Polyelectrolyte-surfactant mixtures as model for understanding the performance of 2-in-1 shampoo formulations

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Abstract

Background: 2-in-1 shampoos are very complex multi-component mixtures used for the cleansing of the hair fibers and the modulation of their tribological properties, contributing to the reduction of the negative charge of damaged hair fibers. This is the result of the combined action of the polyelectrolytes and surfactants that play a central role in the effectiveness of modern 2-in-1 shampoo formulations. Thus, surfactants contribute to the removal of the dust and fatty compounds during the washing process, whereas polyelectrolytes present a strong ability to be deposited on the surface of damaged fibers, and enhance their tribological properties. However, the lack of knowledge about the main forces driving the conditioning process has pushed the research and development strategy of the cosmetic industry towards the design of state-of-the-art experimental and theoretical methodologies for evaluating the behavior of mixtures formed by polyelectrolytes and surfactants in solution and adsorbed onto solid surfaces with negative charge and contact angle for water similar to those appearing in the surface of damaged hair fibers, which have become a very promising tool for obtaining important insights that can be exploited for the optimization of new formulations for hair cleaning and conditioning. **Aims:** This work tries to provide an updated perspective of the current understanding of the behavior of mixtures containing polyelectrolytes and surfactants bearing opposite charges in relation to their performance in hair care and conditioning for providing a link between physico-chemical aspects and the performance of real 2-in-1 formulations. **Conclusions:** Polyelectrolyte-surfactant are powerful tools for obtaining useful information for the optimization of cosmetic formulations for hair care and conditioning. However, the rational design of this type of cosmetic products must be considered a multi-disciplinary challenge, which requires the combined efforts of researchers with very different backgrounds.

Keywords: Conditioning; shampoo; polyelectrolyte; surfactant; deposition; hair

1. Introduction

Hair cosmetic is an industrial field in continuous growth which needs to combine the consumer demands with constrains enforced by the international regulations for the

rational design of optimized products. This has pushed the research and development strategy of cosmetic industry to develop a broad range of formulations and products with an optimal performance for specific applications to meet the high standards demanded for consumers and regulations [1]. These products may be classified into two big categories depending of the duration of the effects associated with their application [2]

- Products providing a temporal modification of the hair, e.g., shampoos, conditioners, sprays or temporary colors.
- Products allowing a permanent or semi-permanent change of hair fiber properties, e.g., permanent waves, relaxers, bleaches or permanent colors.

The application of the above products contributes to the cleansing, promotion of attractiveness, alteration of the appearance and/or protection of the hair fibers. In particular, shampoos are probably the most widely used cosmetic products in our daily life [3]. From a classical perspective, shampoos are cosmetic preparations aimed at washing hair and scalp [4]. However, the current research efforts of the cosmetic industry have evolved towards a rational design of multifunctional shampoo formulations, which allow the removal of the endogenous secretions of sebum and sweat, and exogenous compounds such as dirt from the surface of hair fibers, providing conditioning and temporal reparation (non-biological process) of the damaged hair fiber surface [5-6]. Therefore, a shampoo should be considered a detergent solution containing suitable additives which provides several benefits to the hair, making necessary the formulations of very complex aqueous multi-component mixtures, which contain several polymers and surfactants combined with other chemical compounds, e.g., thickeners, conditioners, foam stabilizers, pH regulators, chelating agents, preservatives, fragrances or colorants, providing specific benefits to the formulations [7-8]. In particular, the combination of cationic polymers (polycations), and anionic and/or zwitterionic surfactants is essential for accomplishing the dual role of most formulations of modern 2-in-1 shampoos. Thus, surfactant molecules contribute to the removal of fatty compounds from the hair fibers and the foamability of the formulations, whereas polycations help on the smoothing of the hair surface and the improvement of the wet combability [9].

The most extended action mechanism of formulations of 2-in-1shampoos involves the deposition onto hair surface of aggregates formed by the interaction of polymers and surfactants [10]. Figure 1 presents a sketch summarizing the steps involved of the polymer-surfactant association in aqueous solution. The coexistence in solution of polyelectrolyte and surfactant bearing opposite charges leads to the emergence of up to three different states characterized by the ratio between surfactant and polyelectrolyte concentration (S/P, with S and P accounting for the concentration of charged surfactant molecules and charged monomers in solution, respectively) [11]. The first region (Region 1) is characterized by S/P values below unity and the presence of a single phase (1ϕ) formed by a solution of polyelectrolyte-surfactant complexes bearing a charge with the same sign than the bare cationic polymer (polycation). The increase of the surfactant concentration push the system to the onset of the second region (Region 2), where neutral insoluble complexes (S/P=1) are formed, leading to a phase separated systems (2ϕ). This region is commonly defined as complex precipitation region, playing a very central role on the performance of 2-in-1 shampoos [12]. The increase of the surfactant concentration up to S/P values above the unity leads to a progressive adsorption of surfactant micelles

