

# Association of oppositely charged polyelectrolyte and surfactant in solution: equilibrium and nonequilibrium features

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## Abstract

The association of polyelectrolytes and surfactants bearing charges of opposite signs has been for long time considered under an equilibrium framework. However, this is far to provide a true description of the physico-chemical rules of the association process when kinetically arrested nonequilibrium states are formed. This is the result of specific interaction pathways between the polyelectrolyte chains and the surfactant molecules determined by the mixing procedure and the mixture composition. In fact, the specific characteristics of the method used for the mixture can induce local inhomogeneities in the mixture composition which can govern the properties of the obtained supramolecular aggregates, driving to the systems to a situation far from the true equilibrium. This topical review tries to provides to the reader a general perspective of the role of the nonequilibrium aspects in the control of the polyelectrolyte-surfactant association process, and how these impact on the obtained supramolecular nanoassemblies, and their properties.

Keywords: association, complexes, Marangoni stresses, nonequilibrium, polyelectrolyte, surfactant

## 1. Introduction

The association of macromolecules bearing opposite charges is prone to drive the formation of nonequilibrium supramolecular complexes [1-3]. These are the result of specific formation pathways that leads to a kinetically trapping of the formed complexes in a dissipative state, instead of driving the formation of true equilibrium structures [4-6].

The formation of kinetically trapped states emerges as a phenomenon of a paramount importance in different

biological processes, including protein folding, hemostasis or ribosomal assembly [7-9]. Moreover, the transition between kinetically trapped states to thermodynamically stable ones, which is not always easy, can lead to the formation of a broad range of transient assemblies. These are, in most cases, inaccessible under conventional equilibrium conditions [10-13].

Complexes obtained by combining oppositely charged polyelectrolytes and surfactants are probably among the most studied supramolecular association nanoassemblies due to their broad range of applications in different fields of technological and industrial relevance, including cosmetic,

food science, painting, tertiary oil recovery, or drug delivery [14-20]. The broad spectrum of application of application of this type of colloidal systems has fostered an extensive research activity trying to understand the physico-chemical bases governing the association process, and how this association process can be tuned for optimizing the composition and properties of the mixtures for specific applications [21, 22]. However, a comprehensive description of the physico-chemical aspects of systems involving oppositely charged polyelectrolytes and surfactant is far from clear [22, 23]. This is the result of the important role of the nonequilibrium in the association process which can push the system to metastable states characterized by the kinetical trapping of the formed aggregates [24, 25]. This type of kinetically trapped aggregates tends to evolve with time towards an equilibrium situation [22]. However, this evolution can involve very lengthy processes [22], and hence attention must be paid to the mixture composition and the mixing protocol used for the mixture preparation to selectively tune the physico-chemical properties of the obtained polyelectrolyte/surfactant aggregates [22, 26].

The crossing of phase boundaries under nonequilibrium conditions has gained attention in recent years due to practical aspects in their applications and fundamental questions [27, 28]. The absence of equilibrium in polyelectrolyte-surfactant mixtures can induce the shifting of the phase boundary, promotion of new phases but also the disassembly of polyelectrolyte-surfactant complexes, or the coexistence between polyelectrolyte and surfactant rich phases [29]. This picture arises from the complex interplay of interactions, e.g., electrostatic, steric, and specific ones, involved in the assembly of the polyelectrolyte-surfactant, making the rationalization of the physico-chemical aspects guiding the behaviour of this type of colloidal systems a very difficult task [21, 22, 28, 30, 31]. Despite the recognized importance of the role of nonequilibrium aspects in the behaviour of polyelectrolyte-surfactant mixtures, up to date the use of classical thermodynamic approaches is very extended for evaluating the phase behaviour of this type of colloidal nanoassemblies [29].

This topical review is intended to provide a general perspective on the current understanding of the association process of oppositely charged polyelectrolyte-surfactant systems, including equilibrium and nonequilibrium aspects involved in this process. It should be noted that the discussion of the aspects related to the interaction of polyelectrolyte-surfactant complexes with fluid and solid interfaces will not be extensively discussed in this work, thus limiting the discussion to the association process occurring within bulk solutions. For a detailed, analysis of the behaviour of oppositely charged polyelectrolyte-surfactant systems in the vicinity of interfaces, we refers readers to the

works by Campbell et al [22, 32-35], Penfold and Thomas group [23, 36-38], or ourselves [21, 30, 39-41].

## **2. Oppositely charged polyelectrolyte-surfactant mixtures: an equilibrium framework**

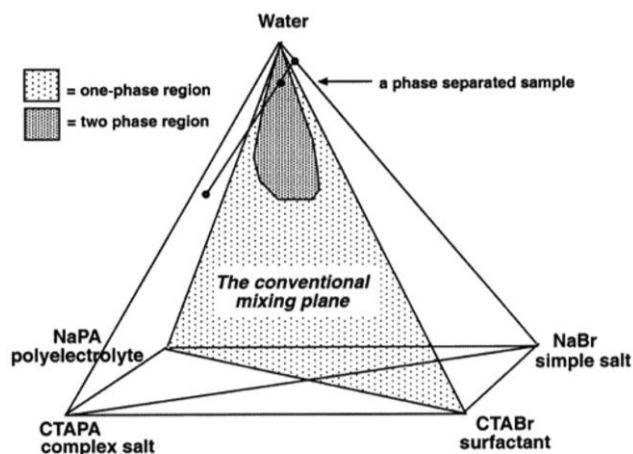
As was stated above, this work is intended to provide a description of the nonequilibrium aspects affecting to the formation of nanoassemblies as a result of the association of oppositely charged polyelectrolyte and surfactants. However, an understanding of the nonequilibrium association requires us to explore the most fundamental aspects related to the equilibrium framework describing the association.

In brief, the association between oppositely charged polyelectrolytes and surfactants is the results of an intricate balance between electrostatic and hydrophobic contributions that govern the binding, structure and phase behaviour of the formed polyelectrolyte-surfactant aggregates. The contribution of the electrostatic interactions can be easily modulated by changing the ionic equilibrium of the system through the modification of the pH or ionic strength. This leads to an association reminiscent of that which is expected for neutral polymers, where hydrophobic interactions control the association process [42]. In systems involving charged species, the electrostatic interactions govern the initial polyelectrolyte-surfactant association, whereas the hydrophobic interactions contribute to the formation of micellar aggregates along the polymer chains. Moreover, hydrophobic interactions can also contribute to the association process when polyelectrolytes with big hydrophobic domains are considered [43, 44].

