant and polymer concentrations, as discussed above. Thus, at a fixed polymer concentration, the foam film stability can have a nonmonotonous behavior, since by increasing $[S]$ the foam film stability can increase or decrease depending on whether the complexes are above or below the 1:1 stoichiometry ($Z = 1$). The same can be said for $[P]$, for high polymer concentrations and thin films, gel-like networks may form in the films increasing their stability[94] (this discussion will be returned to in the next sections). A typical disjoining pressure isotherm and images showing the stratification process are shown in Figure 5. The results in that figure are for mixtures of a copolymer made with acrylamide and acrylamide sulfonate (PAMPS) and dodecyltrimethylamonium bromide (DTAB) at surfactant concentrations bellow cac. At these low surfactant concentrations, long-range repulsive forces are present and, as the pressure increases, a discrete film thickness transition (stratification) is observed. The origin of this stepwise transition was explained as being produced by an interplay between electrostatic repulsion and attractive forces mediated by polymer bridging.[123−125] At concentration above cac, a dense layer of PS complexes is adsorbed to both air−water interfaces, producing very heterogeneous film thicknesses due to a gel-like network within the film. At these high concentrations, the film features strongly depend on the rate of film thinning; at low rates, the films are more homogeneous, probably because the polyelectrolyte chains have enough time to rearrange and accommodate in the confined film.[94] Related to this dynamic is the fact that stratification is generally observed for flexible polyelectrolytes such as PAMPS but not for rigid ones such as DNA or xanthan.[126] This again highlights the role of nonequilibrium states.[73] Gel-like films are also observed when formed from protein mixtures, depending on protein concentration and aggregate size.[127−129] In all cases, gel-like films are more stable than liquid films, which should result in more stable foams; however, more stable liquid films do not always produce more stable foams.[31] The mechanism behind the improvement of foam stability is multifold: as mentioned above, the presence of aggregates could block PB, reducing drainage velocity; the gel-like structure increases the film elasticity, reducing the local fluctuation stabilizing the films, and the presence of large aggregates at the approaching interfaces contribute to stabilize the film thickness by repulsive, electrostatic, or steric forces (see Section 2).

Film thinning dynamics and its dependence on chemical and physical variables is very complex, and it is beyond the scope of this review to discuss it in detail, for which I recommend published reviews[108,117,130] and books.[25,28] As far as I am aware, the impact on macroscopic foams of thinning dynamics in PS foam films has not been addressed. The important point to emphasize here is that such dynamics can be externally modulated, for example, by changing the PS interactions,[117,131] which in turn could be modulated by changing the pH for certain PS mixtures[132] or by irradiating at a specific wavelength.[133] Film stability can also be modified by changing ionic strength[113,134] or temperature.[135] This opens the door to the design of responsive films and, presumably, foams if these physical parameters could be modulated externally and remotely (see Section 6).

4. DYNAMICS OF POLYMER-SURFACTANT MIXTURES AT THE AIR–WATER INTERFACE

Liquid foams are hierarchical soft material that must be studied at different length scales[25] and largely controlled by interfacial properties. Typically, after studying the behavior of PS mixtures in bulk, the first step is to investigate the liquid−gas interfaces and films at equilibrium (see previous section). The second natural step is to do so under dynamic conditions. Finally, macroscopic foams, formed by thousands of such liquid films, are investigated trying to assess their foamability and stability in relation to the characteristic behavior in bulk and at air−water interfaces and liquid films (see Section 5). This section will focus on the dynamics of PS mixtures at the air−water interfaces.

4.1. Adsorption Kinetics and Dynamic Surface Tension. When considering interfacial dynamics in relation to foam formation and stability, two aspects must be taken into account. First, the adsorption process must be considered of surfactants, polymers, and PS complexes to a freshly created air−water interface, that is, the process of migration of these species from bulk to the interfacial region and their adsorption onto the air−water interface. This process results in a temporal evolution of the surface tension (and surface concentration or excess), which is commonly known as dynamic surface tension (DST).

Despite their importance in the understanding of foamability and foam stability, studies on adsorption dynamics and DST in aqueous solutions of PS mixtures are surprisingly scarce. In the 2000s, Ritacco et al. used a homemade maximum bubble pressure tensiometer (MBP) for measuring the DST of aqueous solutions of two statistical copolyelectrolytes with different charge densities, PAMPS25,[105] with 25% charged monomers, and PAMPS10,[136] with 10% charged monomers, both mixed with DTAB. Figure 6 shows a representative example of the temporal evolution of the surface tension for PAMPS25/DTAB at surfactant concentrations below cac. The surface tension goes from that of pure water, 72 mN m^{-1}, to an apparently constant value of about 64 mM m^{-1}. The true equilibrium value is 53 mN m^{-1} for this particular mixture, but the time window of the experiment is not long enough to see the final equilibration process, which last several hours.

In this short-time region, two plateaus are observed; the value of the first one is close to 70.5 mN m^{-1} (marked in the inset as short time) and the second slightly above 64 mN m^{-1} (marked as long time). The two dynamics are clearly separated in time and both are diffusional processes, which are evident from the linear dependencies with the inverse square root of time (see inset in Figure 6). The authors suggested that the shorter time adsorption process is due to the adsorption of the surfactant but slowed by the presence of the oppositely charged polymer. Similarly, the second diffusional process corresponds to the polymer diffusion but accelerated by the presence of the surfactant. This picture is consistent with the synergistic effect observed in the equilibrium surface tension of this system; without the surfactant, the polymer does not adsorb, and without the polymer, the absorbed amount of surfactant molecules is much lower. The final dynamical process to reach equilibrium was not experimentally accessed in the work. The plateau observed in DST curves is really visible at surfactant concentrations above the equivalence point (EP), $Z < 1$. For large surfactant concentrations, the DST curves become complicated and less reproducible, probably due to the adsorption/desorption of bulk aggregates during bubble formation in the course of MBP measurements. Campbell et al.[137] studied mixtures of PDADMAC and SDS. They combined ellipsometry, reflection infrared spectroscopy (ER-FTIR) with the overflowing cylinder technique (OFC) to measure the dynamics of adsorption of these PS mixtures and explained the adsorption dynamics as a consequence of a competition between the surface activity of the adsorbing species and mass transport to the interface. At low surfactant concentrations, below T1 ($Z > 1$), polymer and surfactant synergistically adsorb onto the interface and their dynamics is diffusion controlled, as observed for PAMPS/DTAB (Figure 6). For higher surfactant concentrations, large aggregates form, which are not surface active on the time scale of OFC experiments, due to their slower mass transport to the expanding interface. For $Z \ll 1$, only free SDS adsorbs onto the interfaces.