on the precipitated complexes, driving a resolubilization process in the Region 3 (1φ), where soluble complexes and free micelles are in coexistence in the aqueous phase.
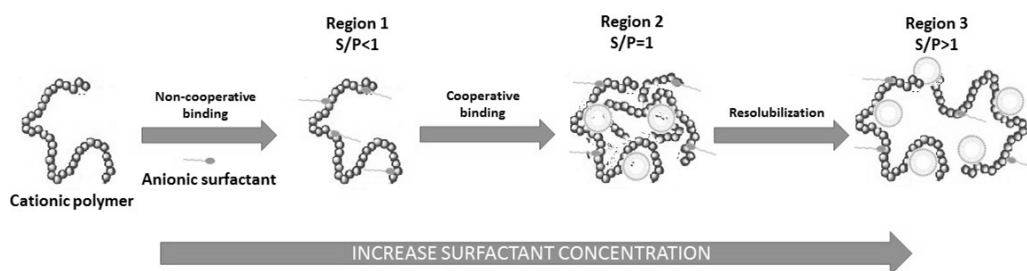
Figure 1. Sketch of the three different states occurring in oppositely charged polyelectrolyte-surfactant mixtures. Region 1 and 3 correspond to one phase solution. Region 2 correspond to the formation of phase separated systems.

2-in-1 shampoos are commonly formulated in such a way that they appear as a one-phase systems (Region 3), which undergo a phase-separation process upon dilution during their application under the shower to reach a composition equivalent Region 2. The emergence of a phase separation phenomenon upon dilution enhances the deposition of conditioning molecules on the surface of the hair fibers, and hence shampoos can be defined as dilution deposition systems [12]. It should be noted that the above process promotes foaming [13-14], reduces the friction between hair fibers [15-16], and stimulates the deposition of other beneficial compounds, such as colloidal particles of silicone emulsions [17-18], playing a very important role on the consumer perception in relation to the shampoo formulation [19].

It is clear that the formation of phase-separated polyelectrolyte-surfactant aggregates, and in particular their ability for being deposited on the hair fiber surface play a central role in the performance of formulations for hair care and conditioning [6, 12, 20-21]. However, the phase separation process, and the type of phase separated aggregates formed depend on different aspects, including the characteristic of the cationic polymer (mainly charge density and molecular weight) and its concentration, the type of surfactant included in the shampoo, the ionic strength, pH and temperature [18]. Therefore, it is necessary to deepen on the deep understanding of the physico-chemical bases underlying the conditioning process for a rational design of formulations, allowing to tune at will the dilution-deposition process [22]. This may help on preparation of formulations with an optimal ability for cleaning the hair fibers, without compromising the sensorial effect associated with the deposition of the conditioning molecules on the hair fiber surface.

2. A simplified perspective of the physico-chemical bases underlying the hair conditioning process

The integrity of the surface of native hair fibers can be altered by the combination of different factors, including the removal of the fatty acid layer covalently linked to the outermost region of the cuticle and the oxidation of the disulfide bonds from the cystine residues to cysteic acid. These processes lead to the emergence of an excess of acid groups

on the outermost surface of the hair fibers, which in contact with water may undergo a dissociation process, providing a hydrophilic character and an effective negative charge to the surface of hair fibers [23].

The anionic residues on the surface of the fibers are susceptible of interacting with positively charged compounds, such as polycations contained in most of the current formulations of 2-in-1 shampoos [1, 5, 10, 23-25]. Thus, the electrostatic interactions occurring between the cationic components and the anionic residues on the hair surface favor the deposition of conditioning molecules. This leads to the formation of a conditioning layer on the hair surface, which enables the reduction of their static electricity as result of the neutralization of the negative charges. Furthermore, the formation of a polymer layer on the hair fiber surface contributes to the improvement of their tribological properties as well as their lubrication, reducing the wet combing force [9]. This may be understood considering that the deposition of the layer of conditioning agents on the hair fiber surface flattens the cuticle scales, which in turn contributes to reduction of the friction between fibers. It should be noted that the size of the phase separation region is not a critical issue on the conditioning performance of 2-in-1 shampoos [18].

The control of the conditioning process makes necessary to analyze very specific aspects related to the morphological and chemical heterogeneity of the surface of the hair fibers, which may influence the deposition process of conditioning species. This has driven important research efforts in the cosmetic industry to disentangle the main physico-chemical bases governing the deposition of conditioning molecules, mainly polyelectrolyte-surfactant mixtures, on the hair fiber surface.

3. Polyelectrolyte-surfactant mixtures in hair conditioning formulations

Conditioning agents included in 2-in-1 shampoo formulations present a broad range of functions, e.g., reduction of the inter-fiber friction, detangling the hair, minimizing frizz and improving the ability for styling. The optimization of such functions is only possible by a careful examination of two very fundamental physico-chemical aspects related to the formulation performance: (i) positively charged molecules neutralize the negative charges emerging on the surface of damaged hair fibers, and (ii) deposition of conditioning species contributes to reduce the hydrophilic character of damaged fibers, providing better lubrication to the cuticle. These goals can be reached by including different antistatic and lubricant agents, e.g. polymers, oils, waxes, hydrolyzed amino acids and other cationic molecules [8], into the formulations of hair conditioning shampoos.