### *2.1 Phase Diagram*

The mutual association of oppositely charged polyelectrolytes and surfactant to form polyelectrolyte-surfactant complexes (PESCs) has been described for a long time in terms of the equilibrium phase diagram. Unfortunately, the thermodynamics description of this type of systems is far from clear due to different aspects. Firstly, the design of a true phase diagram of a polyelectrolyte-surfactant system is a multidimensional problem, involving many variables. In fact, in the most favourable situation when the complexation of a polyelectrolyte and an ionic surfactant in pure water is considered, we must consider up to five different components (water, polyion -ion resulting from polyelectrolyte dissociation-, surfactant ion -ion resulting from surfactant dissociation-, and the two counterions resulting from the polyelectrolyte and surfactant dissociation, respectively) to design a phase diagram. Therefore, assuming that temperature and pressure are constant in the systems. The phase diagram requires at least five degrees of freedom corresponding to the compositions of each component, and hence the phase diagram will be

represented by a tetragonal pyramid [45]. This situation is even more complicated in the presence of inert salts, cosolvents or cosurfactants, making the representation of the phase diagram of polyelectrolyte-surfactant mixtures a very complex multidimensional problem [46-48]. Figure 1 depicts an idealized phase diagram corresponding to the mixture of the anionic polyelectrolyte sodium polyacrylate NaPA and the cationic surfactant cetyltrimethylammonium bromide CTABr.



**Figure 1.** Idealized phase diagram for a polyelectrolyte-surfactant mixture constituted by NaPA and CTABr. In the vertices of the tetragonal pyramid are indicated the five components: water, the polyelectrolyte NaPA, the surfactant CTABr, and the two salts formed by combination of the ions resulting from the dissociation of the polyelectrolyte and surfactant: CTAPA (polyelectrolyte-surfactant complex) and NaBr. Reprinted with permission from Svensson et al. [45]. Copyright (2002) American Chemical Society.

A second aspect that complicates the design of phase diagrams in mixtures of polyelectrolytes and surfactants bearing opposite charges is the broad number of phases occurring in this types of systems, e.g., liquid solutions and dispersions, gels or solids [49]. Moreover, the phase behaviour of polyelectrolyte-surfactant mixtures can present phase separations originated as result of different phenomena. In fact, phase separation can proceed through a segregation mechanism that leads to the formation of two phases enriched in different components, i.e., one phase enriched in the polyelectrolyte and the second one enriched in the surfactant; or following an association process, resulting in the formation of phases containing both components but characterized by their different composition, generally a concentrated phase enriched in polyelectrolyte-surfactant complexes, and a diluted one containing polyelectrolyte and surfactant molecules [49]. It is worth mentioning that in mixtures of polyelectrolytes and surfactant bearing opposite charges, associative phase separation is most common than segregative one, with the

latter occurring almost exclusively in mixtures at high ionic strengths [50].

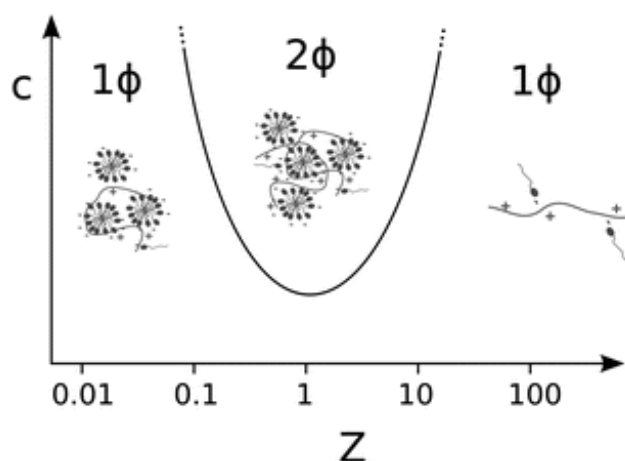
The study of the phase diagram can be enormously simplified taking into consideration that all the phases in equilibrium should fulfill the electroneutrality principle. This makes it possible to simplify the complex multidimensional phase diagrams analyzing the phase behaviour through the conventional mixing plane (see Figure 1). This relies on describing the phase behaviour using 2D maps where information about the compositions of the mixture is provided in terms of the water, the polyelectrolyte or the surfactant, and the complex salt. Thus, it is possible to characterize the main features of the phase behaviour of oppositely charged polyelectrolyte-surfactant mixtures [49]. Li et al. [51] used this approach for elucidating the phase diagram of mixtures formed by the cationic polyelectrolyte JR400 (a chloride salt of the N,N,N-trimethylammonium derivate of the hydroxyethyl cellulose) and the sodium dodecyl sulfate (SDS), which allows them to define the true boundaries of the phase separation region, contributing to explain the discrepancies of previous phase diagram reported in the literature. Moreover, they pointed out that the onset on the phase separation corresponds to a minimum in the system enthalpy.

The simplest alternative to evaluate the phase behaviour of polyelectrolyte-surfactant mixtures relies on the qualitative and/or quantitative determination of the dependence of the turbidity of the samples on the ratio between the number of charged monomers of the polyelectrolyte in solution and that corresponding to the number of surfactant molecules, i.e., the so-called Z ratio. An increase of the turbidity is common as the system approaches to the phase separation, which can be understood in terms of the charge compensation driven by the association of surfactant molecules to oppositely charged polyelectrolyte chains. This compensation takes the system to an isoelectric point characterized by PESC with a zero net charge for  $Z=1$ , and hence lacking stability, leading to the phase separation [22]. Therefore, it can be assumed that the progressive addition of an oppositely charged surfactant to a polyelectrolyte solution, i.e., the decrease of Z ratio, leads to a decrease of the net charge of the polyelectrolyte chains. However, this neutralization process is not relevant below the critical aggregation concentration, CAC, i.e., the threshold concentration where the surfactant binding to the polyelectrolyte starts to be significant (Note: the CAC is generally 2-3 orders of magnitude below the critical micelle concentration, CMC, of the pure surfactant). This means that below the CAC the net charge of the complexes remains close to that of the bare polyelectrolyte chains. Above the CAC, the addition of surfactant molecules drives the neutralization of the polyelectrolyte charges, pushing the system to the onset in the phase separation region in the

vicinity of the isoelectric point ( $Z=1$ ). It should be noted that for  $Z$  ratio values above unity, the mixtures are characterized by the presence of PESCs bearing an excess of charges with the same sign than the bare polyelectrolyte molecules. This is the result of the presence of monomers which are accessible for the compensation upon binding of surfactant molecules or micelles. Therefore, it can be assumed that the decrease of the  $Z$  ratio as the surfactant binding proceeds takes the system from a one-phase region ( $1\phi$ ) to a phase separation region ( $2\phi$ ) for  $Z$  ratio values close to unity. This transition is commonly evidenced by the appearance of phase separated precipitated, coacervates, gels or other type of ordered structures enriched in PESCs [14]. Further decreases of the  $Z$  ratio beyond the phase separation region leads to the resolubilization of the phase separated complexes due to the overcompensation process mediated by the cooperative binding of additional molecules of surfactant in relation to that required for neutralizing all the charges of the polyelectrolyte chains. This pushes the system to a new one-phase region ( $1\phi$ ). This may be easily understood in terms of the net charge of the formed complexes. The addition of ionic surfactant molecules to a oppositely charged polyelectrolyte solution results in a progressive neutralization of the net charges of the complexes up to reaching the isoelectric point or charge neutralization concentration (CNC) where aggregates with a zero net charge are formed. Therefore, it can be assumed that below the CNC, soluble undercompensated aggregates are formed. These present an excess of free monomers of the polyelectrolyte chains, which controls the aggregate charge. Once the CNC is reached, the neutral character of the formed aggregates leads to a reduction of their solubility, pushing the system towards the phase separation (solid-liquid -precipitation- or liquid-liquid -coacervation-) [52]. It is worth mentioning that a part of the surfactant molecules may remain free in solution without contributing to the neutralization of the polymer chain, and hence the CNC would be shifted to a  $Z$  ratio value below unity [16]. The increase of the surfactant concentration above the CNC takes the aggregates to a situation where there is an excess of bound surfactant molecules to the polyelectrolyte chain in relation to that required for the neutralization, and hence soluble overcompensated complexes are formed. These present a charge that is dominated by the excess of bound surfactant molecules. Figure 2 displays a simplified version of the phase diagram for an arbitrary system composed of a mixture of a polyelectrolyte and a oppositely charged surfactant.

