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Non-equilibrium states in polyelectrolyte-surfactant systems at fluid interfaces: A critical review

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Abstract

Over the last two decades, a significant body of research has been developed trying to understand the association and properties of mixtures formed by oppositely charged polyelectrolytes and surfactants. Particular emphasis has been given to their interfacial properties and the intriguing formation of nonequilibrium states. The synergy between these components at interfaces has attracted considerable attention due to its relevance in various industrial and biological applications. The combination of oppositely charged entities leads to complex interactions that influence the stability and behavior of interfaces. This review critically examines recent advances toward understanding the interfacial behavior when polyelectrolytes and surfactants coexist. Emphasis is placed on the existence of nonequilibrium states, shedding light on transient phenomena and kinetic aspects that play a crucial role in the overall system behavior. This will provide insights into the mechanisms governing the interfacial phenomena in these mixed systems. In summary, this review will contribute to the fundamental understanding of colloidal and interfacial science, offering a valuable perspective on designing and optimizing materials with tailored properties.

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Introduction

Oppositely charged polyelectrolyte-surfactant (PE-S) systems are among the most studied colloidal systems due to their potential interest in several areas of scientific and industrial relevance, e.g., personal care, cosmetics, pharmaceuticals, and various other industries that have a significant impact on everyday life [1,2]. In fact, the combination of oppositely charged polyelectrolytes and surfactants represents a fascinating venue for exploring fundamental interactions and designing tailor-made functional colloidal materials [3]. However, to date, there is no comprehensive understanding of the physicochemical bases governing the association processes in this type of mixtures, and how such interactions affect the ability of systems formed by polyelectrolytes and surfactants bearing opposite charges to interact with fluid interfaces [4–8*].

The assembly in oppositely charged PE-S systems involves an intricate interplay among different interactions, including electrostatic, steric, and specific interactions. Understanding the physicochemical aspects that govern the behavior of these colloidal systems poses a significant challenge due to their complexity [*8–12**]. In recent years, several experimental and theoretical methods have been developed to comprehend the physicochemical behavior of mixtures involving oppositely charged polyelectrolytes and surfactants [**9,13,14]. However, there is often a discrepancy between theoretical and experimental results, partly because many theoretical studies are based on an equilibrium thermodynamic framework, which may not accurately reflect the real situation. The reason for this is that the assembly of polyelectrolyte-surfactant complexes (PESCs) in solution frequently leads to the creation of nonequilibrium structures, or kinetically trapped aggregates (metastable states), which tend to evolve towards their equilibrium conformation. However, the equilibration times of PESCs are typically very slow [**9], as in the case of protein refolding [15,16]. This is a very important issue because the transition from nonequilibrium states to equilibrium ones is not always straightforward, and may result in the emergence of a broad range of transient states that are not directly accessible under equilibrium conditions [**9,17]. Therefore, it is necessary to thoroughly examine the mixture composition and mixing protocol to provide a physicochemical description that accounts for their behavior in bulk and upon adsorption at interfaces [**10,11]. As in most nonequilibrium states, the structure and properties of the systems depend on the protocol used for producing them. Therefore, it is crucial to control carefully both the composition of the mixture and the mixing procedure used in its preparation to achieve a selective adjustment of the physicochemical properties of the resulting PE-S aggregates [**9,18]. The nonequilibrium in PE-S association can lead to various phenomena such as the shifting of phase boundaries, the formation of new phases, the dissociation of PESCs, or the coexistence of phases enriched in either polyelectrolytes or surfactants, or coacervation [19]. In particular, the significance of the phase separation phenomena in these systems extends to a wide range of fields, from fundamental understanding of phase transitions to practical applications [3,20]. For instance, the study of phase separation in PE-S systems may be crucial to our understanding of the origin of life. Indeed, this type of phase separation provides a thermodynamically favorable pathway for compartmentalization. The association of oppositely charged species can lead to the formation of phase-separated droplets through an entropically favored release of water and counterions from the aggregates formed, resulting in a membrane-free structure that is chemically enriched and in dynamic equilibrium with an impoverished aqueous phase. However, it is not yet clear whether the above-phase separations occur under equilibrium or non-equilibrium conditions, which may affect various aspects of biological relevance [*21].

Since the chemical potential of the different components at interfaces and bulk are approximately equal for the very long-lived complexes, the non-equilibrium features of the association of oppositely charged polyelectrolytes and surfactants play a key role in the organization of the formed complexes at fluid interfaces. In fact, kinetically trapped aggregates can diffuse from the bulk to the interface, leading to the formation of kinetically trapped films. These films present characteristics that are far from what is expected according to the bulk composition [9**]. The production of kinetically trapped films can impact the ability of a specific PE-S pair to stabilize emulsions and foams [22–26], but also in its role in different applications, including hair conditioning, tertiary oil recovery, or drug delivery [27,28].

This review provides an overview of the impact of nonequilibrium effects in the association process between oppositely charged polyelectrolytes and surfactants on the interfacial properties of the film created through the adsorption of the formed aggregates at fluid interfaces. Before delving into the interfacial aspects of PE-S systems, a brief discussion of the different scenarios that occur in the association of oppositely charged PE-S mixtures will be given, including a clear distinction between equilibrium and nonequilibrium states. The review will then focus on understanding how the formation of nonequilibrium aggregates in the bulk affects the formation of kinetically trapped films, considering various thermodynamic, rheological, and structural aspects. It is worth mentioning that, considering the nonequilibrium nature of PE-S systems, the thermodynamic parameters must be considered as effective magnitudes that provide a mechanical representation of the system but do not inform about the actual thermodynamic behavior of the system. At the end of the review, some remarks will be made to highlight the relevance of non-equilibrium effects in the interfacial behavior of PE-S systems. It is expected that this review will contribute to a better understanding of the nonequilibrium effects in films formed by oppositely charged polyelectrolytes and surfactants and will push research towards the full exploitation of these important effects in the development of potential applications of PE-S mixtures.