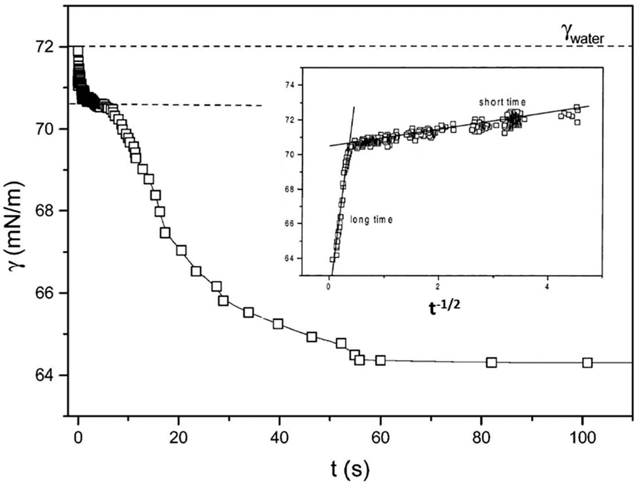


Figure 6. Dynamic surface tension for aqueous solutions of a statistical copolyeletrolyte made from polyacrylamide (75%)-polyacryalamide sulfonate (25% PAMPS25), mixed with 0.2 mM dodecyltrimethylammonium bromide (DTAB). The inset shows the same data but represented as a function of the square root of time (difussional). Adapted from ref 105. Copyright 2003 American Chemical Society.

Ritacco and Busch were the first to propose a two-state model[138] for analyzing the adsorption dynamics of PS mixtures. Their model is based on a model by Fainerman et al. for the adsorption of simple surfactants with two possible orientations.[139] They considered three dynamics: (1) the transport and diffusion of the surface-active agents from bulk to the interface, (2) the adsorption−desorption kinetic process, and (3) the reorganization process of adsorbed molecules on the interface. The authors interpreted the third dynamics not as a reorientation, as in Fainerman's work, but as structural changes of the surfactant as a consequence of complexation with the polymer at the interface. The model works quite well to explain the adsorption dynamics for PAMS/DTAB mixtures, as shown in Figure 7.

Even though at low surfactant concentrations adsorption is controlled by diffusion for the two systems presented above, for other systems and at higher surfactant concentrations, this could be different. In fact, Ritacco et al.[105] mentioned in their work

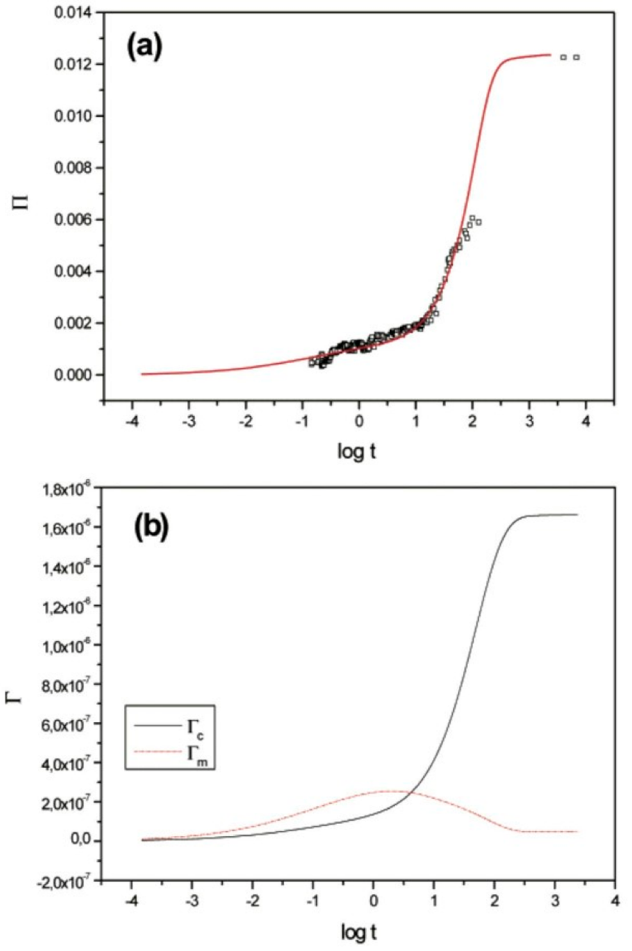


Figure 7. Two-state model. Systems: PAMPS10 175 ppm + DTAB 0.2 mM. (a) Surface pressure as a function of time, $\Pi(t) = \gamma_0 - \gamma(t)$, being γ_0 the surface tension of pure water. (b) Surface concentration for both states of the surfactant at the interface, Γ_m = surface concentration of the surfactant in state 1 and Γ_c = surface concentration of the surfactant in state 2. Reprinted from ref 138. Copyright 2004 American Chemical Society.

that, at [S] > cac, the aggregates might undergo a charge inversion and an electrostatic barrier might build up at the interface, making the adsorption dynamics kinetically controlled. Similarly, it was shown that the adsorption kinetics of poly(ethylene imine) PEI-SDS mixtures can be modulated by changing the pH. Angus-Smyth et al.[140] studied the adsorption dynamics of PEI/SDS at pH 4 and 10 using the OFC technique combined with NR and ellipsometry. They found that the adsorption kinetics strongly depends on the charge density of the polyelectrolyte. PEI charge density is higher, and the PEI-SDS interaction is stronger at pH 4 than at pH 10. At pH 10, aggregate formation in bulk depletes the number of PEI/SDS complexes and free SDS that can adsorb on the time scale of the expanding interface in OFC experiments, the adsorption rate being controlled by diffusion of the small complexes. In contrast, at pH 4, the large aggregates formed by the strong interaction enrich, under the dynamical condition of the OFC experiment, the surface excess by a nondiffusional convection/spreading mechanism. Unfortunately, none of the works commented so far has analyzed the effects of adsorption kinetics on foam formation and stability. This has recently been made by Martinelli et al.[132] for poly(acrylic acid) (PAA) mixed with a cationic surfactant, Gemini 12-2-12 (G12). They have demonstrated the effect of PAA charge density, which they modified by changing the pH, on DST and have shown how this affects foamability and foam stability. Further discussion of this work will be given later within the framework of responsive foams, but it is worth mentioning here that the DST curves present several relaxation times (see Section 6.2) and that the kinetics is not controlled by diffusion except at very low surfactant concentrations. A similar behavior was found for PDADMAC/SDS mixtures for which the DST was measured for several surfactant concentrations, exhibiting very complex dynamics with multiple relaxation times.[98] Another example of complex DST curves can be seen for PAA/DTAB mixtures.[141]

Llamas et al.[142] have recently investigated the adsorption dynamics in concentrated mixtures of PDADMAC with sodium *N*-lauryl-*N*-methyltaurate (SLMT) by NR and pendant drop (PD) tensiometry. Although some of their DST curves seem to insinuate the presence of plateaus similar to those shown by Ritacco et al.[105,138] (Figure 6), they did not mention it, probably because the plateaus seem to be at very short adsorption times. Unlike the maximum bubble pressure technique used by Ritacco et al., PD cannot be used for DST measurements below a few seconds. Even though the authors explained the dynamic adsorption behavior for PDADMAC/SLMT mixtures as the result of a two-step process and they discussed the two-state model, they were not able to fit their data as it was done for PAMPS/DTAB mixtures.[138] The two-step adsorption process was also invoked for PDADMAC/sodium lauryl ether sulfate-(SLES) solutions in order to explain the adsorption dynamics at the air−water interface.[143]