The phase diagram shows the presence of different phases as a function of the concentration ( $c$ ) and the values of the  $Z$  ratio. Therefore for values of  $Z$  ratio different unity, one-phase mixtures are obtained. On the other side, for values of the  $Z$  ratio in the vicinity of the unity, a phase separated

mixture may be expected. It should be noted that the width of the phase separation region, as well as the stoichiometry and structure of the obtained complexes depends on different physico-chemical parameters, e.g., total concentration, molecular weight (and its distribution) of the polyelectrolyte, the stiffness of the polyelectrolyte chain, or the charge density of the polyelectrolyte chains [53-55]. Moreover, the hydrophilicity of the polyelectrolyte plays a very critical role on the onset of the phase separation. In particular, highly hydrophilic polyelectrolytes can undergo phase separation only at very high ionic strengths, whereas for non-polar polyelectrolytes, phase separation can appear in a broad salt concentration range [14, 31].



**Figure 2.** Schematic phase diagram for an arbitrary oppositely charged polyelectrolyte-surfactant mixture as function of the concentration  $c$  and the  $Z$  ratio. Reproduced from Chiappisi et al. [53] with permission from the Royal Society of Chemistry.

Gradzielski's group [28, 56, 57] proposed that the evaluation of the conformational transitions occurring in polyelectrolyte-surfactant mixtures by changing the composition can be very useful for identifying the onset of the phase separation region. They used neutron scattering techniques and found the formation of collapsed clusters of rod-like aggregates for compositions close to the boundaries of the phase separation region. The formation of such type of structures provokes a significant increase of the mixture viscosity, which is reduced as the surfactant concentration is increased within the phase separation due to the formation of more compact structures. Once the phase separation is overcome, i.e., within the one phase region occurring at the highest surfactant concentrations, there is a viscosity increase due to a new conformational transition from compact rod-like aggregates to extended aggregates constituted by polyelectrolyte chains decorated by bound micelles [56].

The correlations between the bulk association and the phase behavior of polyelectrolyte-surfactant systems are a result of the thermodynamic equilibrium condition between phases defined by the equality of chemical potentials

between the coexisting phases. This equilibrium condition can be modulated by the physico-chemical properties of the polyelectrolyte chains (hydrophilic/lipophilic character, charge density, molecular weight, chain flexibility and branching degree) and the surfactant molecules (hydrophobic chain nature and length, type of hydrophilic head, and concentration). Moreover, it is necessary to consider the role of the solution properties, including pH, ionic strength or temperature, in the phase behaviour of polyelectrolyte-surfactant mixtures due to the potential impact of the solution properties on the control of the interactions involved in the polyelectrolyte-surfactant association [30]. In fact, such variables are of a paramount importance because they influence the binding of the surfactant molecules to the polyelectrolyte chains [58]. This was demonstrated by Wallin and Linse using Monte Carlo simulations and Self Consistent Field calculations [59, 60].

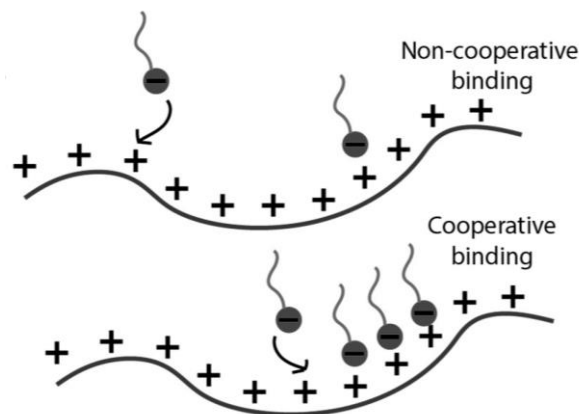
## 2.2 Understanding the polyelectrolyte-surfactant association

Polyelectrolyte-surfactant association is the result of a complex interplay between different interactions (electrostatic, hydrogen bonds, and hydrophobic interactions) that are controlled by the specific chemical nature of the involved species [61-63]. In particular, the understanding of the association mechanism requires us to consider the following aspects: (i) electrostatic binding of the surfactant charged head to the charged monomers in the polyelectrolyte backbone; (ii) hydrophobic interactions involving the surfactant tails, and the hydrophobic residues of the polyelectrolyte backbone; (iii) counterions release, and entropy gain; and (iv) interactions between polyelectrolytes and surfactant micellar-like aggregates that can contribute to reduce the repulsion between micelle charged groups, and the unfavourable interactions of the micelle hydrophobic regions and water [30, 64].

In general, the binding is strongly dependent on the nature of the interactions involved in the system, and can follow three different mechanisms: cooperative, anticooperative and non-cooperative [65]. Figure 3 shows a schematic representation of the situation occurring for cooperative and non-cooperative binding.

The association between polyelectrolytes and surfactants bearing opposite charges can be understood as an ion exchange process, where the release of small counterions due to the surfactant binding to the polyelectrolyte chains results in a strong increase of the entropy of the system from the lowest surfactant concentrations characterized by a non-cooperative binding, i.e., the binding occurs in regions where there are no bound surfactant molecules yet. Therefore, the non-cooperative binding constrains the binding process to positions which are surrounded by free monomers. This

results in the screening of the intra-chain repulsion up to reaching the CAC, where the cooperative binding starts.



**Figure 3.** Schematic representation of the situations expected for non-cooperative and cooperative binding. Reprinted from Khan et al. [31], with permission under Open access CC BY 4.0 license, <https://creativecommons.org/licenses/by/4.0/> (accessed on 24 November 2022).

Cooperative binding is characterized by a sudden occurrence of the binding process in a very narrow range of surfactant concentration. This type of binding can be understood considering the existence of secondary interactions with increasing importance as the electrostatic binding progresses. For instance, the participation of hydrophobic interactions between the hydrophobic tails of the surfactant molecules, can lead even to the formation of complexes where surfactant-like micelles are bounded to the polyelectrolyte chains. This leads to a sudden increase of the number of surfactant molecules linked to the polyelectrolyte chains, and hence plays an essential role in the redissolution of phase separated equilibrium mixtures (mixtures with  $Z < 1$ ). Therefore, cooperative binding does not introduce any constraint to the position where a new surfactant molecule is bonded, i.e., the binding can occur with independence of the existence of surfactant molecules in adjacent positions.

The binding becomes more complex when solutions with high ionic strength are considered. In this situation, the charge screening weakens the electrostatic interactions, and the polyelectrolyte and surfactant undergo an association that may be considered similar to that expected for neutral molecules, where the hydrophobic interactions play a very central role [43].