Association in oppositely charged polyelectrolyte-surfactant mixtures: a complex picture

The association in mixtures including oppositely charged polyelectrolytes and surfactants mixtures has usually been approached from several perspectives. These include mainly the analysis of the phase diagrams or the binding of the surfactant to the polyelectrolyte chains [11,12**]. This type of approach generally assumes an equilibrium framework, which is inadequate due to the recognized role of the formation of kinetically trapped states in the bulk. Indeed, they are the result of the combination of convective and diffusive contributions that occur during the mixing of the components, thus leading to a composition and structure that are not those expected from the surfactant/polyelectrolyte compositional ratio or, most commonly, the Z-ratio (hereinafter Z) [29]. This parameter defines the composition of PE-S mixtures as the ratio between the number of surfactant molecules and the number of charged monomers within the polymer chains in solution [8*]. This section will present the different scenarios that can emerge in mixtures of polyelectrolyte and surfactant mixtures bearing opposite charges as a function of Z, and how the phase behavior can be modified depending on a subtle balance of parameters modulating the binding and structure of the resulting PESCs.

Equilibrium systems

The association in oppositely charged PE-S systems from an equilibrium perspective has been extensively developed following two different approaches: (i) evaluation of the phase diagram [**30,31], and (ii) analysis of the binding process [**12]. Here, a simplified perspective to describe the general features of the association process will be provided. Figure1 displays a schematic view of the phase diagram of oppositely charged PE-S mixtures in terms of a surfactant concentration (c)-Z ratio representation [*32,33*].

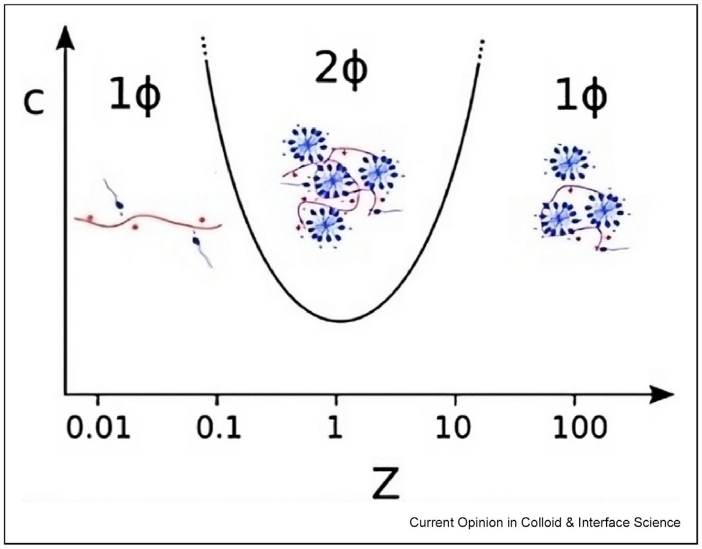
Assuming mixtures with a fixed concentration of the polyelectrolyte and increasing concentrations of surfactant, when the number of surfactant molecules is smaller than the number of charged monomers in the polyelectrolyte chain ($Z < 1$), the system remains in a single-phase region (1ϕ). However, as the cooperative binding of surfactant molecules to the polyelectrolyte proceeds, the value of Z tends to the unity, where the number of surfactant molecules and charged monomers are the same (isoelectric point), a stoichiometric binding between the polyelectrolyte and the surfactant takes place. At this point, the neutral character of the PE-S aggregates is accompanied by a lack of stability, and therefore the mixture becomes unstable, showing a biphasic character (2ϕ) as a result of liquid/liquid (coacervation) or liquid/solid (precipitation).

Further increases in the amount of surfactant beyond $Z = 1$ bring the system again to a single-phase region (1ϕ) as a result of the redissolution of the phase-separated complexes. In fact, the excess of surfactant molecules in relation to the number of charged monomers leads to the formation of overcharged complexes, with the same charge as the surfactant molecules, characterized by the association of surfactant molecules as aggregates with different conformations, e.g., micelles, vesicles or bilayers, depending on the specific nature of the surfactant [*8]. These surfactant aggregates can act in some cases as bridges between different polyelectrolyte chains, resulting in multichain PESCs [34].

It is worth mentioning the importance of considering the effectiveness of the binding process to define the true composition at which the phase separation is expected. In fact, the isoelectric point can appear to be shifted beyond the composition corresponding to the stoichiometric mixing (charge equivalence point). This is important because the true charge neutralization point of the PESCs occurs in conditions where there is a stoichiometric binding of surfactant molecules to the polyelectrolyte chains [9**]. Therefore, it is possible to find systems where the isoelectric point is not located for a value of $Z = 1$. This can impact specific features of the phase diagram, such as the compositional region where the phase separation occurs [34], which is indicative of the complex interplay between the components of the mixture and their cooperative association [11].

The association process depends on the physicochemical properties of both the polyelectrolyte and surfactant, which affects to different aspects of the behavior of PE-S systems, including the width of the phase

Figure 1



Graphical representation displaying a cartoon of the phase diagram of an arbitrary oppositely charged PE−S mixture in terms of concentration (c) and the Z ratio. Adapted from Chiappisi et al. [34] with permission from the Royal Society of Chemistry.

separation region, the stoichiometry, and the structure of PESCs. In fact, the chain stiffness (persistence length), charge density along the chain, proximity of the charge to the backbone, and molecular weight of the polyelectrolyte together with the packing parameter as well as the type of head group and hydrophobic group of the surfactant influence the association, behavior an properties in PE-S systems [*8,12**]. In addition, the role of polyelectrolyte concentration, ionic strength, temperature, and pH cannot be considered as negligible in the control of the association of oppositely charged polyelectrolytes and surfactants.