4.2. Surface Rheology. When dealing with foams, the dynamics related to surface rheology[57] must be considered. Surface rheology for soluble species depends on the adsorption/desorption dynamics (inside and outside the interface), as well as the dynamics and interactions of the adsorbed species at the interface (in plane).[144] For pure surfactant solutions, it has been shown that compression elasticity plays a role in the dynamics of bubble coalescence (see eq 5) and in the dynamics of coarsening.[57] High frequency surface compression (dilational) elasticity controls coalescence, and low frequency surface compression elasticity is involved in the dynamics of coarsening. For pure surfactants, shear elastic moduli are generally close to zero and shear viscosity is small,[144] but when the interface layer contains polymers, they can confer high interfacial shear viscosities. This might change the boundary conditions (i.e., the interfacial mobility) on the liquid flow through PB[145] from slip to nonslip condition, modifying the drainage dynamics in foams,[146,147] and thus their stability (see section 2, eq 1, α parameter). Therefore, the study of interfacial rheology, both dilational and shear, at the air−water interfaces for PS mixtures is of fundamental importance to understand the features of foams stabilized with them. Noskov and co-workers wrote some fine reviews on surface dilational rheology in PS mixtures, some from a historical perspective,[148] some including protein−surfactant systems,[149] and some focusing on heterogeneities of the adsorption PS layers and kinetically trapped aggregates.[98] PS complexes often give rise to strongly heterogeneous surface layers[98] that result in highly nonlinear responses in interfacial rheological experiments.[150] To illustrate their behavior, only a few examples of PS systems in the context, whenever possible, of foams will be described.

Probably the first study relating dilation surface elasticity of PS mixtures to foam stability is the one by Bhattacharya et al.[151]

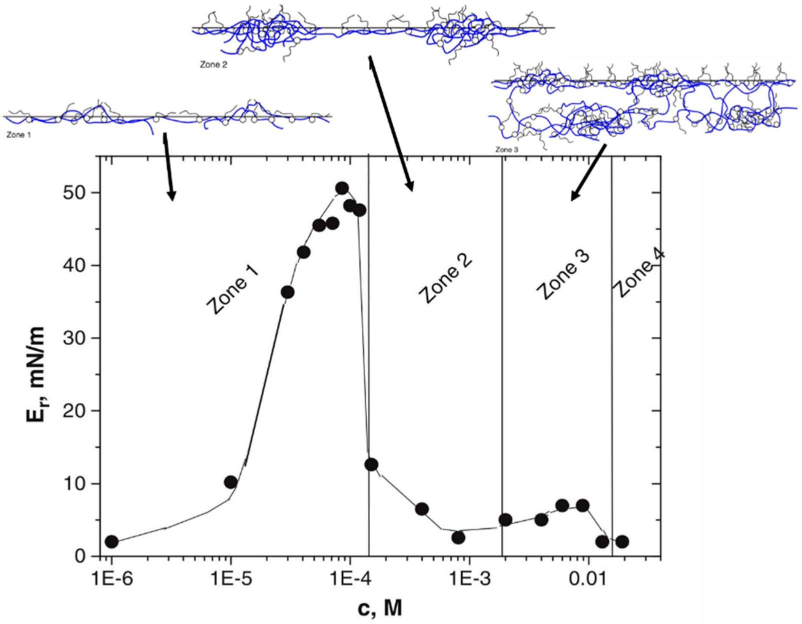


Figure 8. Elastic moduli (Er) at a frequency of 0.075 Hz (oscillating ring) of PAA/DTAB solutions as a function of surfactant concentration (c). The structural transitions of the surface layer from each zone to the other are schematized in the figure. Adapted from ref 141. Copyright 2009 American Chemical Society.

They used an excited capillary wave (ECW) setup to measure the elastic compression and loss moduli of DTAB mixtures with three polymers: PAMPS10, PAMPS25, and xanthan. All mixtures present peaks in the moduli measured at 600 Hz as surfactant concentration increases (at $[P]$ = cte). The peaks occur at surfactant concentrations close to cac (T1) for PAMPS25 and xanthan (for PAMPS10, the cac is not well-defined). However, these peaks do not correlate with the foamability and foam stability of PS mixtures. Ritacco et al.[96] revisited these same systems but characterized the interfaces by X-ray reflectometry (XRR) and ECW and found that it is not straightforward to compare foaming behavior with the properties of interfacial layers in these systems. They also found that the layers are viscoelastic for PAMPS and xanthan. At $[S]$ < cac, they behave as incompressible layers, similar for both polymers. Differences in mechanical responses are observed only under large-area deformations: xanthan still behaves as insoluble layers, even above cac, whereas PAMPS is partially soluble. The authors ascribe this to the backbone rigidity of the polymers and use it to explain the observed differences in foam film stabilities. PAMPS films are very stable, whereas xanthan films are impossible to form. Peaks and abrupt decreases in surface elasticity are observed with increasing surfactant or polymer concentration in many other PS systems.[141,152,153] It has been suggested that abrupt changes in surface dilational elasticity are related to the formation of heterogeneous surface layers with spatially separated regions of high and low concentrations of complexes.[98,141] Figure 8 shows as an example the elastic modulus for PAA/DTAB solutions as a function of surfactant concentration.[141] As for xanthan/DTAB and PAMPS/DTAB, there is a peak.[98] For some systems, however, the behavior is more complicated and more than one peak may be seen.[141] Four zones or regions are identified in Figure 8. In zone 1, surface elasticity increases continuously until it reaches a maximum, indicating the formation of a rigid interface. In zone 2, elasticity drops abruptly, and the surface tension response to sinusoidal oscillations in the area contains higher harmonic contributions, and the systems become nonlinear.[141] The drop in surface elasticity coincides exactly with the beginning of nonlinear surface tension responses to area oscillations. It is assumed that, under compression, aggregates form at the interface (see scheme in Figure 8) and mass exchange between the aggregates at the interface keep the local concentration constant under compression/expansion cycles, and the elasticity drops. These in-plane relaxations eventually make the surface layers viscoelastic in zone 2. In zone 3, the DST curves show a plateau, as in PAMPS/DTAB in Figure 6 but at longer times, after which equilibrium is reached. The size of these plateaus decrease as surfactant concentration increases. In this region, surface elasticity as a function of surface age presents two local maxima (see Figure 9 in ref 141) corresponding to the times at which surface tension plateaus begin and end. This behavior is related to surface layer heterogeneity and nonlinear responses (see structural schemes in Figure 8). In this region, as surfactant concentration increases further, the number and size of complexes in the surface region augment; they start to interact with each other, and the surface elasticity increases again (see the scheme in Figure 8). NR showed the formation of multilayers at surfactant concentrations of zone 3.[154] The process involved in the formation of these multilayers could explain the second maximum observed in the curves of surface elasticity as a function of surface age mentioned above.[98] Finally, in zone 4, the surfactant concentration surpasses the surfactant cmc (>T4), and the interfacial dynamics becomes controlled by the excess of free surfactant monomers. At these low frequencies and concentrations, the elasticity is close to zero.