A last type of binding mechanism is the so-called anticooperative one and occurs in those systems where the binding is guided by specific interactions between the polyelectrolyte chains and the surfactant molecules [21, 30, 31, 53, 66, 67]. In fact, anticooperative binding is strongly influenced by the specific architectures of polyelectrolyte and surfactant molecules [68], and hence can lead to situations in which the formation of free micelles can be

favoured in relation to polyelectrolyte-surfactant association [69]. Therefore, there may be a different degree of cooperativity for the binding of ionic surfactant to oppositely charged surfactant depending on the nature of the interactions involved in the association, which is strongly dependent on the specific nature of the considered polyelectrolyte-surfactant pair [70]. For instance, the association can change strongly depending on the polymer rigidity as demonstrated Leung et al. [51]. They found that in the association of SDS with rigid cationic modified cellulose, the intermolecular association is extremely favoured whereas for mixtures with more flexible polyelectrolytes, e.g., vinyl polycations, the intramolecular association is predominant, giving as a result a weakening of the intermolecular interactions.

It is worth to stress that the binding of the surfactant to the polyelectrolyte chains is of a paramount importance for understanding different physico-chemical aspects of the behaviour of polyelectrolyte-surfactant mixtures, impacting even the phase diagram as was briefly discussed above. In fact, it may be expected that the physico-chemical properties of polyelectrolyte-surfactant systems undergo an important modification for surfactant concentrations close to the CAC, and hence the evaluation of the binding in terms of any property providing information about the concentration of free surfactant molecules ( $c_f$ ), i.e., unbound molecules remaining in solution with respect to the total concentration of surfactant molecules in the mixture ( $c$ ) can help to understand the complexation mechanism. The most common approach for binding evaluation is the use of the binding isotherms which are defined in terms of the surfactant dependence of the fraction of bound surfactant molecules ( $\beta$ ), i.e., the so-called binding degree, defined as a ratio between the concentration of bound surfactant molecules ( $c_b=c-c_f$ ) and the total monomer concentration ( $c_p$ ) according to the following expression [39, 71, 72]

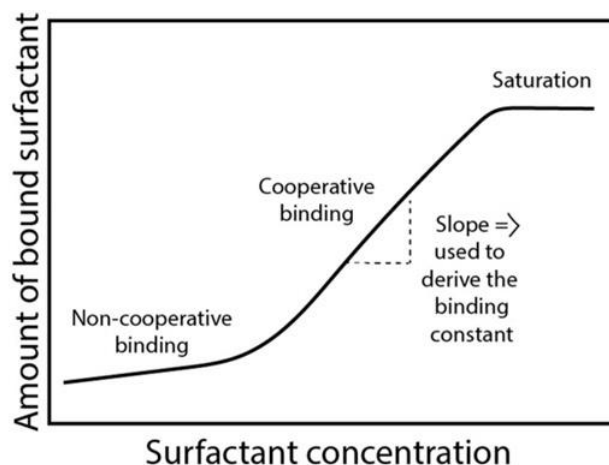
$$\beta = \frac{c_b}{c_p} \tag{1}$$

There are currently available a broad range of techniques that can be exploited for extracting information about the binding process, e.g., electrophoretic mobility measurements, potentiometric titration, isothermal titration calorimetry [39, 71-75]. In most cases, the obtained binding isotherms present a sigmoidal-like shape, in which regions appear of different slope depending on the type of binding occurring for the specific concentration range. Figure 4 show an idealized sketch of a binding isotherm where regions of different cooperativity are indicated.

The cooperative binding region is characterized by a sharp increase of the fraction of bound molecules with the increase of the surfactant concentration. The slope of this sharp

increase on the binding isotherm is related to the equilibrium constant for cooperative binding ( $Ku$ ), which provides information about the strength of the binding. In the non-cooperative binding, the concentration dependence of the fraction of bound molecules is weaker than for the cooperative regime. This can be understood considering the constrains to the binding in the non-cooperative regime. On the other hand, the anticooperative binding is commonly associated with the absence of any significant increase of the binding with the surfactant concentration [31].

It should be stressed that surfactant binding is associated with the thermodynamic aspects of the association process, and can be described in terms of different enthalpic contributions,  $\Delta H$ . These include, among other factors, the dissociation of surfactant micelles (demicealization), the binding of surfactant to the polymer chains, conformational changes in the polymer and dilution effects, the latter being much smaller than the other ones [76, 77].



**Figure 4.** Schematic representation of a binding isotherm where a non-cooperative binding regime and a cooperative one are represented. Adapted from Khan et al. [31], with permission under Open access CC BY 4.0 license, <https://creativecommons.org/licenses/by/4.0/> (accessed on 24 November 2022).

The most common methodology followed for evaluating the polyelectrolyte-surfactant association process is in terms of the binding isotherm [36, 78], which is commonly interpreted in terms of thermodynamic or statistical models, e.g., Satake–Yang equation [67, 79]. This approach considers the polyelectrolyte chain as a lattice with  $N$  sites where surfactant molecules can bind [66, 80, 81], providing a description of the concentration dependence of  $\beta$  according to the following expression,

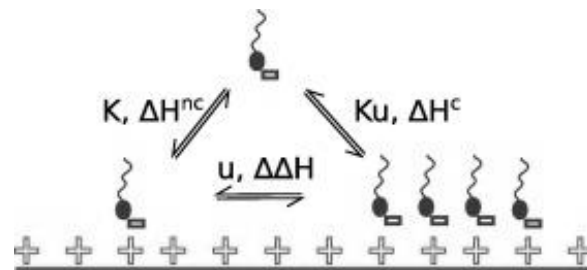
$$\beta = \frac{1}{2} \left[ 1 + \frac{Kuc - 1}{\sqrt{(1 - Kuc)^2 + 4Kc}} \right], \tag{2}$$

where  $K$  is the equilibrium binding constant for a single surfactant to a binding site,  $u$  is a parameter accounting for the cooperativity of the binding process, and  $Ku$  is the constant for cooperative binding. Despite the interest of the use of the above model for the description of the binding isotherm of many polyelectrolyte-surfactant mixtures, enabling the comparison of the binding strength in different systems, it provides an oversimplified picture of the binding process [51, 66, 74, 82]. This is because the model does not consider the role of the steric hindrance or the interactions between surfactant hydrophobic tails across non-occupied sites. Moreover, it does not account for multibody interactions, and considers the polymer as a rigid linear array of binding site, which is far from the real situation characterized by the possible interactions of surfactant placed in very distant positions as result of the chain flexibility [80, 81]. In fact, the specific architecture of the polymer plays a very important role on the surfactant binding. Banerjee et al. [83] using mean-field calculations demonstrated that the polymer chemical nature, and its specific structural arrangement govern the association process for a particular mixture, controlling the final structure and morphology of the obtained complexes. This agrees, at least qualitatively, with the findings by Liu and Wagner [84] who found a series of semiempirical correlations between the strength of the cooperative binding, and the polyelectrolyte charge density and the surfactant hydrophobicity. The results showed that the cooperative binding strength increases with the square of the polyelectrolyte charge density, and linearly with the surfactant hydrophobicity. The presence of specific interactions during the binding process provokes a deviation of the mentioned general trends.