In recent years, different theoretical and simulation studies have been carried out to improve the understanding of the interactions within PE-S systems. These efforts aim to provide valuable insights into the intricate mechanisms governing the association of these systems, shedding light on the complex interplay between polyelectrolytes and surfactants in the presence of electrostatic interactions. Banerjee et al. [35] investigated the modulability of the association between anionic surfactants and cationic polymers through structural modifications in the polyelectrolyte chain using self-consistent mean field calculation. They predicted that the association occurs due to the interaction of the polyelectrolyte charged monomers with charged micelles. Notably, the results show that the polyelectrolyte chains form a corona around the surfactant micelles, resulting in cooperative behavior during the association process. This cooperative behavior contributes to an increase in the aggregation number of polymer and surfactant within the complexes, potentially leading to a situation characterized by complete pairing of charges, thereby pushing the system toward phase separation. Further studies using self-consistent mean field calculations for studying the PE-S association demonstrated that together with the molecular structure of the polyelectrolyte chains that correspond to the surfactant plays a very important role in the control of the association process [14].

Coscia et al. [36] using Molecular Dynamics simulations reported a scenario compatible with mean field self-consistent calculations. This is characterized by the wrapping of the polymer chains around spherical micelles, with the positive charges associated with the negatively charged groups of the surfactant micelles. This leads to the formation of aggregates where the polymer can bridge several spherical micelles. This situation was also found by using self-consistent mean-field calculations in the proximity of the phase separation. It is true that from an experimental point of view, the molecular aspects of the association process described from the self-consistent mean field calculations and the molecular dynamics simulations may seem unrealistic, particularly given that the association between micelles and polyelectrolyte chains is anticipated only at high values of Z. Despite this, these modeling efforts effectively capture the ability of the system to undergo phase transitions in the proximity of the isoelectric point.

Nonequilibrium equilibrium systems

The description of the association of oppositely charged PE-S systems is less straightforward than in the case of the typical equilibrium association [**9,11]. In general, nonequilibrium is characterized by the emergence of phase separation for compositions that should correspond to a single-phase region, i.e., phase separation for $Z \neq 1$. This is generally attributed to the creation of Marangoni stresses during the mixing process of polyelectrolyte and surfactant that lead to a local accumulation of surfactant molecules higher than the nominal concentration. Thus, the association process leads to a situation characterized by a heterogeneous distribution of the surfactant molecules along the polyelectrolyte chain, resulting in the formation of locally neutral complexes, despite, on average, they present a net charge. These aggregates can undergo a gravitational phase separation process even though the composition of the mixture may correspond to a single-phase region [7].

The formation of nonequilibrium states can appear in different ways. The most studied appears at a relatively low polyelectrolyte concentration and can present two different manifestations. The former is related to the persistence of phase-separated complexes at surfactant concentrations that are well above those corresponding to the phase-separation, i.e., phase-separated complexes remain even though $Z > 1$. This is commonly associated with an irreversible collapse of the formed aggregates which cannot undergo reswelling even though they are overcharged by the addition of additional charged species [37,38]. On the other hand, it is also possible to obtain charge-stabilized kinetically trapped aggregates for compositions corresponding to a two-phase-phase region in the equilibrium conditions. These aggregates are formed due to the heterogeneous distribution of surfactant molecules that results in the formation of complexes where there is an excess of bound surfactant molecules, resulting in overcompensated particles with a large hydrophobic core that remain stable in the aqueous medium [38–40]. Again, the preparation of the mixtures requires careful attention to concentration gradients, as they play a crucial role in determining the heterogeneous distribution of components. This can lead to a system that is far from its equilibrium composition.

The formation of nonequilibrium states in PE-S mixtures is even more pronounced when the concentration of polyelectrolyte is high. In this case, it is possible to find phase-separated mixtures for compositions that in some cases are more than one order of magnitude below the isoelectric point, i.e., $Z = 1$ [41,42]. This can only be understood by considering that the concentration gradient of the surfactant during the mixing process leads to a situation characterized by the formation of complexes with an overcharged inner core and a neutral outer region. These aggregates can easily undergo phase separation even though the composition of the mixture remains far from the two-phase region.

The above discussion has shown that nonequilibrium in PE-S mixtures can have different manifestations, although it is generally assumed that their occurrence is associated with Marangoni stresses during sample preparation. The effect of these gradients can persist after mixing maintaining the system outside the equilibrium for weeks or even longer [9**]. However, nonequilibrium features can be minimized by controlling the ionic equilibrium in the medium by changing the ionic strength or pH, but also by changing the effective charge density of the polyelectrolytes or by adding non-ionic amphiphiles [18,39,40].

Dilution-control of the phase behavior

A third scenario found in mixtures of oppositely charged polyelectrolyte and surfactant is the occurrence of phase separation and redissolution of phase-separated aggregates as a result of a dilution process [*32,43]. This involves the control of the phase diagram under Z constant conditions. Therefore, the phase separation and subsequent redissolution cannot be understood as a consequence of a neutralization process, and the nonequilibrium aspects may have a critical influence on the control of changes in the phase behavior of PE-S systems on dilution [44,45]. However, to date, the true physical mechanisms behind the control of the phase separation process in PE-S mixtures at constant Z and different than unity are not clear.

From a simple perspective, the behavior of PE-S mixtures under dilution can be described by considering that the dilution of a highly concentrated single-phase (1ϕ) mixture leads to the appearance of a phase separation (2ϕ) without changes in Z. This separation can then be reversed by further dilution to take the sample into a new single-phase region (1ϕ). It is generally assumed that the dilution process leads to a disruption of the charge equilibrium within the dissolved complexes. This leads to the release of shielded ions and the dissociation of bound micelles associated with the charged polymer chains [32*]. In cases where both the surfactant and polymer carry significant charges, the polymer chains pack tightly together due to recombination at multiple sites. Conversely, as the charges decrease, the polymer chains adopt a less compact mesh-like structure due to a decrease in the number of recombination sites [46–48]. These densely packed structures are depleted from the solution, resulting in the formation of phase-separated complexes (precipitates or coacervates), even though the nominal composition of the mixtures corresponds to a single-phase region. The understanding of the physics behind dilution-induced phase separation plays an important role in the optimization of the performance of several commercial products, e.g., shower gels and shampoos [47].

The above discussion has evidenced the richness that can be found in the bulk phase behavior of PE-S mixtures. In the following, the discussion will focus mainly on the effect of nonequilibrium aspects on the formation of PE-S films at fluid interfaces. This is important because access to equilibrium conditions is usually difficult from an experimental point of view.