From the theoretical point of view, to the best of my knowledge, there are no theoretical models capable of fully describing the experimental results on surface rheology in polymer-surfactant solutions. Theoretical expressions were derived for the complex dynamic surface elasticity, E, in the case of a single adsorbing entity (surfactant molecule, polymer, complex) for which mass transport to the interface is controlled

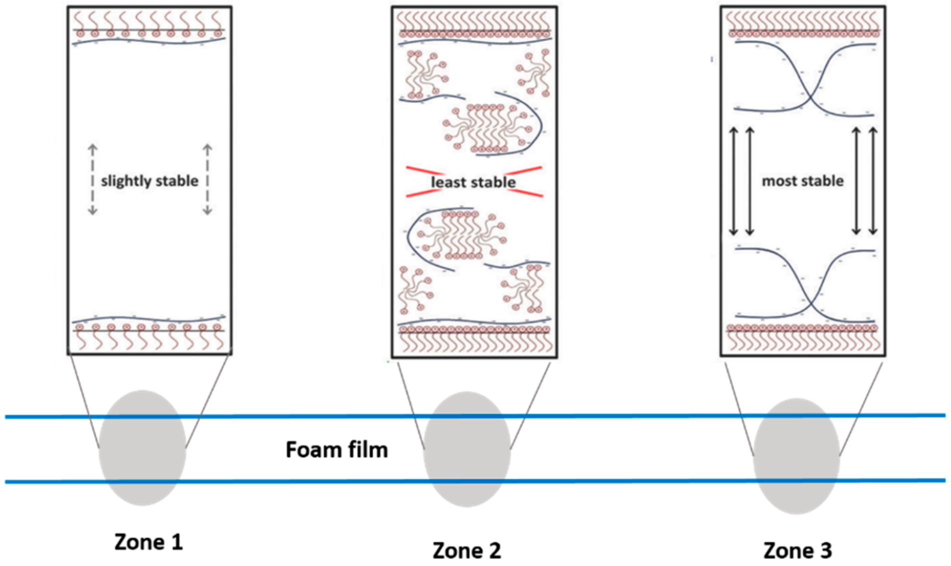


Figure 9. Schematic representation of the different surface layer structures for the three zones of the (sPSO2−220)/TTAB mixtures in relation to foam film stability. Adapted from ref 159. Copyright 2020 Royal Society of Chemistry, Creative Commons.

by diffusion and, once adsorbed, can undergo a single relaxation process inside the interfacial layer at the liquid−gas interface[155]

$$E = E_0 \frac{i\omega\tau + (1 + i)/2\zeta}{1 + i\omega\tau + (1 + i)/2\zeta} \tag{6}$$

where

$$E_0 = -\frac{d\gamma}{d\ln\Gamma};\ \omega_D = \frac{D}{2}\left(\frac{dc}{d\Gamma}\right)^2;\ \zeta = \left(\frac{\omega_D}{\omega}\right)^{1/2}$$

γ is the surface tension, Γ is the surface concentration or excess, D is the diffusion coefficient of the adsorbing entity in bulk, τ is the relaxation time of the process inside the interfacial layer (in plane), and ω is the angular frequency. Note that this model is somehow the counterpart for the complex surface elasticity of the two-state model for DST discussed above. In the limiting case of $\tau \approx 0$, eq 4 reduces to the Lucassen-van den Tempel model.[156] However, given the complexities of PS dynamics in bulk and interfaces, the applicability of these simple models is very limited. For example, for PS mixtures, there are several adsorbing species: surfactant monomers, polymer chains, PS complexes of different composition and size, and the relative amount of each of them changes with polymer and surfactant concentrations; this makes the model in eq 6, which considers only one adsorbing species, too simple to explain the dynamics. Additionally, as described above, the dynamics within the surface layer, which for some concentrations include the formation of multilayers, are by far much more complex than the single relaxation considered in eq 6.

The description provided above is certainly incomplete, covering only a few examples of experimental systems, whereas other PS mixtures present many different particularities. For a more complete discussion of surface rheology in PS mixtures, please consult the specific reviews.[98,148,149]

5. FILM AND FOAM STABILITY IN POLYMER/SURFACTANT SYSTEMS

The usual historical approach to studying and rationalizing the stability of macroscopic foams is in terms of individual liquid films and interfaces: stable films should give rise to stable macroscopic foams, consisting of thousands of such films. This approach works relatively well when dealing with solutions of simple surfactants. Stable foams[28] are expected when there are low surface tension values (reducing the energy to create bubble surfaces), fast adsorption dynamics (favoring foamability), and when the dilational interfacial elasticity is high, which helps the film to resist fluctuations (see section 2, eq 5) and reduce coarsening rates (Gibbs criterium: for $E \sim \gamma/2$[28]). Similarly, high shear viscosities and small interfacial mobilities should reduce drainage dynamics, like high bulk viscosities. However, even for simple surfactant solutions, many foams stabilized with them do not show the expected correlation among foam stability, interface features, and individual film stabilities. The stability of some foams is mainly controlled by collective dynamics, quite independent of film and interfacial features.[41,61]

For PS mixtures, the correlation between interfaces and films properties and macroscopic foam stability is indeed worse because even for isolated foam films no clear correlation between film stability and, for example, surface tension, surface elasticity, or surface potential could be established.[117,153,157,158] A step forward in understanding foam film stability was recently made by Uhlig et al.[159] with well-designed NR experiments using different isotopic contrast conditions that allowed them to establish the different surface layer structures for mixtures of sulfonated poly(phenylene sulfone) (sPSO2−220) with tetradecyltrimethylammonium bromide (TTAB). They focused on how the surface layer structure of the two approach interfaces in foam films interacts and related them to liquid film stability. (sPSO2−220)/TTAB mixtures present, like PAA/DTAB in Figure 8, three zones in the curves of surface elasticity, surface tension, and surface excess versus polymer concentration. Note that the authors in their experiments kept the surfactant concentration constant and varied the polymer concentration, whereas in Figure 8 the polymer concentration is constant and the surfactant concentration varies. The fourth zone shown in Figure 8 is not mentioned in this work because the only surfactant concentration used is below cmc. In zone 1, in which the polymer concentration is below the equivalence point ($Z \ll 1$), the surface layer structure corresponds to a layer of surfactant molecules adsorbed at the interface with their chains facing the air and with a thin layer of polymer molecules attached below to the solvated head groups (thickness ~10 Å). This structure provides weak electrostatic and steric stabilization to the films when the two interfaces approach, making the films barely stable (see Figure 9). In zone 2, which is at concentrations close to $Z = 1$, the NR-derived structure is a monolayer of surfactant molecules attached to a lower compact polymer layer, followed by a low-coverage TTAB bilayer and, finally, an additional outer PS mixed layer (thickness ~50 Å). In this region, due to the outer PS mixed layer, there is no electrostatic or steric stabilization, and the films are not stable (see Figure 9). In zone 3, the structure is similar to the one in zone 1, but the polyelectrolyte layer is thicker (total thickness ~80 Å), and the polymer adopts an extended conformation with a volume fraction of less than 10%. The foam films in this region are very stable; however, the stoichiometry of the complexes at the interface is 1:1, indicating that it is not the double-layer repulsion between both interfaces in the film that stabilizes them. The extended polyelectrolyte conformation at the interface and the free polyelectrolyte coils in bulk within the thin film can interpenetrate, locally increasing the polymer segment densities, resulting in high osmotic pressure. This gives rise to steric forces that stabilize the films against drainage and produce very stable foam films (see Figure 9).