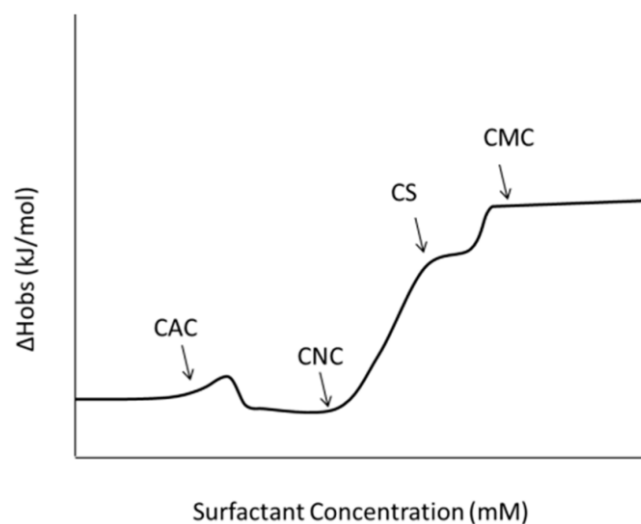
According to the above discussion, an accurate description of the binding process of ionic surfactant molecules to oppositely charged polyelectrolyte chains requires an extension of the Satake–Yang model by including additional enthalpic contributions accounting for different physico-chemical aspects involved in the association. The simplest approach considers that together with the enthalpic contributions associated with the non-cooperative binding region ( $\Delta H^{nc}$ ) and the cooperative one ( $\Delta H^c$ ), it is necessary to include an enthalpic contribution accounting for the transition between these two regimes ( $\Delta\Delta H$ ). Figure 5 represents the three enthalpic contributions, and the corresponding binding equilibria describing the association of a polyelectrolyte with an oppositely charged surfactant.

The best option to evaluate the binding process from a thermodynamic perspective is the use of microcalorimetric measurements [75]. This is important because it helps to understand the driving forces involved in the association process from a semiquantitative point of view. This is possible because the microcalorimetric curves display different regions which give information on the enthalpic

changes occurring within the different steps of the binding process. Figure 6 shows a sketch of a typical curve obtained during an isothermal titration experiment.



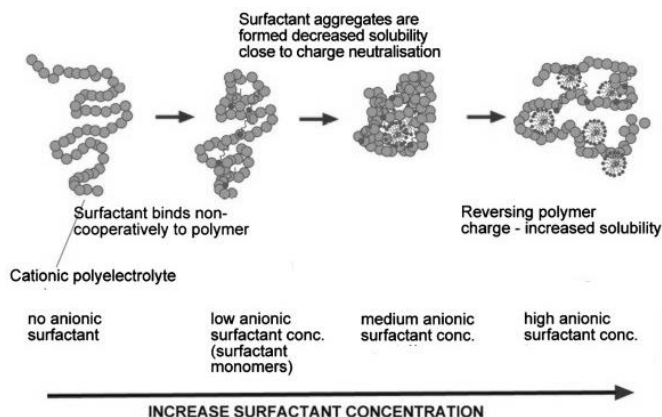
**Figure 5.** Sketch of the three equilibria involved in the binding of ionic surfactants to oppositely charged surfactants. Reprinted from Chiappisi et al. [75], Copyright (2014) with permission from Elsevier.



**Figure 6.** Schematic representation of the enthalpic changes for the association of oppositely charged polyelectrolyte-surfactant systems. Adapted from Khan et al. [31], with permission under Open access CC BY 4.0 license, <https://creativecommons.org/licenses/by/4.0/> (accessed on 4 December 2022).

At the lowest surfactant concentrations, the enthalpy change remains constant with the concentration increase due to the absence of enthalpic contribution associated with the non-cooperative binding. Then, the enthalpy increases sharply, the association becoming highly endothermic, in the vicinity of the CAC, which is characterized by the presence of a maximum in the calorimetric curve, the so-called cooperative peak. This reflects the strength of the cooperative binding, and it is the common signature for the transition from a non-cooperative binding regime to a cooperative one. The increase of the surfactant concentration beyond the CAC leads to a decrease of the enthalpic contribution down to a value close to zero, i.e., the binding

becomes endothermic up to reaching the isoelectric point or charge neutralization concentration (CNC). Further increases of the surfactant concentration push the system to a new endothermic region that takes the system to a situation characterized first by the saturation of all the binding sites of the polyelectrolyte chains (concentration of saturation, CS) and then by the formation of surfactant micelles free in solution, allowing to define the critical micelle concentration (CMC) [84, 85]. Figure 7 displays a sketch of the different steps occurring during the association of polyelectrolytes and surfactant bearing opposite charges.



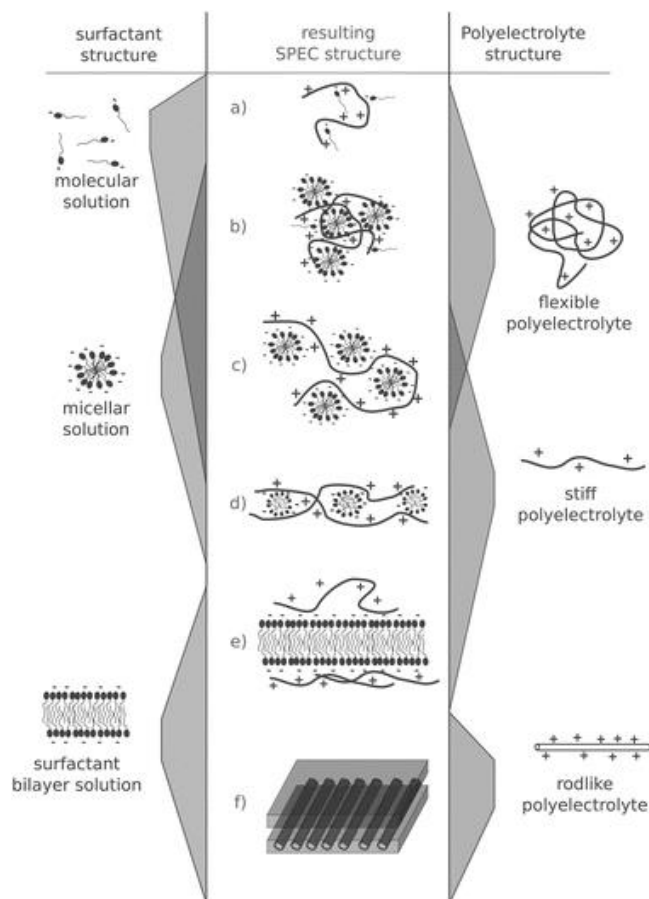
**Figure 7.** Sketch of the different steps involved during the association of polyelectrolytes and surfactant bearing opposite charges. Reprinted from Bain et al. [64], Copyright (2010) with permission from Elsevier.