Polycations and silicones are widespread compounds in shampoo formulations, with the former being water soluble polymers included at a relatively reduced concentration (0.1 to 1 wt%), presenting good compatibility with other ingredients of the product. On the other side, silicones do not present good compatibility with the rest of the components included into the 2-in-1 shampoo formulation, which makes necessary their emulsification as discrete droplets using different thickeners molecules, such as ethyleneglycol distearate and stearic monoethanolamide [26]. Contrary to that what is

expected for other ingredients, conditioner species (mainly cationic polymers and silicones) should be retained on the hair surface after the washing process [6].

It should be noted that the cosmetic industry is currently seeking eco-sustainable ingredients to manufacture products for hair care and conditioning with minimal impact on human health. This is particularly important because current international regulations limit the number of chemicals that can be used for the preparation of new products or the design of new processes involving humans as final consumer [27]. Therefore, it is necessary to seek new chemical compounds that can substitute those currently used with minimal impact over the performance of the product to ensure the consumer satisfaction. Some examples of these new trends can be found in the use of biopolymers, mainly polysaccharides, as conditioners [9, 28], or different type of biosurfactants (e.g., rhamnolipids or sophorolipids) as detergents [9, 29-30].

Table 1 summarized the complexity of the chemical composition of three different formulation for hair conditioning. It should be stressed that the chemical complexity of current 2-in-1 shampoos makes necessary to explore simple models including a reduced number of components. This type of study may provide important insights on the most fundamental physico-chemical aspects guiding the performance of commercial products. The study of the behavior of polyelectrolyte-surfactant aqueous mixtures can be considered as a very simplified approach understanding some fundamental aspects about the performance of 2-in-1 shampoos. In the following, a brief description of the role of surfactant and polymers in current shampoos will be presented.

Table 1. Example of three different compositions of hair conditioning products. Adapted from Llamas et al. [10] with permission from Elsevier, Copyright 2015.

Ingredient	1 (wt%)	2 (wt%)	3 (wt%)
Cetyl alcohol	0	3	5
Cetearyl alcohol	2.8	0	0
Cetyl esters	0	0.25	1
Glyceryl stearate	0.5	0	0
Lanolin	0.5	0.15	0
Mineral oil	0	0	0
Avocado oil	0	0	0
Hydroxyethylcellulose	0	0.2	0.2
Amodimethicone (and) trideceth-12 (and) cetrimonium chloride	0	0.7	0
Amodimethicone (and) trideceth-6 (and) cetrimonium chloride	0	0	1.1
Behentrimonium chloride	0	0	3
Cetrimonium chloride	0.55	0.45	0
Steramidopropyldimethylamine	0	0.75	0
2-oleoamido-1,3-octadecanediol	0	0	0.1
Lauryl PEG/PPG-18/18 methicone (and) dodecene (and) poloxamer 407	0	0.25	0

Ingredient	1 (wt%)	2 (wt%)	3 (wt%)
PEG-180	0	2	2
Glycerin	0	0	2
Water	ad. 100	ad. 100	ad. 100
pH	4	5.5	3.2

3.1. Surfactants

Surfactants included in 2-in-1 shampoos influence the amount of phase separated aggregates formed upon dilution, as well as the deposition of conditioning species on the hair. Thus, it may be expected that surfactant can present a very strong impact on the final sensorial perception upon shampoo application. It is known that the formulation of the surfactant blend included into the 2-in-1 shampoo influence strongly the conditioning performance of cationic polymers as well as the silicone deposition [18]. Furthermore, anionic surfactants also play a very central role on the weakening of the adhesion forces between different fatty materials and dust and hair, contributing to the solubilization of such compounds within the hydrophobic core of surfactant micelles [8-9]. It should be noted that the cleansing properties of surfactant, including penetration, solubilization, roll-up, and spontaneous emulsification, are very different depending on the type of hair [31]. Sulfate based surfactants, such as sodium dodecyl sulfate (SDS), due to their excellent capacity as detergent and foaming agent has been, for long time, the most commonly used surfactant in shampoos. On the other side, cationic surfactant are very common as conditioning agents because they present a strong ability to cling to the negatively charged surface of damaged fibers [9]. However, the irritant character for skin and mucosa of ionic surfactants has limited their applications in recent years, which has driven their progressive substitution for different mixtures of surfactants. In particular, sugar-based surfactants are gaining importance in shampoos due to their mildness in the skin and eyes as well as result of their reduced environmental impact [30]. This allows improving the formulation performance, its eco-sustainability and toxicological profile. Surfactant belonging to several categories are currently found in shampoo, and their classification is commonly based on their charge [8, 32-33]