Unfortunately, as mentioned above, no correlation between the stability of isolated films and macroscopic foams made with them can generally be established.[31] Macroscopic foams are a large collection of films and PB, all interconnected and interacting with their neighbors in a dynamic and continuously evolving state driven by drainage, coarsening, and coalescence. Although these three dynamics act, when considered independently, on different time scales, they affect each other. For example, when a film ruptures within a foam, it releases liquid and energy (surface energy); the liquid is collected by neighboring films and PB, and the liquid fraction and thickness of those films and PB increase locally. This, in turn, modifies locally the coarsening dynamics, as the coarsening rate is inversely proportional to the film thickness (section 2, eq 3). Additionally, the forces that stabilize the films are also modified (in the disjoining pressure isotherm, they move to higher values of h, and so on. The rupture of a film and the energy released in that rupture can trigger topological changes and new film ruptures in avalanche-like dynamics. When this occurs, the lifetime of the macroscopic foam might become independent of the foam film features and be dominated by the collective behavior,[41] making it impossible to correlate the stability of single isolated foam films with that of a macroscopic foam. In this respect, energy dissipation mechanisms within the foam might play a key role, but they are rarely studied in relation to foam stability.[61,62] All the described dynamics depend on other factors such as bubble size, bubble size distribution, and liquid fraction[28] (see section 2). Foams containing PS mixtures have their peculiarities. The presence of PS complexes at interfaces and thin films can act as more effective barriers to gas diffusion, changing the effective gas diffusion coefficient in eq 3. PS aggregates can additionally produce, as discussed above, very rigid interfaces, slowing down or arresting the coarsening dynamics when $E \sim \gamma/2$. Thus, the presence of PS complexes might help stabilize foams regardless of the stability of individual films. To my knowledge, no systematic studies have yet been published on the effect of PS complexes on coarsening dynamics. On the other hand, the presence of large PS aggregates or precipitates within PB could reduce the permeability constant (see eq 2) or directly clog the liquid channels, modifying the drainage dynamics and, as a consequence, foam stability in a way not related to the stability of isolated films. Obviously, this will depend on the region of the phase diagram in which the mixtures are located, which in turn depends on the type and strength of polymer-surfactant interactions and total and relative P/S concentrations, as well as on system history (nonequilibrium states). As is the case with coarsening, there are no systematic studies on drainage dynamics of PS mixtures in macroscopic foams or in single PB channels. Regarding the stability of macroscopic foams in PS systems, as a general trend, it seems that strong P−S interactions and thick interfacial layers containing PS complexes favor the formation of stable macroscopic foams.[31]

Finally, it is important to stress here that foamability and foam stability are not necessarily correlated for polymer-surfactant mixtures. The ability of polymer-surfactant complexes to produce foams on the one hand and to stabilize them on the other is related to the kinetics of their adsorption (or complexation) onto the fluid interfaces and their behavior under dynamical conditions,[76,96,98,148,149,160] which in turn depends again on the polymer-surfactant interactions in bulk and at interfaces.[71,75,103,158,161] Mixtures of neutral or low-density charged polymers with ionic or nonionic surfactants usually interact weakly. These weakly interacting mixtures generally produce systems that increase the ability to form foams when compared to the polymer or the surfactant alone; they have a synergistic effect.[158,161] This enhanced performance is due to a first fast adsorption dynamic of surfactant molecules and small PS complexes on the liquid−air interface, which is responsible for foam formation. On the contrary, when the interactions between polymer and surfactants are strong, as for polyelectrolyte mixed with oppositely charged surfactants, it is frequently observed that foamability is reduced; however, once the foam is produced, by performing more work in the dispersion process, its stability is usually higher than that of the surfactant or polyelectrolyte alone. This behavior for strongly interacting systems can be explained by the strong complexation of polymer and surfactants in bulk, which slows down adsorption onto the interface, reducing the ability to form foams. However, when complexes adsorb onto the interface, they stabilize films, as is the case with weakly interacting mixtures. These interactions can be modulated to produce responsive foams based on polymer-surfactant mixtures by modifying the first steps in the adsorption dynamics,[132] as will be shown in the following section.

6. SMART FOAMS BASED ON POLYMER-SURFACTANT MIXTURES

This section will deal with three PS systems used to successfully formulate responsive or smart foams. The first one is a mixture capable of modulating foam stability with temperature, the second is pH responsive, and the third is light responsive.

6.1. PNIPAAm/Surfactant Mixtures: Thermal Responsiveness. Poly(*N*-isopropylacrylamide), PNIPAAm, is a synthetic polymer that undergoes a conformational transition at a low critical solution temperature (LCST) of about 35 °C, being in a coil conformation below this temperature and collapsing to form globules above it. PNIPAAm is a water-soluble polymer but is not a polyletrolyte. It is surface active and adsorbs at water−air interfaces. It was shown that, once adsorbed at the air−water interface, PNIPAAm transitions from a fluidlike to a solidlike surface layer when the LCST temperature is crossed.[162,163] Because the transition is reversible both in bulk and at the interfaces, PNIPAAm aqueous solutions were considered as candidates for the formulation of smart foams whose stability could be switched on/off by changing the temperature. Unfortunately, the foaming properties of PNIPAAm aqueous solutions are quite poor and the foams produced from them were found to be unstable,[164] precluding their use as a stabilizing agent in foam formulations. Guillermic et al.[164] tried to overcome this problem by mixing PNIPAAm with surfactant sodium dodecyl sulfate (SDS) to improve the foaming properties of the solutions. Foamability and foam stability were indeed improved; however, the thermal responsiveness of the interfacial layer was lost because the surfactant displaced PNIPAAm from the liquid−air interface.