### 2.3 Structure of PESCs : Generalities

The richness in structure and properties of polyelectrolyte and surfactants makes it predictable that their combination to form PESCs can lead to the formation of a broad range of potential structures [28, 53, 86, 87]. These are controlled by structural parameters of polyelectrolyte and surfactant molecules, including the chain stiffness of the polyelectrolyte, its charge density. Moreover, the proximity between the charge residue and the polyelectrolyte backbone, and the molecular weight of the polyelectrolyte can play a very important control over the final structure of the complexes. For the surfactant, the packing parameter, and the nature of the headgroup are central parameters for controlling the formation of polyelectrolyte-surfactant nanoassemblies [53, 83, 88]. It is worth mentioning that the structure of PESCs plays a key role in the control of the properties of polyelectrolyte-surfactant mixtures [57].

It is common that the structure of PESCs results from the arrangement of individual surfactant molecules or micelles in relation to the polyelectrolyte chains [89]. This can drive the formation of different types of structures, including gel-like systems or precipitates. Moreover, it may be also possible the formation of more complex structures, including lamellar

structures, or nanoassemblies containing cylindrical micelles or spherical vesicles with the polyelectrolyte chains forming a cross-linked network with surfactant micelles or vesicles joining several chains. Under specific conditions it is also possible to obtain core-shell structures, with the polyelectrolyte decorating the core of the obtained nanoassemblies [28, 88, 90]. Examples of possible structural arrangements for PESCs are shown in Figure 8.



**Figure 8.** Sketch of some of the potential structures that can be expected in PESCs as a function of polyelectrolyte and surfactant characteristics. (a) surfactant decorated polyelectrolyte ; (b) densely packed micelles "glued" by a polyelectrolyte; (c) pearl-necklace structure; (d) rod-like aggregation of micelles with a stiff polyelectrolyte; (e) flexible polyelectrolyte attached to a bilayer; and (f) rod-like polyelectrolyte incorporated between bilayers. Reproduced from Chiappisi et al. [53] with permission from the Royal Society of Chemistry.

For large values of  $Z$ , i.e., complexes with an excess of uncompensated monomers, the formation of aggregates is possible with the presence of single surfactant molecules or surfactant micellar aggregates bound to the polyelectrolyte chains. The formation of the latter structures even at concentrations well below the CMC is guided by the hydrophobic effect as result of a locally enhanced surfactant concentration. However, the formation of aggregates with



bound micelles for relatively low surfactant concentrations requires flexible polyelectrolytes, otherwise the formation of aggregates where individual surfactant molecules are bound to the polyelectrolyte chains would be favoured. In general, it can be assumed that the structure of PESC is determined by the complex interplay between the loss of energy associated with the bending of the polyelectrolyte chains and configuration entropy during the association process, and the free energy associated with the hydrophobic effect. When the concentration overcomes the CMC, it is possible to find similar structures, existing micelles are arranged in solution as a result of the presence of the oppositely charged polyelectrolyte.

The association between micelles and polyelectrolyte chains can occur to generate a broad range of structures, including pearl-necklace structures or densely packed micelles “glued” together by the presence of a polyelectrolyte. The most probable configuration is defined mainly by the charge density of the used polyelectrolyte [91]. In some cases, the formation of liquid crystalline like structures may be even possible [92]. This requires the assembly of polyelectrolytes characterized by a persistence length smaller than the micelle radius, which enables the formation of dense polyelectrolyte arrangements surrounding the micelles. For polyelectrolytes with a rather high persistence length, the formation of nanoassemblies characterized by the formation of micellar arrangements along a preferential axis is frequent, resulting in the formation of tube-like polyelectrolyte-micelle aggregates [53].

The increase of the rigidity of the polyelectrolyte backbone, accompanied by the reduction of the charge density of the chain as commonly occurs in polysaccharides, reduces the polyelectrolyte ability for compensating the charge of micellar aggregates. Therefore, for this type of PESC the formation of elongated nanoassemblies may be expected [93]. The situation becomes just the opposite when flat surfactant structures are considered instead micelles, where stiff polyelectrolytes result in a more efficient interaction with the surfactant aggregates. If the polyelectrolyte is not stiff enough, an inefficient interaction may occur due to the important loss of configurational entropy [94].

### 3. Non-equilibrium in oppositely charged polyelectrolyte-surfactant mixtures

The above discussion present a description of the association between oppositely charged polyelectrolyte and surfactant considering an equilibrium perspective. However, this equilibrium cannot be reached under specific conditions. For instance, the experimental protocol followed for mixing the polyelectrolyte and the surfactant can introduce convective and diffusive contributions to the association

process [95], which drives the formation of PESC (the so-called kinetically trapped aggregates) characterized by a composition and structure far from that expected for equilibrium nanoassemblies. The emergence of non-equilibrium effects does not influence the qualitative characteristics of the phase diagram. However, they modify the boundaries between the different phases and the structure of the complexes. Moreover, the formation of kinetically-trapped aggregates can shift the phase separation to  $Z$  values far from the unity, i.e., phase separation can occur in systems containing non-neutral aggregates [21, 22, 96, 97]. It should be noted that kinetically-trapped aggregates correspond to a metastable conformation of PESC, and hence it is expected that they can evolve towards the true equilibrium conformation. Unfortunately, up to date there are no general rules providing a comprehensive description of the equilibration process, and no information about the equilibration times, which are expected to be strongly dependent on the specific polyelectrolyte-surfactant pair, are available.

It is common to consider the formation of kinetically trapped aggregates as a result of the existence of local compositional heterogeneities during the mixing of the components. In fact, the presence of concentration gradients in the mixture causes its local composition to differ substantially from the equilibrium composition, which is reflected in the composition and structure of the obtained PESC. For instance, the presence of composition heterogeneities can be simply a result of how the complexes are obtained, i.e., how the polyelectrolyte and surfactant are mixed [22, 24, 39, 96]. In fact, the formation of kinetically trapped aggregates can be considered a very complex process that can result from the formation of aggregates with a local composition similar to that expected for the two-phase equilibrium region together with aggregates resulting from the lack of colloidal stability of PESC, followed by a charge stabilization process once a sample with excess of polyelectrolyte and surfactant is fully mixed [21].

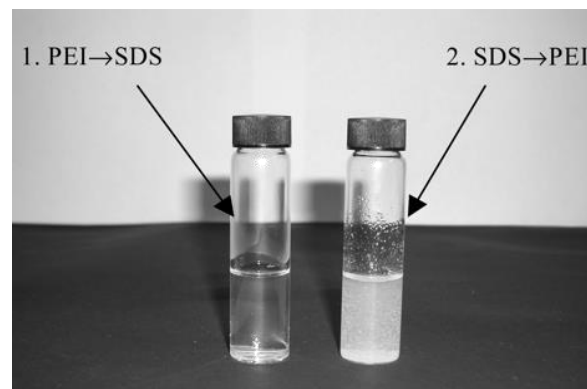
Very recently, Bezrukov and Galyametdinov [95] using microfluidic devices have explored the nonequilibrium character of the association of different polyelectrolyte-surfactant mixtures, and found that the main limitation to fix a true equilibrium is the diffusivity of the components, which is too high, and makes difficult to establish true equilibrium mixing conditions. Therefore, the hydrodynamic conditions of the mixing process becomes a very critical aspect to control the nature of the obtained aggregates (true equilibrium vs. arrested states).