Polyelectrolyte-surfactant mixtures at fluid interfaces

Nonequilibrium effects in PE-S association play a very important role in shaping the properties and structures of interfacial layers after adsorption of the complexes at fluid interfaces. In fact, their nonequilibrium nature leads to a variety of phenomena that significantly influence interfacial behavior [**9,10**]. From a fundamental perspective, it can be expected that the behavior of mixtures at the fluid interface reflects, at least in part, their behavior in solution. The cooperative binding of surfactants to polyelectrolyte chains produces synergistic effects, resulting in a decrease in surface tension when complexes are adsorbed at the fluid interface [7,41,49]. At high surfactant concentrations, it has been observed that there is competition between PESCs and free surfactant molecules for the available interfacial area, which can limit the synergistic effects [41]. The interfacial properties of PE-S mixtures in solution are influenced by various factors, such as polymer and surfactant nature, charge density, ionic strength, and temperature. However, the effect of the polymer concentration and molecular weight is comparatively restricted [4,5,9**]. It should be noted that the interfacial properties of mixtures containing oppositely charged polyelectrolytes and surfactants are significantly dependent on the specific characteristics of the system under study [*5,7,9**].

A very significant effect frequently observed is the non-regular surface tension dependence on surfactant concentration, where peaks or plateaus are present as shown in Figure 2. These distinctive patterns in surface tension behavior at varying surfactant concentrations underscore the complexity of molecular interactions occurring at the interface. Additionally, they allow for clear differentiation between equilibrium and nonequilibrium complexes in the bulk. The origin of this non-regular behavior has been a very controversial topic for a long time. However, it has been interpreted in terms of thermodynamic models [50], even though in most cases nonequilibrium plays a crucial role in the structure and properties of the interfacial layers.

Figure 2

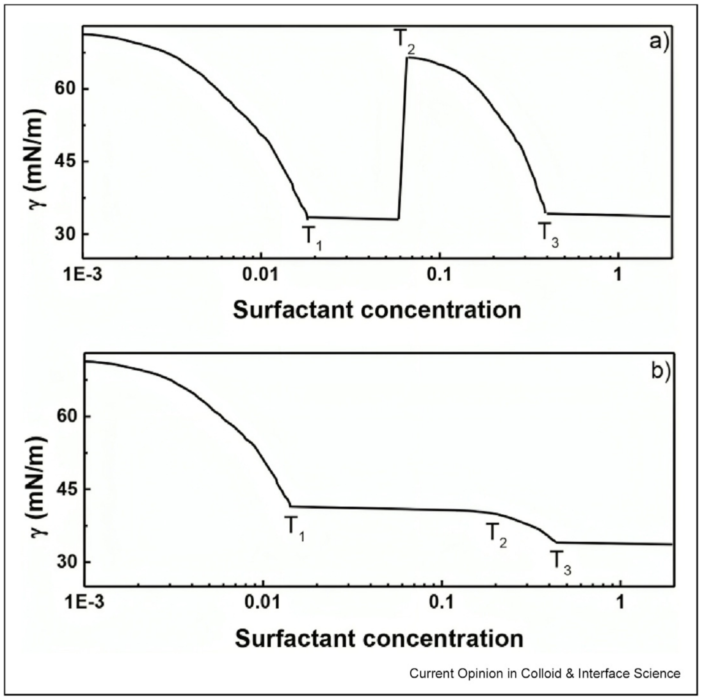


Illustration depicting the two distinct surface tension isotherm types observed in mixtures of oppositely charged polyelectrolytes and surfactants: **(a)** isotherm featuring a surface tension peak and **(b)** isotherm characterized by a surface tension plateau. Reprinted from Guzmán et al. [10**], Copyright (2020), with permission from Elsevier.

The nonregular trends in the surface tension curve generally include three characteristic points labeled T1, T2, and T3 (see Figure 2). The definitions of these points vary depending on the nature of the system considered. In some systems, the surface tension decreases until it reaches a surfactant concentration T1, after which it remains constant. The region of constant surface tension extends up to a surfactant concentration T2, where a sharp peak in surface tension is observed. This type of behavior was originally observed in mixtures of poly(diallyl-dimethylammonium chloride) (PDADMAC) and sodium dodecyl sulfate (SDS). As the surfactant concentration increases beyond T2, the surface tension decreases again until T3. At concentrations beyond T3, the surface tension remains relatively constant as the surfactant concentration increases. Another type of behavior includes a surface tension plateau between surfactant concentrations corresponding to T1 and T2, with no evidence of surface tension peaks. This phenomenon is typically observed in weakly interacting systems, such as mixtures of poly(4-styrene sulfonate of sodium) (PSS) and alkyltrimethylammonium bromides. Once the surfactant concentration surpasses the value corresponding to T2, surface tension decreases to reach a new constant value at T3. The variations in surface tension curves are also reflected in the lateral organization of molecules at the interface, with maximum adsorption observed in systems featuring a peak corresponding to a monolayer. On the other hand, for systems with a plateau, maximum adsorption can be explained in terms of a loosely packed bilayer [4].

General perspective of nonequilibrium polyelectrolyte-surfactant films

The presence of surface tension peaks, commonly known as cliff-edge peaks, is probably the most common signature in the interfacial properties of the non-equilibrium nature of PE-S mixtures. Penfold's group provided a seminal interpretation of the non-regular dependences of surface tension on surfactant concentration for PE-S mixtures [*5,51]. In particular, they analyzed the surface tension peaks appearing in the surface tension curves of mixtures of poly(diallyl-dimethylammonium chloride) (PDADMAC) and sodium dodecyl sulfate (SDS) [4,5,9**]. For this purpose, they used an equilibrium framework that is compatible with an extended version of the Gibbs description of interfacial layers for linking the association occurring in the bulk with the behavior of the films at fluid interfaces [52]. Thus, the appearance of the surface tension peak was explained assuming a bulk phase transition, or pseudo-phase transition, that leads to the formation of 3D PESCs with a low surface activity. This is suggested to be formed as a result of the transition between a non-cooperative surfactant binding to a cooperative one. The adsorption of these complexes was assumed negligible, and therefore the surface tension was supposed to be determined by the surfactant molecules that remain free in the solution. They observed that increasing the concentration of surfactant can lead to the re-establishment of surface activity of the complexes, which in turn facilitates their incorporation into the interface. As a result, a decrease in surface tension to values similar to those observed before the peak was observed.