The work of Guillermic et al. inspired Lencina et al.[135] to develop a related PS system. They hypothesized that thermoresponsive foams might be formulated with such a mixture if a charged surfactant was used to anchor an oppositely charged brush-type polyelectrolyte, with PNIPAAm incorporated as side chains, to the interface. To this end, the authors synthesized a brush-type negatively charged copolyelectrolyte (Cop-L) using sodium alginate as the main chain and PNIPAAm as side chains. They mixed Cop-L with the opposite-charged DTAB surfactant and used the mixture to formulate foams. The idea was that the adsorption of DTA+ to the interface might anchor the Cop-L by complexation with alginate-charged groups, leaving the PNIPAAm side chains underneath in the surface layer and perpendicular to the interface. The hope was that these complexes would improve foamability without losing the thermoresponsiveness. Lencina et al. used a battery of techniques to characterize the system in bulk and at interfaces: surface tension, step-compression surface rheology on a Langmuir balance, and dynamic light scattering. They performed their measurements at fixed and constant polymer concentrations, varying the surfactant concentration over the entire range, from T0 (the concentration at which surface tension starts to decrease) to T4 (see Figures 2 and 3), and at two temperatures, below (20 or 25 °C) and above (45 °C) LCST. They were able to produce thermoresponsive foams due to the coil-to-globule transition at the interface, but in a limited range of surfactant concentrations, from 0.3 to 1.6 mM. The surface tension isotherm is of type 1, as in Figure 3a, and these concentrations fall exactly between T1 and the middle of the surface tension plateau ($[S] <$ T2), well below the onset of phase separation ($[S] \sim 8$ mM). At concentrations below 0.3 mM, foams are not stable, and at concentrations above 1.6 mM, the thermal responsiveness is lost because DTAB induces the collapse of the complexes. By means of multiple light scattering, they studied the dynamics of coarsening and coalescence in foams as well as foam stability. They correlated the results with those of surface compression elasticity to understand the described behavior. Figure 10a shows an example of the storage and loss moduli as a function of frequency at two temperatures, below and above LSCT. In the inset of that figure, the high frequency limit of the elastic modulus as a function of surfactant concentration is plotted; this limit elasticity is related to coalescence dynamics (eq 5). Note first that the elastic modulus changes appreciably when temperature changes and that this change decreases as surfactant concentration increases. This could explain both the loss of responsiveness and the change in foam stability as temperature exceeds LSCT. Figure 10b shows the temporal evolution of the light transmitted through the foam. These experiments allow studying the coarsening and collapse dynamics, but I would like to stress here only the difference in the behavior observed at the two temperatures. For $T = 20$ °C, the change is monotonous presenting only one inflection point, which the authors relate to a combination of coarsening and coalescence dynamics. For $T = 45$ °C, the light fluctuates, which is due to the occurrence of avalanches of film ruptures followed by bubble rearrangements inside the foams. Thus, based on these results, the authors conclude that the thermal response is a consequence of the change in the surface compression elasticity passing below a certain threshold that makes the films unable to resist the mechanical stress induced by the rupture of a neighboring film giving rise to local cascades of ruptures that accelerate the collapse of the whole foam, this being the main response mechanism. To my knowledge, this is the first PS system used to remotely control foam stability without changing the chemical composition.

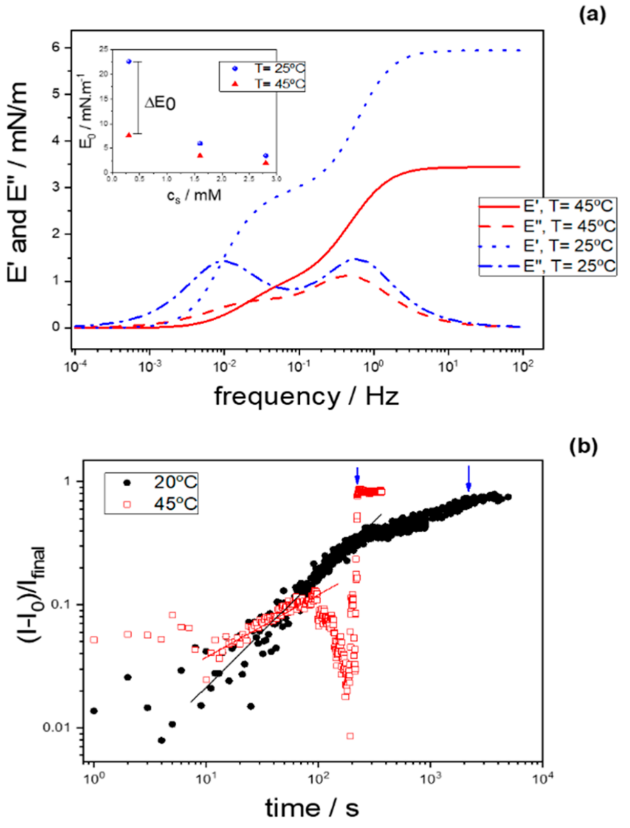


Figure 10. (a) Storage (elastic) and loss (viscous) compression modulus obtained from step-compression experiments. Results correspond to Cop-L 400 mg L^{-1} + DTAB 1.6 mM. The inset shows the high-frequency limit of elasticity, E_0, as a function of DTAB concentration. Note that ΔE_0 is appreciable when T exceeds LSCT, only for $[S] < 1.5$ mM. (b) Relative light intensity transmitted through the foam sample as a function of time for a Cop-L/DTAB mixture, Cop-L 400 mg L^{-1} + DTAB 1.6 mM, at two temperatures, one below and one above LSCT. Blue arrows indicate the half time of the foams (i.e., the time required to reach half the initial foam height), which is a measure of foam stability. Note the oscillations of light intensity for $T = 45$ °C; this is due to cascades of film ruptures and reorganization inside the bulk of the foam bubbles. Reprinted with permission from ref 135. Copyright 2018 Elsevier.

6.2. PAA/G12 Mixtures: pH Responsiveness.

Martinelli et al.[132] studied mixtures of poly(acrylic acid) (PAA) and a cationic surfactant, Gemini 12-2-12 (G12), in aqueous solutions. PAA is a weak acid, the charge of the carboxylic groups can be modulated by changing the pH, which could modify the interactions with the oppositely charged G12 surfactant; this in turn may change the structure and properties of the complexes, both in bulk and at interfaces. Martinelli et al. hypothesized that this might produce pH-responsive foams. They used equilibrium and DST, surface dilational rheology, and X-ray reflectometry (XRR) to characterize the interfaces. Then, they formulated foams with these complexes at three different pH (~3, 6, and 11) and studied the stability of these foams by means of multiple light scattering and CCD cameras. The foams are pH responsive, very stable at pH 3, and at surfactant concentrations as low as 4×10^{-2} mM, which is about 1/25 cmc. Maximum stability at this pH is reached for a surfactant concentration range of $0.01 < [S] < 0.5$ mM. At pH 6, the systems do not form foams at all. At pH 11, they form very small and unstable foams. The response to pH is fully reversible; by adding hydrochloric acid (HCl) or sodium hydroxide (NaOH) to cyclically change the pH, they cyclically produce stable and unstable foams that can be seen in a video that accompanied the publication or in ref 165. The authors demonstrated that the response mechanism is entirely due to interfacial dynamics. Figure 11a shows DST measurements as a function of pH for a PAA/G12 mixture with $[S] = 0.5$ mM and $[P] = 1$ mg L^{-1}. Figure 11b shows the corresponding XRR results at the three pHs. These results show that the complexes are surface active at all pHs, but the adsorption dynamics is much faster, by far, at pH 3. The kinetics follows the order pH 6 < pH 11 < pH 3, the same trend in foam stability.