Meszáros et al. [98] studied mixtures of poly(ethyleneimine) (PEI) and SDS, and found that the speed of the polyelectrolyte-surfactant mixture mixing was critical for the final nature of the mixture. In fact, a fast mixing of the components, regardless of the addition order, resulted in

the formation of perfectly clear solution. However, for the same final composition, a slow addition of the SDS solution to the PEI one drives the system to the phase separation. Similar results were found when the surfactant solution is added to the PEI in two steps, i.e., first a small amount of SDS is added, and then after a delay time for ensuring the stabilization of the mixture, the rest of the SDS is added. The above differences can be interpreted considering that a fast mixing favors the binding of the SDS excess to the PESC, which provides an additional kinetical stability to the formed aggregates as a result of the formation of electrostatically stabilized colloidal aggregates, limiting the phase separation events [22, 99]. Figure 9 shows the appearance of PEI-SDS mixtures obtained using protocols involving different order of addition during the mixing of the components. The above results agrees with the finding by Mezei et al. [99] for the same mixture, and demonstrated that a rapid mixing favours the formation of colloidal aggregates stabilized by an excess of surfactant molecules, whereas less efficient mixing procedures result in the formation of large clusters of individual PEI-SDS particles, and favour the onset of the system in the phase separation region. The above discussion suggested that the presence of concentration gradients during the mixing of the components is of paramount importance in the formation of kinetically trapped aggregates. However, there are additional parameters that can affect the non-equilibrium character of the polyelectrolyte-surfactant association, e.g., shearing. For instance, the use of a different stirring speed during the mixing process can induce the formation of aggregates with very different characteristics. If the stirring is maintained slow, the formation of true equilibrium is favoured against the production of kinetically trapped aggregates, whereas the opposite is true when the mixing is performed vigorously [100]. Therefore, the modulation of the mixing speed provides a mechanism for shifting the compositional range corresponding to the phase separation in agreement with the finding by other authors [71, 101-107].

Further studies on the nonequilibrium effects induced by different mixing methods were performed by Mezei et al. [108] on poly(vinylamine)-SDS mixtures. They found that a high local concentration of surfactant molecules favors the formation of kinetically trapped aggregates. This is favored by using very efficient mixing methods (the so-called stop flow mixing), whereas it prevented using a gentle mixing procedure. Moreover, the obtained results suggested that polyelectrolyte-surfactant mixtures cannot be described as true solutions including solvated PESC, it is most appropriate to call them colloidal dispersion. It should be noted that the formation of kinetically trapped aggregates can be also favoured by using high polyelectrolyte concentrations, leading to different situations depending on the polyelectrolyte charge density. Thus, for polyelectrolyte

with a reduced charge density, the formation of thermodynamically stable solutions is common, whereas the formation of kinetically trapped aggregates stabilized by the uncompensated monomers is the most usual scenario when highly charged polyelectrolytes are used [109].



**Figure 9.** Effect of the mixing order in PEI-SDS mixtures of final composition (PEI concentration 0.05%w/w, and SDS concentration 10 mM): PEI on SDS (left) vs. SDS on PEI (right). Reprinted with permission from Meszaros et al. [98]. Copyright (2020) American Chemical Society.

The production of kinetically trapped aggregates can be also controlled by changing the value of the Z ratio [24]. In fact, the preparation of dispersions with a large surfactant excess can favor the formation of overcharged kinetically trapped aggregates in such a way that depends on the gradients of the polyelectrolyte concentration during mixing. Moreover, kinetically trapped aggregates can be also obtained in the opposite situation, i.e., when there is a large polyelectrolyte excess. In this latter case, the production of kinetically trapped aggregates is the result of a heterogeneous distribution of the bound surfactant molecules within the polyelectrolyte backbone [39, 71, 103]. The aggregates formed under large polyelectrolyte excess conditions are extremely persistent, and their approach to the equilibrium state is very slow due to the existence of constraints for the reorganization within the polyelectrolyte chains of the bound surfactant molecules [24]. This is in agreement with the results by Guzman et al. [102] for PDADMAC-sodium laureth sulfate (SLES) mixtures. They found that for mixtures with elevated polyelectrolyte concentration very stable kinetically trapped aggregates can be produced. In this type of systems, even though the binding efficiency of the surfactant to the PDADMAC chains was found to be extremely high, there is an excess of free polyelectrolyte charges, which provides stability to the formed kinetically trapped aggregates. In fact, PDADMAC-SLES mixtures displayed phase separation for surfactant concentrations well below to that corresponding to the equilibrium phase separation, i.e., CNC. This was the result of the Marangoni

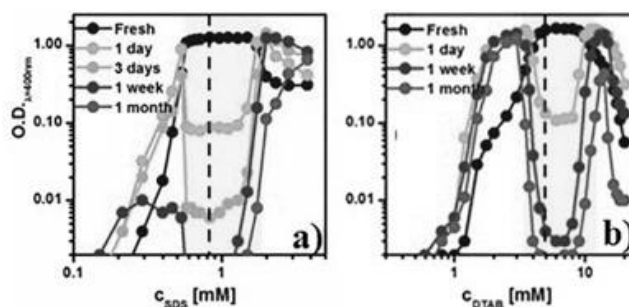
stresses created during the initial stages of the component mixing, which are originated from a local excess of surfactant molecules. Thus, it was possible to produce kinetically trapped PESCAs that resist the dilution, and present an inner core with a composition reminiscent to that corresponding to a true equilibrium phase separation, even though they maintain an external corona formed by the excess of polymer chains, resulting in the formation of charged aggregates with colloidal stability.

Llamas et al. [101] reported a strategy to fabricate very stable and reproducible kinetically trapped aggregates by combining the cationic polyelectrolyte (polydiallyldimethylammonium chloride, PDADMAC) and the anionic sodium lauroyl-N-methyltaurate (SLMT). They showed that the formation of this kinetically trapped aggregates pushes the system to a phase separation state for a surfactant concentration 100 times lower than that expected for true equilibrium conditions. This means that phase separation occurs under conditions in which undercompensated complexes are formed in the medium. Using the same protocol, Fernández-Peña et al. [105] demonstrated that for mixtures of PDADMAC and rhamnolipids of different hydrophobicity (both mono- and di-rhamnolipids) it was also possible to shift the onset of the phase separation to lower surfactant concentrations (up to 20 times lower, depending on the considered pair) than that required for equilibrium mixtures. Therefore, the production of kinetically trapped aggregates makes possible the fabrication of phase separated systems for compositions that are far from the electroneutrality conditions, and hence the phase separation appears even when the composition corresponds to a one-phase equilibrium region. This requires us to introduce some consideration about the timescale, on which the concentration gradients evolve. Unfortunately, up to date there are no general correlations between the timescales of the different phenomena involved in the mixing process and the formation of kinetically trapped aggregates, even though it is clear that the specific nature of the polyelectrolyte-surfactant pair plays a key role in the control of the association process and the timescale involved in the equilibration of the solution/dispersion. For instance, in mixtures of cetyltrimethylammonium bromide (CTABr) and sodium polyacrylate (NaPA), the PESCAs reach their equilibrium configuration just after the mixing [110], whereas the equilibration time may be of up to several months for other systems, e.g., poly[2-(propionyloxy)ethyl]trimethylammonium chloride (PCMA) and SDS (two months of equilibration) [96].