- Anionic surfactants are used in numerous shampoo formulations, having as main characteristic the presence of a negatively charged moiety (carboxylates, sulfates, sulfonates or phosphates) which is directly bound to a hydrophobic tail, commonly an alkyl one, e.g. sodium laureth sulfate (SLES), sodium lauroyl methyl isethionate (SLMI) or sodium methyl lauroyl taurate (SLMT) [34-39]. In particular, the use of sulfate surfactants is widespread in shampoos because they have excellent foaming ability both in hard and soft water, contributing to an efficient washing process. The role of these surfactant is to ensure an efficient cleaning of fatty compounds and dirt from the hair fibers. However, an excessive content of this type of surfactants may be detrimental for the conditioning performance of the formulation because they can remain trapped on the surface of the hair fibers during the washing process, which leads to an increase of the

number of negative charges on the fiber surface, increasing the friction between fibers and making difficult the combing process.

- Cationic surfactants present as main characteristics the presence of a positively charged polar group (generally a quaternary ammonium group). The presence of such positively charged groups provides to the cationic surfactant a very important role in the charge neutralization process required for conditioning (it is worth recalling that damaged fibers present an excess of negative charge), contributing to the minimization of frizz. Furthermore, cationic surfactants can also play a very important role as softeners in the formulations. Among the cationic surfactant accepted for their use in hair conditioning products are included benzalkonium chloride, trimetrhylalkylammonium chloride or cetylpyridinium cetrimonium chloride [32, 40].

- Non-ionic surfactants do not present any hydrophilic dissociable groups, and hence have a null charge in aqueous solutions. They are less aggressive for skin and mucosa than other surfactant categories, and play a very important role on the emulsification and solubilization of other components in shampoos formulations, becoming the preferred surfactants in sulfate-free products. However, their application appears very times limited due to their limited foamability. Some commonly used non-ionic surfactant in the formulation of shampoos are compounds derived from ethylene oxides (ethoxylated surfactants), and some "multihydroxy" molecules, including glycol esters, glycerol and polyglycerol esters, glycosides and polyglycosides, and sucrose esters [39].

- Zwitterionic surfactants include both cationic and anionic moieties within their polar heads. This allows tuning their net charge almost at will by changing the pH of the solutions. Zwitterionic surfactants are included in cosmetics formulations for their good foaming, detergency and wetting properties. Furthermore, they are milder than other types of surfactant, which makes them excellent candidates for the minimization of the dermatological impact associated with an extensive use of anionic surfactants. N-alkyl betaines, derived from trimethylglycine (betaine) [38-39, 41], are probably the most common zwitterionic surfactants included in shampoos and conditioning products.

3.2. Polymers

The choice of the most suitable polymers for 2-in-1 shampoo formulations is influenced by a set of parameters that can be summarized as follows: (i) ability of the polymer for binding to the surface of the hair fibers, i.e., ability as film forming molecule; (ii) chemical nature; (iii) rheology of the solutions, and (iv) adhesion properties of the layers of the polymer to the surface of the hair fibers [1]. Table 2 reports some examples of polymer used as conditioners in 2-in-1 shampoos.

Cationic polymer or polycations are accounted as the most widely used polymers in formulations for hair conditioning products. Nevertheless, it is possible to include other polymers which play very specific roles in the formulation performance, e.g., fixative, thickeners, etc. Among polycations, those having a quaternary ammonium as charged groups (polyquaternium) are the preferred one for conditioning purpose due to their good ability for adhering to the keratinous structure of the hair fibers [42]. Furthermore, polyquaternium polymers present a very strong interaction with anionic and zwitterionic

surfactants, which favors the association of polyelectrolyte and surfactant molecules to form supramolecular aggregates. It should be noted that the rich phase behavior of the aggregates formed by the interaction of the polyelectrolyte and surfactant molecules plays a very central role on the performance of conditioning products [43-47]. Yong-jian and Jordan [48]reported that highly charged cationic polymers leads to the formation of solid-like phase separated aggregates with low water content over a very narrow dilution range, providing body to hair, whereas cationic polymer with low charge density leads to the formation of liquid-like aggregates with a high water content over larger dilution range, providing softness and volume to the hair. Furthermore, the molecular weight of the conditioning polymer present a strong influence on the amount of conditioning aggregates.

Table 2. Example of some polymers used as conditioners in 2-in-1 shampoos. Adapted from Fernández-Peña et al. [20] with permission under License of Attribution Creative Common 4.0 (2020).