They rationalized the behavior as follows: first, the fast adsorption process that changes rapidly the surface tension is responsible for the initial foam formation; surface compression elasticity accounts for foam stability (data not reproduced here; see original paper). Both the adsorption velocity of complexes at the liquid−air interface and surface viscoelasticity are modified by pH, the pH responsiveness of foam stability being well correlated with these interfacial dynamics and not with the equilibrium surface activity of the chemical stabilizer. These results contrast with the response mechanism of foams formulated with colloidal polystyrene-PAA particles,[166] for which the hydrophobicity/hydrophilicity balance at different pH modifies the surface activity of the particles, this being the main pH response mechanism of those foams.

Martinelli et al. ended their article by suggesting the possibility of using mixtures of polyelectrolytes with oppositely charged photoresponsive surfactants to make light-responsive foams. This has been achieved by another group very recently.

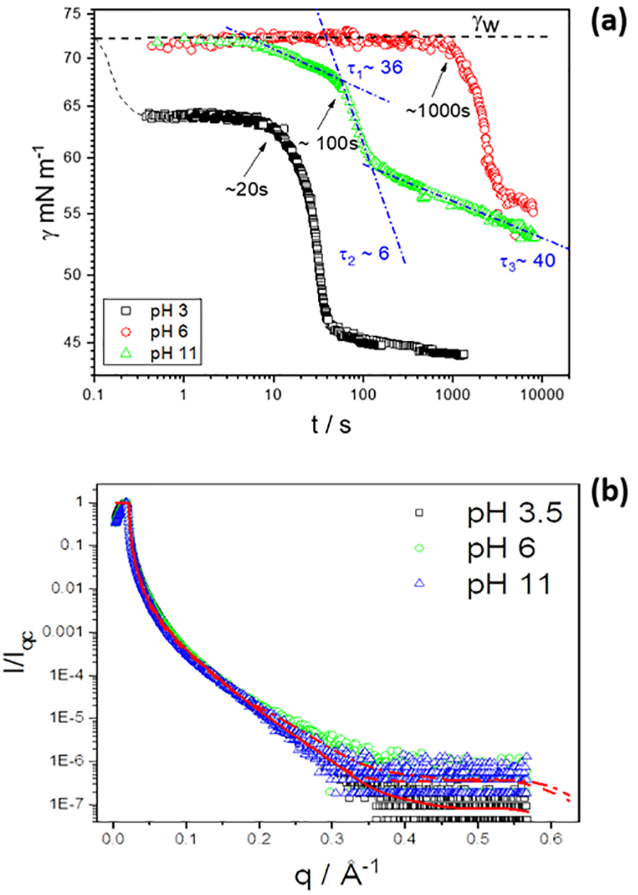


Figure 11. (a) Dynamic surface tension curves measured by the pendant drop technique, at three pHs for PAA/G12 mixtures with $[S] = 0.5$ mM and $[P] = 1$ mg L^{-1}. Note that the adsorption dynamics is complex, with several processes and characteristic times. At pHs 6 and 11, there is an induction time before the surface tension starts to decrease. (b) X-ray reflectivity curves for the same solution at the three pHs at equilibrium (>24 hs). Reprinted from ref 132. Copyright 2021 MDPI, Creative Commons.

6.3. PSS/AAP-TB Mixtures: Light Responsiveness.

Schnurbus et al.[133] were able to formulate a photoresponsive foam with a mixture of poly(sodium styrenesulfonate) (PSS) and arylazopyrazole tetraethylammonium bromide (AAP-TB). AAP-TB is a photoswitchable surfactant that undergoes a reversible E/Z photoisomerization reaction under illumination with green (wavelength = 520 nm, E-AAP-TB) and UV (365 nm, Z-AAP-TB) light. They worked at a fixed surfactant concentration of 7 mM, which is half the cmc, and varied the polymer concentration. The authors' starting hypothesis was that by illuminating the PSS/AAP-TB mixtures with the appropriate wavelength, they would be able to modulate polymer-surfactant interactions, thereby tuning the features of PS complexes both in bulk and at interfaces impacting foam stability. They measured the surface potential and hydrodynamic diameter of the aggregates at different $Z = [P]/[S]$ ratios and showed that by irradiating with UV or green light, they could modulate the net charge of the complexes because E/Z photoisomerization of AAP-TB results in different extents of the surfactant binding to PSS. Modulation of the net charge of the complexes has a direct impact on aggregate size and phase behavior. The most remarkable modification of these properties under irradiation occurs at a $Z \sim 1/2$ for this surfactant concentration. Irradiation also has an impact at the air−water interface. They performed DST measurements, vibrational sum-frequency generation (SFG) spectroscopy and NR, all in freshly prepared solutions, that is, not necessarily at thermodynamic equilibrium, which needs days or weeks to establish. After reaching a stationary state under green light, the surface tension rises and passes through a transient peak under UV irradiation, to return to the initial stationary value. On the basis of SFG results, the authors concluded that light affects the charging state of the complexes at the air−water interface, as it does in bulk. However, because the stoichiometry of the interfacial complexes is not necessarily the same as in bulk, they decided to study the structure and composition of the surface layer by NR. They chose three different $[P]/[S]$ ratios to study: $Z = 1/2$, where the most drastic changes in bulk are observed, $Z = 1/5$, which lies within the mixing ratio zone where, according to SFG, the net charging state at the interface can be reversed by light irradiation, and $Z = 1/140$, for which the differences between the E and Z states are minimal in bulk and at the interfaces. They used a three-layer model (chain-head-third layer) to analyze NR results and showed that there are drastic changes in the surface concentration of surfactant and polyelectrolyte as well as in the chain layer thickness when AAP-TB is switched between its E and Z conformation; for example, at $[P]/[S] = 1/2$, the chain layer thickness changes by a factor greater than 2 when illuminating with UV. The authors hypothesized that these changes are not due to a modification in the stoichiometry of the complexes but to structural changes that produce the modification of the net charge (see Figure 12). To test the light responsiveness of PSS/AAP-TB complexes, they produced aqueous foams at different $[P]/[S]$ ratios. Figure 12 shows the foam half-life time (time elapsed until the foam height is half of the initial one) as a function of mixing ratios and light irradiation. The maximum response to light is observed for $[P]/[S] = 1/2$, for which the net charge of the complexes is close to zero, indicating that it is not the electrostatic repulsion term in the disjoining pressure that stabilizes the macroscopic foam. The authors vaguely proposed that Pickering stabilization is the main mechanism involved in the stability of these foams. The manuscript comes, as supporting or additional information, with a video showing how UV irradiation locally destroys the foams (see Figure 12).