Bodnar et al. [100] have recently extended the studies on the impact of the specific nature of the polyelectrolyte-surfactant pair on the formation of nonequilibrium PESCAs. Their results show that the modulation of the degree of the surfactant binding to the polyelectrolyte chains can be

exploited as a tool for producing nonequilibrium aggregates. In particular, the increase of the importance of specific interactions such as those of hydrophobic origin between the hydrophobic tails of alkyltrimethylammonium bromides and the hydrophobic domains of the polymer backbone can contribute to an enhanced cooperative binding, which favors the formation of electrostatically stabilized kinetically trapped aggregates [100, 111]

As was stated above, turbidity measurements are very useful to evaluate different aspects of the phase diagram of polyelectrolyte-surfactant mixtures, but from its time evolution it is possible to elucidate the equilibrium or nonequilibrium of PESCAs [22, 24]. This requires us to distinguish between the turbidity of the samples as a result of a true equilibrium phase-separation and that associated with the formation of kinetically trapped aggregates. This can be easily understood in terms of experimental results following the methodology proposed by Varga and Campbell [22]. Figure 10 shows the optical density measured at 400 nm ( $OD_{\lambda=400\text{ nm}}$ ) for mixtures of PDADMAC-SDS, and poly(4-styrene sulfonate of sodium) (PSS)-dodecyltrimethylammonium bromide (DTABr) mixtures with different surfactant concentration and fixed polyelectrolyte one as was measured at different times after mixing.



**Figure 10.** Dependence of the optical density recorded at 400 nm for different polyelectrolyte-surfactant mixtures: (a) PDADMAC (100 ppm)-SDS mixtures in NaCl (0.1 M) and (b) PSS (100 ppm)-DTABr mixtures in pure water. Notice that the measurements were obtained after different times from the preparation. The shadowed zones in both panels correspond to the phase separation region. Adapted with permission from Varga and Campbell [22]. Copyright (2017) American Chemical Society.

It may be expected that the onset of the equilibrium phase separation region can be evidenced by a high initial optical density of fresh mixture followed by a decreases as the sample is aged. This can be understood considering the sedimentation of solid-separated complexes. However, this is not the situation that appears when kinetically trapped aggregates in an equilibrium one-phase region are formed. Dispersions containing this type of nonequilibrium structures are characterized by a moderate optical turbidity of the fresh

dispersions that does not undergo a significant decrease with time. This can be interpreted considering that the formation of kinetically trapped aggregates is not associated with a complete charge matching, and hence the obtained aggregates have a non negligible net charge. Therefore, kinetically trapped aggregates present a colloidal stability that is absent in true equilibrium complexes, and hence their depletion from the aqueous solutions is minimized [39, 71]. According to the above discussion, it may be expected that the reduction of turbidity during the aging of the mixture provides the bases for considering the system in equilibrium two-phase region, whereas the absence of significant changes may commonly suggest the formation of kinetically trapped aggregates formed just after mixing as a result of concentration gradients. Therefore, it is clear that the origin of the turbidity is very different for equilibrium and arrested mixtures. In fact, the results by Campbell and Varga [22] allow assuming that the time evolution of the turbidity of polyelectrolyte-surfactant mixtures can help the evaluation of the transition of the mixtures towards equilibration, which is strongly dependent on the specific polyelectrolyte pair and the solution conditions. Therefore, it is possible to assume that the onset of turbidity from kinetically trapped aggregates is not the same at the equilibrium phase boundary [22]. Thus, on the basis of the aforementioned results, it is possible to assume that the evaluation of the turbidity at different times provides insights on the evolution through the equilibration of polyelectrolyte-surfactant systems, with the equilibration process being strongly dependent on the specific mixture considered.

The above discussion has stated clearly the importance of kinetically trapped aggregates in polyelectrolyte-surfactant mixtures, emphasizing importance of defining the true equilibrium in this type of systems to avoid any interpretation lacking physical meaning. This is controversial as evidenced by the disagreement between the interpretation provided by Varga and Campbell [22] and that by Thomas and Penfold [23] of the results in Figure 9. Thomas and Penfold [23], on the basis of the phase diagram proposed by Hansson and Almgren [112], suggested that the reported phase separation is not a true equilibrium situation. However, in the results, it is possible to find several signatures of the equilibrium character of the phase separation and the formation of kinetically stable aggregates: (i) high optical turbidity of fresh dispersions that undergo a significant reduction as the samples are aged (equilibrium two phase-region), and (ii) moderate turbidity of fresh samples that remains almost unaltered for aged samples (production of kinetically trapped aggregates in an equilibrium one phase region). Therefore, for the particular case of PSS-DTABr mixtures, the results displayed in Figure 9 allow defining the phase boundary for a surfactant concentration around 3 mM, whereas the CNC in the equilibrium two-phase region is fixed around 6 mM

(according to independent electrophoretic measurements). Moreover, the results suggest that kinetically trapped aggregates are formed for surfactant concentration below 1 mM (evidenced by a sudden turbidity increase that does not evolve with time). This is not in disagreement with the results obtained by Hansson and Almgren [112] which were obtained before the identification of nonequilibrium kinetically trapped states in polyelectrolyte-surfactant [96], and represent a physical picture that does not consider the strong impact that can present this type of aggregates on the association process of polyelectrolyte-surfactant systems.

The production of kinetically trapped aggregates and the formation of equilibrium mixtures can be modulated by the addition of salt. At small and moderate ionic strengths, the ability to obtain kinetically trapped aggregates is reduced, whereas the increase of the salt concentration affects mostly to the equilibrium properties of the mixture, even suppressing the equilibrium phase separation as result of the limited binding of the surfactant to the polyelectrolyte chains [113].

#### 4. Concluding remarks

Mixtures of polyelectrolyte and surfactant bearing opposite charges are probably among the most studied colloidal systems in recent years. However, the physical principles underlying their formation process remain unclear yet, and there is a strong controversy related to the equilibrium or nonequilibrium character of their association process. For a long time, most of the studies in polyelectrolyte-surfactant systems have considered a thermodynamic approach assuming that the result of the complexation process can be described in terms of the formation of equilibrium PESCs, which depending on the mixture composition can drive the formation of equilibrium one-phase solutions, and phase separated mixtures containing solid precipitates or liquid coacervates. However, this traditional perspective has been overcome due to an extensive research effort, and it is currently accepted that PESCs cannot be always true equilibrium systems, which can result in the appearance of phase separated mixtures even for concentrations that are far from the boundaries of the equilibrium phase separation. This is commonly associated with the existence of compositional heterogeneities during the mixing of the components. Therefore, a careful examination of the properties and composition of PESCs is required when their equilibrium character is defined.

This review has tried to present a rigorous analysis on the key features of the association of oppositely charged polyelectrolyte-surfactant mixtures, considering both the general equilibrium description, and the most recent advances in the understanding of nonequilibrium PESCs. It is clear that the field is really open, and much more work is required for a comprehensive understanding of the association mechanisms. This is of a paramount importance

for tuning the production of PESCs with specific properties that can be exploited for different technological applications.

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