Name	Composition
polyquaternium 2	poly[bis(2-chloroethyl) ether-alt-1,3-bis [3-(dimethylamino)propyl]urea] quaternized
polyquaternium 6	homopolymer of poly(diallyl-dimethyl-ammonium chloride)
polyquaternium 7	copolymer containing 50 wt% diallyl-dimethylammonium chloride and 50 wt% acrylamide
polyquaternium 10	hydroxyethyl cellulose quaternized with 2,3-epoxypropyl-trimethyl-ammonium chloride
polyquaternium 17	poly[oxy-1,2-ethanediyl(dimethyliminio)-1,3-propanediylimino-(1,6-dioxo-1,6-hexanediyl)imino-1,3-propanediyl(dimethyliminio)-1,2-ethanediyl dichloride]
polyquaternium 18	poly[oxy-1,2-ethanediyl(dimethyliminio)-1,3-propanediylimino-(1,6-dioxo-1,6-heptanediyl)imino-1,3-propanediyl(dimethyliminio)-1,2-ethanediyl dichloride]
polyquaternium 22	copolymer containing 50 wt% diallyl-dimethylammonium chloride and 50 wt% acrylic acid
polyquaternium 39	copolymer containing 50 wt% diallyl-dimethylammonium chloride, 25 wt% acrylamide and 25 wt% acrylic acid
polyquaternium 53	copolymer containing 40 wt% methacrylamidopropyltrimonium chloride, 50 wt% acrylamide and 10 wt% acrylic acid
polyquaternium 67	hydroxyethyl cellulose quaternized and polymerized with n-propyl-2-hydroxy-3-trimethyl ammonium and n-propyl-2-hydroxy-3-dimethyl dodecyl ammonium monomers
polyquaternium 86	copolymer of vinyl pyrolidone, vinyl imidazole, vinyl imidazole quaternized with methyl chloride and methacrylic acid (25 wt% of each type of monomer)

It should be noted that cosmetic industry is trying to replace cationic polymers and surfactants, and in particular those obtained from petroleum chemical sources, for eco-friendly conditioner molecules. This can be done by using cationic amino lipid as demonstrated Ajayi et al. [49], or biopolymers as shown the study by Hernández-Rivas

et al. [28]. However, at the current point the substitution of cationic polymers is far from the incorporation in commercial 2-in-1 shampoos.

4. Towards the understanding of the phase behavior of polyelectrolyte-surfactant mixtures

The association of polyelectrolyte and surfactant molecules bearing opposite charges to form polyelectrolyte-surfactant aggregates is the result of an intricate balance of interactions including different attractive and repulsive contributions [50-54]: (i) electrostatic interactions between charged monomers and the ionic head groups of the surfactant molecules; (ii) hydrophobic interactions between the surfactant tails, and between such tails and the hydrophobic domains existing within the polymer backbone; (iii) entropy gain as result of the release of counterions as result of the binding of surfactant molecules to polyelectrolyte chains, leading to the formation of colloidal aggregates; (iv) screening of the repulsive interactions between the polar groups of the surfactant micelles due to the formation of polymer-surfactant aggregates, and (v) reduction of the contact between the surfactant molecules and water as result of the polymer-surfactant association. The complex interplay between the above mentioned contributions leads to a very strong association of the surfactant molecules and the oppositely charged polyelectrolyte chains [53, 55]. This depends on molecular parameters of the polymer chains (molecular weight, flexibility and branching degree, hydrophobicity or charge density) and the surfactant molecules (nature of the polar head or length of the hydrophobic tail), and on the solution characteristics (concentration of polymer and surfactant, ionic strength, pH or temperature). The modification of such parameters allows a controlled modulation of different aspects, including the interactions between the components of the mixtures, the association mechanism and the phase behavior [56-58].

The formation of aggregates by the interaction of polyelectrolytes and surfactant molecules having charges with different signs may be understood as an ionic exchange process, which leads to a strong increase of the system entropy due to the release of counterions from the polyelectrolyte and surfactant molecules. This occurs from very low surfactant concentrations, initially through a non-cooperative association between surfactant molecules and polymer chains, i.e. surfactant molecules start to bind only in the vacancy sites of the polymer chains. The non-cooperativity of the polyelectrolyte-surfactant association continues up to the so-called critical aggregation concentration (CAC), which corresponds to the transition between non-cooperative association to cooperative one. The cooperative association is characterized by the binding of the surfactant molecules either in vacancy sites existing in the polyelectrolyte chain or in regions where there are previously bound surfactant molecules. This is possible considering the existence of secondary attractive interactions, commonly hydrophobic ones, which contributes to the formation of surfactant micelles for surfactant concentrations that are very far from the normal critical micelle concentration (CMC) of pure surfactants (almost 3 orders of magnitude lower). These micelles can bind to the polymer chains [55, 59]. This association leads to the progressive reduction of the average net charge of the polyelectrolyte chains as result of the increase of the number of

surfactant molecules bound to the polymer chains with the increase surfactant concentration of the bulk mixture, i.e., the increase of the S/P value. Thus, the increase of the surfactant concentration beyond the CAC leads to a fast dropping of the charge of the aggregates down to a quasi-null value in the vicinity of the isoelectric point or charge neutralization concentration (CNC) characterized for a S/P value about the unity (Region 2 in Figure 1) [11, 55, 58, 60]. This point is associated with the onset of a phase separation region (2ϕ), which can be easily understood considering that when the S/P value assumes a value around 1, the aggregates dispersed in the bulk present a very reduced net charge and hence they colloidal stability becomes very poor.