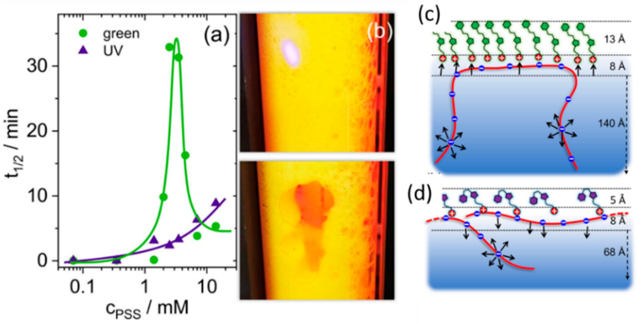


Figure 12. (a) Foam half-life time $t_{1/2}$ as a function of P/S molar mixing ratio and light irradiation. The AAP-TB concentration was fixed at 7 mM, whereas the PSS monomer concentration, c_{PSS}, was varied. (b) Local destruction of an aqueous foam from a P/S mixture with a molar mixing ratio of 1/2 using local UV irradiation for 10 min. (c) Schematic drawing of interfacial structure at the air−water interface under green light, with dangling polyelectrolyte chains underneath. (d) The structure changes upon UV irradiation to a layer with chains more parallel to the surface plane. Note that the thicknesses of the chain layers (from NR) change by a factor of 2 under UV light. Adapted from ref 133. Copyright 2022 American Chemical Society.

7. FINAL REMARKS AND PERSPECTIVES

The use of PS mixtures to produce foams has advantages over other stabilizing agents. They can produce stable foams at very low concentrations of surfactants and polymers, which is highly desirable from an economic and environmental point of view. Furthermore, because PS interactions can be externally modulated by different stimuli (pH, light, temperature), they can be used for the design of smart foams. Unfortunately, little is known about the mechanisms of foam formation and stabilization using these mixtures. Foam formation and stability of PS mixtures in aqueous solutions depend on a multiplicity of factors; one of them, which is not very well understood, is the presence of aggregates, both at equilibrium or kinetically arrested, in bulk and at fluid−gas interfaces. In this regard, the particular surface layer structure of the two interfaces of a foam film and how they interact with each other as liquid drains and film thins play a very important role in the stability of individual isolated films. The size, net charge, and structure of aggregates affect the different contributions, DLVO and non-DLVO, to the disjoining pressure and thus film stability. However, film stability and macroscopic foam stability are generally poorly correlated. In this respect, cooperative phenomena with the occurrence of avalanche-like ruptures and topological changes could play a role, not yet well explored.

Foam stability, and particularly foamability, depends on the adsorption kinetics of all surface-active species in a multistep process involving sequential or coadsorption of surfactants, polymers, small or large aggregates, via diffusion or convection, and the relaxation processes occurring at the interfaces once adsorbed (e.g., surfactant reorganization, conformational changes of the polymer chain or disassembly, and spreading of PS complexes). Despite its importance, the adsorption kinetics of polymer-surfactant mixtures in aqueous solutions is really scarce and rarely studied in a single work, in relation to foam formation and stability.

Surface viscoelasticity of PS air−water interfaces, both dilatational and shear, plays a fundamental role in the dynamics of macroscopic foams and their stability: drainage, for which shear surface viscosity is important in defining the slip/nonslip condition for the liquid flow in PB; coarsening, for which low frequency interface dilational elasticity is important in light of the Gibbs' criteria for arresting gas diffusion ($E \sim \gamma/2$); and coalescence, in which high frequency interface elasticity defines the lifetime of films under thermal fluctuations (eq 5). The presence of PS aggregates can affect the dynamics of macroscopic foams, as is the case for single isolated films. They could modify drainage dynamics by modifying foam permeability (eq 1) or by clogging PB and/or coarsening rate acting as an effective gas barrier (eq 3). To my knowledge, no systematic studies have been conducted on the gas diffusion rate and coarsening dynamics in macroscopic foams and foam films covered with PS surface layers.

All the above-mentioned dynamics and processes ultimately depend on the type and strength of PS interactions in bulk, at interfaces and within the confined geometry of thin films, which in turn depends on the particular chemical systems. The huge complexity of behavior is, in my opinion, not necessarily a problem but an opportunity because these interactions, being mainly of physical origin, can be modulated externally, opening the way to the design of responsive, smart foams (and other systems) with an enormous potential in technological applications.

Three examples of such systems have been discussed: one that is capable of responding to temperature changes, which is, as far as I know, the first PS systems used to modulate remotely the stability of a foam; another one that is responsive to pH changes; and a third that responds remotely to irradiation with light of a particular wavelength. Of these three systems, only two trigger a response using an external, noninvasive stimulus that does not modify the chemical composition of the mixture. For the pH-responsive PS mixture, the addition of NaOH and HCl to change the pH in order to modulate foam stability is not really convenient if the repetition of unlimited cycles is desired. The addition of acids and bases in repeated cycles would continuously increase the ionic strength, changing the system composition and eventually affecting its behavior. To overcome this issue, it would be possible to explore the use of diphenyl yondonium salts in the formulation of these systems.[167] These salts are photoacid generators; they photolyze by UV light generating an acid that, in water solution, causes a pH decrease. Thus, we could in principle change the basic pH-responsive system to a light-responsive foam. Similar approaches can be thought of to transform PS temperature-sensitive systems into light- or magnetic-field-sensitive ones, by mixing them with the appropriate nanoparticles.

The challenge for foam researchers in this field is to find triggers to modulate PS interactions in bulk and at interfaces by remotely activated triggers to produce smart foams whose stability can be turned on/off at will in a noninvasive and reversible manner.

To conclude, a special very important case of polymer-surfactant systems used in foams, particularly in food, cosmetic, and pharmaceutical industries, the protein−surfactant mixtures should be mentioned. Although many aspects discussed in this review also apply to proteins, they have some particularities that turn them into a case apart. However, everything said about the design of smart foam systems also applies to protein mixtures.

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Notes

The author declares no competing financial interest.

ACKNOWLEDGMENTS

This research was funded by the Agencia Nacional de Promoción Científica y Tecnológica (AN-PCyT), Argentina, [PICT-2019-3185], by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina, [PIP 11220200101754CO], and by the Universidad Nacional del Sur (UNS), Argentina, [PGI-UNS 24/F080].

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https://doi.org/10.1021/acsomega.2c05739