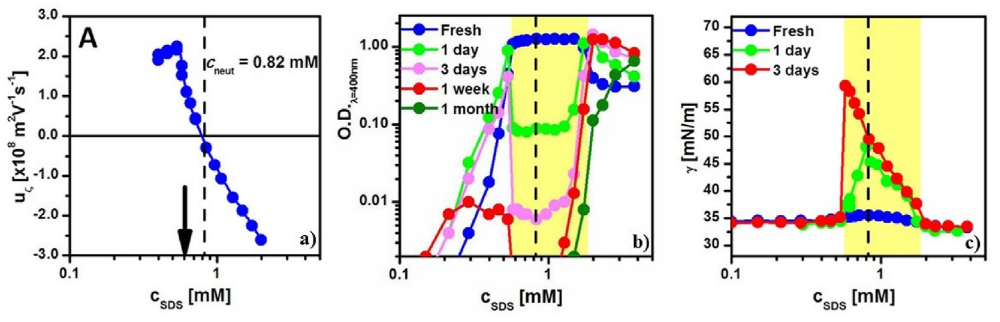
The framework discussed above does not consider any possible influence of nonequilibrium aspects on the formation of interfacial layers. However, Campbell et al. [53]. Proposed an interesting approach to understanding how nonequilibrium aspects impact the formation of PE-S films at fluid interfaces. Their study was focused on the evaluation of the surface tension of PDADMAC-SDS mixtures that had the same age but were subjected to different handling procedures. The surface tension measurements of samples prepared using different procedures indicated that, in the absence of aging, the surface tension curve does not exhibit any peaks within the explored range of surfactant concentrations. This observation suggests that the sample contains sufficient surface-active material to guarantee a fast formation of an interfacial layer, and rules the possible formation of complex with low surface activity proposed by the framework discussed above [*5,51]. The importance of nonequilibrium on the formation of the interfacial layers was confirmed by the evaluation of the surface tension of samples aged for three days, ensuring that the sedimentation of aggregates can occur. The surface tension curve of aged samples showed a surface tension peak for surfactant concentrations in the range of that corresponding to the appearance of precipitate in the bulk samples. The redispersion of the precipitate by light mechanical stress leads to a shifting of the surface tension peak. This finding suggests that the adsorption kinetics may be constrained by mass transport. In fact, the shifting of the surface peak can be understood by assuming that only a small quantity of the surface-active material is redispersed into the solution phase during the redispersion process. Based on the above, it appears that the cliff edge peak can be eliminated by agitating the solid material and releasing surface-active material into the solution phase. This suggests that the peak may result from the gradual precipitation process, which depletes the solution phase of surface-active material, and therefore a clear manifestation of the nonequilibrium nature of PE-S mixtures. It should be emphasised that the above discussion corresponds to one of the seminal works by Campbell's group [53] where they demonstrated that the redispersion process of sedimented aggregates can be exploited as a non-equilibrium supply of surface-active material back to the air/water interface. This was important because this study showed that sample handling had a critical effect on the experimental results obtained when considering PE-S mixtures. The study and exploitation of this type of behaviour has been further developed and extended by Campbell's group [**9,54,55].

Campbell et al. [56] extended their research by using neutron reflectometry measurements, which allowed them to assess the surface excess of the polyelectrolyte and the surfactant at the interface. Their results evidence that the loss of interfacial activity of the PESCs is the result of the sedimentation of the complexes due to their reduced charge. In these conditions, neutron reflectometry experiments evidenced, as expected, a sharp reduction in the surface excesses of polyelectrolyte and surfactant, which agrees with the findings by Penfold's group [4,5,50,57]. However, the results by Campbell et al. [56] evidenced that the presence of complexes with high surface activity can be only a transient state (nonequilibrium effects) because at the specific composition of the mixture, where they were formed, the system is close to the electroneutrality, and therefore the equilibrium situation corresponds to a phase-separated mixture.

Based on the above discussion, it can be inferred that the equilibrium situation corresponds to a liquid phase where the surface-active material has been depleted due to its lack of colloidal stability resulting from its proximity to the isoelectric point, accompanied by a fluid interface containing the unbound fraction of surfactant, and a solid precipitated phase. It is worth noting that the surface excess and composition at fluid interfaces may stabilize relatively quickly, within minutes or hours, while the bulk aggregation may continue to evolve over days or even longer. This is clear from more recent studies by Varga and Campbell [9**]. They observed two different effects on the surface tension of PDADMAC-SDS samples at different times after preparation. The first issue was related to the appearance of a surface tension peak as the sample ages, while the second issue was related to the increase in surface tension at the peak maximum and the shift in concentration at which this maximum appears towards the composition corresponding to the charge equivalence. These findings are consistent with previous results that underscore the importance of sample aging and handling in their bulk and interfacial properties. Figure 3 displays the surfactant concentration (c_{SDS}) dependence of the electrophoretic mobility, as well as concentration dependences of the optical density ($\mathrm{OD}_{\lambda\ =\ 400\ \mathrm{nm}}$) and surface tension of PDADMAC-SDS samples measured at different times. From the results displayed in Figure 3, it is clear that the system tends to evolve until a complex equilibration of PESCs in bulk is reached.