The increase of the S/P value beyond the CNC drives the system to a new one-phase region (1ϕ, Region 3). The emergence of this new one-phase region can be rationalized considering that the binding of additional surfactant molecules to the aggregates, leads to their rehydrophilization, which allows their re-solubilization and re-stabilization of the phase-separated complexes [29, 61]. It should be noted that when the surfactant concentration is high enough, the addition of surfactant molecules does not induce any additional binding. This occurs for surfactant concentrations above the so-called saturation concentration (CS), and is accompanied of the formation of free micelles in solution [62-63].

The above discussion has shown that the phase behavior of oppositely charged polyelectrolyte-surfactant mixtures is characterized for the emergence of three different regions: (i) two one-phase regions (1ϕ) appearing when the concentration of surfactant is lower or higher than that corresponding to that of the charged monomers, and (ii) a phase separation region (2ϕ) characterized by a 1:1 stoichiometry between the number of charged monomers and the number of surfactant molecules in the mixture (S/P=1). Thus, the one-phase regions correspond to mixtures having a mixing ratio above or below the unity, whereas the phase separation generally emerges when the value of the mixing ratio is close to 1 [61]. It should be noted that the performance of formulations of shampoos for hair care and conditioning is mainly based on the control of the transition between the commercial product commercialized as a one-phase mixture with an excess of surfactant (high S/P ratio), and the phase-separated mixture emerging upon dilution of the commercial product under the shower.

5. Adsorption of polyelectrolyte-surfactant mixtures on solid surfaces

The understanding of the adsorption process of polyelectrolyte-surfactant systems on solid surfaces presents a broad interest for cosmetic industry due to its recognized impact in the performance of 2-in-1 shampoos. It is worth recalling that the deposition of polymer–surfactant aggregates onto hair fiber surface plays a very important role on the conditioning ability of cosmetic formulations, and the final sensorial perception obtained upon their application [64-65].

The adsorption of polymer-surfactant aggregates on solid surfaces is a very complex process which is affected by different factors, including molecular characteristics of the polymer (charge, molecular weight), surfactant molecules and surfaces (charge, surface energy) and properties of the solution (concentration of the species, pH, temperature,

solvent quality, ionic strength) as well as the nature and concentration of the surfactant [10, 66]. Furthermore, the proximity of the mixture composition to the phase separation region also emerges as a very important aspect for controlling the efficiency of the adsorption process [67].

Polyelectrolyte-surfactant mixtures are a broad family, and the study of the adsorption of all the possible combinations emerges a very difficult issue. Therefore, this section will be only focused on presenting a brief analysis of the adsorption on negatively charged surfaces of mixtures formed by the combination of polycations and anionic surfactants. This choice is not arbitrary, considering that damaged hair fibers present a negative surface charge, and hence the understanding of the adsorption processes on negatively charged surfaces may help to deepen in the most fundamental bases governing the performance of conditioning formulations.

The analysis of the adsorption requires to consider two type of interactions: (i) attractive interactions between polyelectrolyte chains and surfaces bearing opposite charge, and (ii) repulsive interactions between the negatively charged surfactants and the surface with a charge of the same sign. These interactions are governed by the composition of the specific mixture, which allows defining three different adsorption regions depending on the zone of the phase diagram.

At low surfactant concentration, the solution is formed by overcharged aggregates with positive charge, and hence their adsorption onto a negative surface is mainly governed by the electrostatic interaction between the free positively charged monomers and the negatively charged surface [68-69]. This leads to the formation of adsorption layers (region 1: pre-phase separation) in which the amount of surfactant is very reduced and increases with the S/P value, i.e. with the surfactant concentration in the mixture [68]. This appears reasonable considering that within this region, there is a high excess of positively charged monomers in the complexes and a very low binding of surfactant molecules to the polyelectrolyte chains. The increase of the surfactant concentration drives the formation of aggregates in which the compensation of the polyelectrolyte charges occurs as result of the binding of the surfactant molecules to the charged monomers. This takes the system to a destabilization point due to the formation of neutral complexes (turbid dispersions) with a limited colloidal stability, which in turns favors the depletion of the aggregates from the aqueous phase, and enhances their deposition on the surface due to their sedimentation onto the surface (region 2: phase separation). This sedimentation leads to a maximum on the adsorption curve. The increase of the surfactant concentration beyond the phase-separation region drives the system to a new one phase region characterized by the re-solubilization of the neutral aggregates due to the binding of an excess of surfactant molecules to the polymer chains. This leads to a situation in which overcharged aggregates bearing a charge of the same sign than the surfactant appears in solution. These aggregates present an enhanced solubility which favors their dispersion within the aqueous environment, leading to the dropping of the adsorbed amount as the S/P value increase (region 3: post-phase separation). Therefore, the overcompensation of the charges occurring for S/P values above that corresponding to the phase separation region hinders the adsorption of the aggregates. This can be explained considering the emergence of interactions with repulsive origin between the negatively charged aggregates and the surface with the same sign [69].The above

discussion evidenced that the worsening of the solubility of the polymer-surfactant aggregates due to the decrease of their charge density leads to an enhancement of their deposition onto solid surface [70-71].

6. Adsorption of polyelectrolyte-surfactant mixtures enhanced for dilution

The phase separation occurring for oppositely charged polyelectrolyte-surfactant mixtures is one of the most relevant aspects for the industrial application of these mixtures. This phase separation occurs commonly as result of the increase of the surfactant concentration within the mixture. However, more relevant from a cosmetic perspective is the emergence of phase separation in transparent mixtures containing a surfactant excess (Region 3). This situation is that what appears in most of the formulations of 2-in-1 shampoos and conditioner products. These formulations contain several surfactants (anionic, neutral and zwitterionic) and polymers, appearing as one-phase transparent mixtures.

The shampoo should be considered a dilution deposition system. This may be understood considering that the dilution occurring during its application under the shower can induce a precipitation-enhanced deposition (Lochhead effect) [12]. Thus, the application of the shampoo on the hair fibers, and their subsequent rinsing with water takes the mono-phasic shampoo to the onset of the phase-separation region, which makes possible an enhanced deposition due to the depletion of the conditioning molecules from the solution to the hair fiber surface. From a physico-chemical point of view, the above process can be understood considering that the dilution of a mixture of overcompensated aggregates formed by oppositely charged polyelectrolytes and surfactants pushes the system from a one phase composition to a liquid/liquid phase separation, leading to the formation of gel-like particles with a high content of polymer and a poor solubility in water. This low solubility drives the deposition of such aggregates onto hair fiber surface [12].

7. Conclusions

This review provides a brief perspective on how the study of oppositely charge polyelectrolyte-surfactant mixtures can contribute to the understanding of the most fundamental bases underlying the performance of hair conditioning formulations. This relies mainly on the deposition on hair fiber surface of aggregates of conditioning molecules (mainly complex mixtures of polyelectrolytes and surfactants), which reduce the static electricity of damaged hair fibers, and enhance the lubrication of the hair, facilitating the wet combing. Thus, optimal conditioning results may be only obtained by preparing formulations which combine good cleansing properties and specific rheological properties with a facilitated deposition of condition species on the hair fiber surface upon dilution under the shower. This can be optimized by exploring the physico-chemical bases governing the association of polyelectrolyte and surfactant molecules in solution to form aggregates as well as the deposition of such aggregates on the hair fiber surface. This has become the formation of products for hair care and conditioning in an inter-disciplinary challenge that brings together fields of physics, chemistry and biology to guide to the

cosmetic industry for a rational design of new multifunctional products. The field is open to research, and nanotechnology has opened new avenues to the application of novel nanomaterials for enhancing the effectiveness of hair conditioning process.

Consent for Publication

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Acknowledgements

References

1.   Robbins, C. R., *Chemical and Physical Behavior of Human Hair*. Springer Science+Business Media: New York, NY, USA, 1988.
2.   Alessandrini, A.; Piraccini, B. M., Essential of Hair Care Cosmetics. *Cosmetics* **2016,** *3*, 34.
3.   Ishii, M. K., Objective and Instrumental Methods for Evaluation of Hair Care Product Efficacy and Substantiation of Claims. In *Hair and Hair Care*, Johnson, D. H., Ed. Routledge: New York, NY, USA, 1997; pp 261-302.
4.   Arora, P.; Nanda, A.; Karan, M., Shampoos based on synthetic ingredients vis-a-vis shampoos based on herbal ingredients: A review. *Int. J. Pharm. Sci. Rev. Res.* **2011,** *7*, 41-46.
5.   Hössel, P.; Dieing, R.; Nörenberg, R.; Pfau, A.; Sander, R., Conditioning polymers in today's shampoo formulations - efficacy, mechanism and test methods. *Int. J. Cosmet. Sci.* **2000,** *22*, 1-10.
6.   Luengo, G. S.; Fameau, A.-L.; Léonforte, F.; Greaves, A. J., Surface science of cosmetic substrates, cleansing actives and formulations. *Adv. Colloid Interface Sci.* **2021,** *290*, 102383.
7.   Mainkar, A. R.; Jolly, C. I., Formulation of natural shampoos¶. *Int. J. Cosmet. Sci.* **2001,** *23*, 59-62.
8.   Gavazzoni Dias, M. F. R., Hair cosmetics: an overview. *Int J Trichology* **2015,** *7*, 2-15.
9.   Yorke, K.; Amin, S., High Performance Conditioning Shampoo with Hyaluronic Acid and Sustainable Surfactants. *Cosmetics* **2021,** *8*, 71.

10.	Llamas, S.; Guzmán, E.; Ortega, F.; Baghdadli, N.; Cazeneuve, C.; Rubio, R. G.; Luengo, G. S., Adsorption of polyelectrolytes and polyelectrolytes-surfactant mixtures at surfaces: a physico-chemical approach to a cosmetic challenge. *Adv. Colloid Interface Sci.* **2015,** *222*, 461-487.