The above discussion of PDADMAC-SDS mixtures highlights the significant impact of nonequilibrium

Figure 3



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Results for PDADMAC-SDS mixtures with polyelectrolyte concentration of 100 ppm and a NaCl concentration of 100 mM. **(a)** Surfactant concentration dependence of the electrophoretic mobility. The arrows indicate the nominal bulk composition corresponding to charge equivalence. **(b)** Surfactant concentration dependence of the optical density of the samples measured at 400 nm at different times after the sample preparation. The shaded area is indicative of the equilibrium two-phase regions in the recorded data. **(c)** Surfactant concentration dependence of the surfactant tension of the samples measured at different times after the sample preparation. The shaded area is indicative of the equilibrium two-phase regions in the recorded data. The vertical dashed line in the three panels denotes the composition at charge neutrality. Adapted with permission from Varga and Campbell [9**]. Copyright (2017) American Chemical Society.

factors on the properties of their interfacial layer. However, it is possible to reconcile the equilibrium and nonequilibrium frameworks by considering the timescales associated with the measurements and the aging of the samples. However, when studying weakly interacting systems, such as mixtures of PSS and dodecyltrimethylammonium bromide (DTAB), it can be challenging to conclude the role of nonequilibrium effects on interfacial properties due to discrepancies in the results. Different studies have reported varying results regarding the presence of surface tension peaks. In fact, the results of some authors do not show any peak in the surface tension isotherms [58,59], whereas a very evident surface tension peak was found by Abraham et al. [60]. This can be rationalized because PSS-DTAB samples take longer to precipitate than PDADMAC-SDS samples. Therefore, extreme care must be taken when handling the samples to observe similar behaviour to that reported for PDADMAC-SDS mixtures. In particular, a longer aging period of the samples (1 month as opposed to three days) is required when considering PSS-DTAB to ensure similar conditions to those found in PDADMAC-SDS mixtures [**9].

Abraham et al. [60] also found a clear plateau in the surface tension curves corresponding to fresh samples. However, when aged samples were evaluated, a surface tension peak appears having its maximum at the onset of the phase separation region. Therefore, it can be expected that the absence of the surface tension peak in the measurements of fresh samples can be the result of the nonequilibrium state of the mixtures considered. However, this is the source of an important discrepancy with the studies by Thomas and Penfold [5*]. They claimed that there is no possible scenario leading to the appearance of a surface tension peak under equilibrium conditions, and therefore the surface tension peak should be considered as a nonequilibrium feature. However, previous results from the same group pointed out the presence of surface tension peaks as the length of the alkyl chain of the surfactants is increased [61]. The appearance of those peaks was ascribed to a nonequilibrium effect as a result of the decrease of the solubility of the complexes as the length of the alkyl chain increased [5*]. It should be stressed that, although the work of Penfold's group neglects the role of nonequilibrium effects in the adsorption of PSS-DTAB mixtures, they found poor reproducibility in the determination of the surface tension plateau between different series of measurements [62]. The origin of this variability can be understood in terms of two different scenarios: (i) it was difficult to reach equilibrium in the system considered, or (ii) the experiments were carried out far from real equilibrium conditions. Consequently, the results of Taylor et al. [62] underlined the significant influence of non-equilibrium conditions on the interfacial behavior of PE-S mixtures, although the physical model proposed by the authors overlooks such an influence.

According to the above discussion, it can be assumed that the equilibration of PE-S films at fluid interfaces is the result of the complex interplay between three different competitive processes: (i) surface trapping; (ii) surface affinity, and (iii) transport under gravity. Therefore, when kinetically trapped states are considered, the mere diffusion of the complexes from the bulk to the interface is not enough to explain the formation of interfacial films [55]. Thus, having solved the cliff-edge peak problem as a general phenomenon related to the precipitation of aggregates over different timescales for different systems, research interest turned to the processes that might occur when aggregates contact a relevant interface. At the interface, PESCs can undergo a myriad of transformations influenced by the interplay of various factors such as specific chemistry, interactions, and hydrodynamic conditions [**9,49,54,63]. Understanding these dynamics is essential to elucidate the behaviour of PE-S mixtures in diverse environments ranging from biological systems to industrial processes.

Films of kinetically trapped aggregates close to technologically relevant conditions

Despite the significance of PE-S systems in numerous industrial and technological fields, there is a noticeable lack of research on systems that closely resemble those utilized in practical applications. The interest in deepening the interfacial properties of these concentrated systems emerges from the potential of these interfaces to stabilize foams and emulsions.

Llamas et al. [49] studied the bulk association and interfacial properties of concentrated mixtures formed by PDADMAC and sodium *N*-lauroyl-*N*-methylatorate (SLMT) using a combination of techniques, including surface tension measurements, neutron reflectometry or potentiometric titration. They found important differences in the behavior of concentrated mixtures in relation to traditional diluted ones. The main reason for this discrepancy arises from the extremely low concentration of free surfactants found within the measured range of bulk surfactant concentrations. Consequently, a physical framework involving the adsorption of bulk complexes becomes more pertinent in comparison to systems with lower bulk polyelectrolyte concentrations, where a synergistic co-adsorption of complexes and free surfactant is expected. Despite this, there is evidence of stoichiometric binding at the interface even at bulk compositions significantly distant from stoichiometric binding in the bulk. This underscores that the synergistic effect can wield considerable influence on interfacial behavior, even in more concentrated mixtures, particularly when the free surfactant concentration is only a few percent. Moreover, the impact of kinetically trapped aggregates on interfacial properties was substantial. In fact, PE-S particles were observed at the fluid interface, even though bulk compositions were several orders of magnitude away from the equilibrium two-phase region. The relatively large size of the observed islands indicated lateral coalescence of the aggregates at the interface.

Llamas et al. [42] extended their study to evaluate the dynamic aspects of the formation of the layers of PDADMAC-SLMT mixtures. Their results show that the layer formation at the fluid interface undergoes a two-step process. Initially, the adsorption of bulk-formed complexes takes place, followed by an interfacial reorganization of the adsorbed material until the equilibrium of the adsorbed layer is reached. However, the reorganization mechanism is strongly dependent on the specific PE-S pair [7]. In fact, for PDAMDAC-SLMT mixtures, the results suggest that the kinetically trapped aggregates remain unchanged after their incorporation at the fluid interface, and their reorganization is mainly associated with the packing of the trapped particles [42]. However, in other systems, such as mixtures of PDADMAC and sodium laureth sulfate (SLES), once the kinetically trapped aggregates arrive at the interface dissociation and spreading phenomena control the formation of the interfacial layers [41]. A similar mechanism to that found for PDADMAC-SLES mixtures was also reported by Angus-Smyth et al. [64] for mixtures of polyethyleneimine (PEI) and SDS in diluted conditions.

A last concentrated system studied was formed by mixtures of chitosan and SLES [65]. These mixtures present a very different scenario to the above described, which is possibly related to the low binding efficiency during the association. This leads to a non-negligible concentration of free surfactant in solution, establishing a competition between the PE-S aggregates and the free surfactant for covering the interface. This competition is shifted toward the complete depletion of the complexes from the interface for the highest surfactant concentrations where the fraction of free surfactant in the solution is above 50% percent of their nominal concentration [66].

Films formed by the direct spreading of aggregates from the bulk to the interface

The coverage of the interface by kinetically trapped aggregates may be predominantly influenced by the Marangoni spreading mechanism as demonstrated by Angus-Smyth et al. [64] using an overflowing cylinder and by Akanno et al. [41]. Thus, the interaction of aggregates with the fluid interface starts a material spreading which drives the accumulation of kinetically trapped aggregates at the interface. However, this can be influenced by the specific nature of the PE-S pair as was above discussed. Given the potential for material spreading from aggregates to induce significant surface excess at dynamic air/water interfaces, Campbell et al. [54,63,67**] opened a new avenue of research. Recognizing the importance of this phenomenon, they undertook pioneering research to elucidate the mechanisms underlying the spreading of PE-S aggregates directly onto a water surface. By exploiting the intricate dynamics of Marangoni flow, Campbell et al. [54,63,67**] developed a method to precisely control the deposition and spread of PE-S aggregates on the water surface. By exploiting the interplay between surface tension gradients and the hydrophilic or hydrophobic properties of the aggregates, they controlled the formation of spread films with remarkable precision and efficiency.

The direct spreading of kinetically trapped aggregates was demonstrated as a more effective route for the fabrication of kinetically trapped films than the direct adsorption of aggregates from the solution [67**]. Campbell et al. [67**] used direct spreading of an aqueous solution of a PSS-DTAB mixture with a composition corresponding to isoelectric point, at the fluid interface. This allows the production of films that can lead to interfacial confinement of over a third of the macromolecules in the system. Their results showed that the surface excess always remains below that corresponding to a complete surface layer of each component. However, the importance of the developed approach lies in the efficiency of the surface loading. In fact, a significant surface excess can be achieved with a minimal amount of material compared to systems based on direct adsorption from the bulk. In addition, the authors analyzed the dynamic properties of the films using an innovative implementation of neutron reflectometry, which improves the accuracy and time resolution in measuring interfacial stoichiometry during dynamic surface cycling. Using this new methodology, stoichiometric charge binding was observed at the interface, and after an initial compression cycle to the surface tension minimum, excess material was squeezed out over a complete surface layer. However, this material remains trapped at the interface during subsequent compression cycles. It should be noted that during the expulsion of material, the films exhibit linear ripples of hundreds of microns. They then adopt characteristics similar to perfectly insoluble membranes, maintaining a stable stoichiometric charge binding. These findings suggest the potential to control film coverage by adjusting the dynamic surface area, a factor that has previously been inferred only indirectly from surface pressure measurements.

More recently, Tummino et al. [68] extended the above approach to the preparation of interfacial films by direct spreading of positive and negative PSS-DTAB complexes. They also investigated the effect of ionic strength on the formation of interfacial films as a result of the spreading of the aggregates. The result showed that the spreading of compact positively charged aggregates on pure water leads to the formation of extended structures at the interface. These structures can be obtained either by spreading enough aggregates or by compressing a film beyond monolayer coverage. However, the morphologies produced in each scenario are different, with the formation of disordered structures as a result of successive Marangoni flows at the interface during spreading, and linear structures perpendicular to the compression direction during film compression. The exact nature of these extended structures, whether they are reservoir loops or multilayer stacks, was not clear from the results obtained. Conversely, films prepared from swollen negatively charged aggregates on pure water do not exhibit such extended structures, suggesting that the formation of these structures can be modulated by the charge/structure of the aggregates used in film preparation. On the one hand, the increase of the ionic strength suppresses the formation of extended structures. However, loops of polyelectrolyte stabilized by excess small ions are formed regardless of the charge/structure of the aggregates used in film formation. The exchange of material between the subsurface and the film occurs faster than the period of the surface cycles, but the energy barrier in the process results in extreme hysteresis in the surface pressure isotherms.

Carrascosa-Tejedor et al. [69] studied the interfacial structure and morphology of films resulting from the spreading of hyperbranched PEI-SDS aggregates at the air/water interface at two different pH values (4 and 10) to control the charge density of the polyelectrolyte. The results show that, regardless of pH, the spread films undergo similar structural changes upon compression of the surface area. These changes involve the formation of a surface monolayer with bound discrete PEI-decorated surfactant extended structures. Both Brewster angle microscopy images and ellipsometry together reveal the rigidity of the films at pH 4 and their mobility at pH 10. Ellipsometry further reveals the high heterogeneity of the films at pH 10, which is attributed to the presence of embedded aggregates, consistent with findings from a previous study of bulk adsorbed PEI-SDS complexes [70]. In addition, neutron reflectometry measurements suggest the formation of a diffuse layer of PEI loops exclusively at pH 10. On the other hand, the density of PEI associated with the surface monolayer is higher at pH 4 than at pH 10, possibly correlating with the differences in mobility of the films at these respective pH values. The results also show a greater amount of PEI in spread films at pH 10 than at pH 4, which is consistent with charge binding by an electrostatic driving force, indicating a lower charge density that facilitates a greater amount of PEI binding to the surfactant in the monolayer at pH 10 than at pH 4.

The comparison of the results obtained for spread films of hyperbranched PEI-SDS mixtures with those obtained for mixtures of poly(L-lysine) (PLL) and SDS reflects similarities in the interfacial structure [54]. Indeed, the presence of extended structures with comparable thicknesses (around 20 Å) and compatible with the characteristic dimensions expected for a surfactant bilayer (or hemimicelles) was found independently of the mixture considered. However, the polyelectrolyte layer beneath the extended structures is significantly thicker for PEI-SDS films, especially at pH 10 where polyelectrolyte loops are observed. This difference is attributed to the polyelectrolyte's hyperbranched structure and partially charged nature. Unlike PLL-SDS films, which exhibit a plateau in surface pressure during compression coinciding with the onset of extended structure formation, expanded PEI-SDS films continue to exhibit an increase in surface pressure after the onset of extended structure formation. Furthermore, although the surface pressure is higher at pH 10, the surface excess of surfactant is lower than at pH 4, suggesting that extended structures are formed with varying proportions of surfactant in the surface monolayer during spreading. This contrasts with PLL-SDS films where the onset of the formation of extended structures occurs upon compression beyond a discontinuity in surface pressure.

Carrascosa-Tejedor et al. [63] extended their work by comparing the behavior of spread layers of PLL-SDS with that found when the polypeptide is substituted by poly(L-arginine) (PLA). This was done to determine the effect of the different interactions between the surfactant and the polypeptide on the interfacial properties. PLA shows a stronger association with SDS than PLL due to the formation of hydrogen bonds between the guanidinium group and its oxygen atoms. In addition, SDS induces bulk β-sheet and α-helix conformations in the respective polypeptides. The underlying premise for this study was that exploiting such different interactions provides a way of fine-tuning film properties when subjected to compression to form extended structures. The results showed that while PLL-SDS films exhibit discrete extended structures after collapse to form a solid film, PLA-SDS films exhibit linear regions of higher material content associated with film folding. In particular, at the highest compression ratios, PLL-SDS films form more stable solid aggregates which are more difficult to redispersing on expansion and may become trapped at the interface. The morphology of the expanded structures varies depending on the maximum compression ratio applied. PLA-SDS films show reversible collapse regardless of the compression ratio applied, whereas PLL-SDS films show irreversible collapse at the highest compression ratio applied. The differences in the ability to reincorporate material at the interface are closely related to the flexibility of the polyelectrolyte chains. A refined analysis of the structural features of the films by neutron reflectometry showed that PLL-SDS mixtures can nucleate films with a high coverage of extended structures up to a sufficiently high compression ratio. Furthermore, the reduced water content in these films, together with the presence of two distinct layers of extended films, is consistent with observations of solid films using Brewster angle microscopy. Based on the results, it is not possible to confirm the retention of the secondary structure of polypeptides in the extended structures of the expanded films. However, the results suggest that the films in this study are stiffer than those obtained using flexible random coil polyelectrolytes, consistent with the higher stiffness of the β-sheet and α-helix conformations relative to the random coil.

The body of research discussed in this section, together with the wider investigations into the origins of surface tension peaks and the influence of nonequilibrium conditions on the adsorption behaviour of PE-S systems at fluid interfaces by Campbell et al. [**9,54,55,64,67**], represents a concerted and sustained effort to unravel the intricate implications and unexploited potential inherent in the interaction of PE-S aggregates with interfaces.

Concluding remarks

Mixtures of oppositely charged polyelectrolytes and surfactants are extensively studied colloidal systems with immense potential in industries as diverse as tertiary oil recovery, paper production, cosmetics, food processing, and drug delivery. Despite their widespread applications, realizing the full potential of PE-S systems has been hampered by the complex physical principles governing both their bulk and interfacial behavior. A particular challenge is to accurately define the true equilibrium conditions within these systems.

It is clear that the discussion in this review has revealed notable similarities in the general behavior of oppositely charged mixtures of polyelectrolytes and surfactants, especially when the bulk phase dynamics and the kinetics of aggregation are concerned. However, the association involves dynamic processes with different time scales depending on the specific mixing protocols employed and the specific PE-S pair. This variability in time scales dictates the approach to true equilibrium in such systems and significantly influences the properties resulting from the adsorption of the formed complexes at fluid interfaces. In fact, the nature of bulk binding interactions and the specific characteristics of the precipitate dictate the specific characteristics of the films formed at the fluid interface. Importantly, this dynamic nature often results in the formation of kinetically trapped films, further complicating the understanding and manipulation of these systems. In fact, the true equilibrium conditions are dictated by a complex interplay between different aspects, with the depletion resulting from precipitation in the equilibrium two-phase region playing a crucial role.

It is noteworthy that, despite reproducible steady-state properties can be measurable over days and weeks, the system can remain trapped far from equilibrium for an extended period. This underscores the potential limitations of the use of equilibrium considerations in the interpretation of the behavior of complex systems. The long-term non-equilibrium effects emphasize the need for a deeper understanding of the intricate interplay between bulk and interfacial dynamics in such colloidal systems. Further research is essential to unravel the underlying mechanisms that contribute to the observed prolonged departure from equilibrium and to refine the current conceptual frameworks for interpreting the system equilibration. In addition, a comprehensive understanding of the dynamic processes, equilibrium conditions, and subsequent properties of the formed complexes is essential to fully exploit the potential of polyelectrolyte-surfactant (PE-S) systems in various applications. Research efforts aimed at elucidating these complexities will pave the way for the design and optimization of tailored PE-S systems, unlocking their full potential across a spectrum of technological applications. In this direction, different studies in recent years have focused on the behaviour of systems under technologically relevant conditions, revealing a complex landscape characterized by a complex interplay between bulk composition, interfacial phenomena, and kinetic processes. Indeed, even in concentrated mixtures, the presence of kinetically trapped aggregates can significantly affect interfacial properties, leading to the formation of large aggregates at the fluid interface. In addition, recent advances in the coverage of interfaces by kinetically trapped aggregates have helped to elucidate the pivotal role of the Marangoni spreading mechanism and enabled the fabrication of kinetically trapped films with remarkable efficiency. Overall, the current research directions represent a concerted effort to unravel the multiple implications and unexplored potential of PE-S aggregate interactions with interfaces. In the future, further research in these directions promises to provide new insights into the design and optimization of materials for applications ranging from foam stabilization to emulsion control, thereby pushing the boundaries of colloid and interface science.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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