11.	Bain, C. D.; Claesson, P. M.; Langevin, D.; Meszaros, R.; Nylander, T.; Stubenrauch, C.; Titmuss, S.; von Klitzing, R., Complexes of surfactants with oppositely charged polymers at surfaces and in bulk. *Adv. Colloid Interface Sci.* **2010,** *155*, 32-49.

12.	Miyake, M., Recent progress of the characterization of oppositely charged polymer/surfactant complex in dilution deposition system. *Adv. Colloid Interface Sci.* **2017,** *239*, 146-157.

13.	Cohen-Addad, S.; di Meglio, J.-M., Stabilization of aqueous foam by hydrosoluble polymers. 2. Role of polymer/surfactant interactions. *Langmuir* **1994,** *10*, 773-778.

14.	Kristen, N.; von Klitzing, R., Effect of polyelectrolyte/surfactant combinations on the stability of foam films. *Soft Matter* **2010,** *6*, 849-861.

15.	Jordan, S. L.; Zhang, X.; Amos, J.; Frank, D.; Menon, R.; Galley, R.; Davis, C.; Kalantar, T.; Dow, M. L., Evaluation of novel synthetic conditioning polymers for shampoos. *J. Cosmet. Sci.* **2009,** *60*, 239-250.

16.	Fernández-Peña, L.; Guzmán, E.; Ortega, F.; Bureau, L.; Leonforte, F.; Velasco, D.; Rubio, R. G.; Luengo, G. S., Physico-chemical study of polymer mixtures formed by a polycation and a zwitterionic copolymer in aqueous solution and upon adsorption onto negatively charged surfaces. *Polymer* **2021,** *217*, 123442.

17.	Svensson, A. V.; Huang, L.; Johnson, E. S.; Nylander, T.; Piculell, L., Surface Deposition and Phase Behavior of Oppositely Charged Polyion/Surfactant Ion Complexes. 1. Cationic Guar versus Cationic Hydroxyethylcellulose in Mixtures with Anionic Surfactants. *ACS Appl. Mat. Interface Sci.* **2009,** *1*, 2431-2442.

18.	Lepilleur, C.; Mullay, J.; Kyer, C.; McCalister, P.; Clifford, T., Use of statistical modeling to predict the effect of formulation composition on coacervation, silicone deposition, and conditioning sensory performance of cationic cassia polymers. *J. Cosmet. Sci.* **2011,** *62*, 161-177.

19.	Marchioretto, S.; Blakely, J., Substantiated synergy between silicone and quats for clear and mild conditioning shampoos. *SOFW J.* **1997,** *123*, 811-818.

20.	Fernández-Peña, L.; Guzmán, E., Physicochemical Aspects of the Performance of Hair-Conditioning Formulations. *Cosmetics* **2020,** *7*, 26.

21.	Luengo, G. S.; Guzman, E.; Fernández-Peña, L.; Leonforte, F.; Ortega, F.; Rubio, R. G., Interaction of Polyelectrolytes and Surfactants on Hair Surfaces. Deposits and their Characterization. In *Surface Science and Adhesion in Cosmetics*, Mittal, K. L.; Bui, H. S., Eds. Scrivener Publishing: Berveley, MA, USA, 2021; pp 401-449.

22.	Faucher, J. A.; Goddard, E. D.; Hannan, R. B., Sorption and Desorption of a Cationic Polymer by Human Hair: Effects of Salt Solutions. *Textile Res. J.* **1977,** *47*, 616-620.

23.	Bhushan, B., Nanoscale characterization of human hair and hair conditioners. *Progr. Mat. Sci.* **2008,** *53*, 585-710.

24.	Andre, V.; Norenberg, R.; Hossel, P.; Pfau, A., The role of polymer-surfactant interactions in the adsorption process of hair-conditioning polymers. *Macromol. Symp.* **1999,** *145*, 169-179.

25.	Pfau, A.; Hössel, P.; Vogt, S.; Sander, R.; Schrepp, W., The interaction of cationic polymers with human hair. *Macromol. Symp.* **1998,** *126*, 241-252.

26.	Savary, G.; Grisel, M.; Picard., C., Cosmetics and personal care products. In *Natural Polymers: Industry techniques and applications*, Olatunji, O., Ed. Springer Intl. Pub. : Basel, Switzerland, 2016; pp 219-261.

27.	Fisk, P., *Chemical risk assessment: a manual for REACH*. John Wiley & Sons: Chichester, UK, 2013.

28.	Hernández-Rivas, M.; Guzmán, E.; Fernández-Peña, L.; Akanno, A.; Greaves, A.; Léonforte, F.; Ortega, F.; G. Rubio, R.; Luengo, G. S., Deposition of Synthetic and Bio-Based

Polycations onto Negatively Charged Solid Surfaces: Effect of the Polymer Cationicity, Ionic Strength, and the Addition of an Anionic Surfactant. *Colloids and Interfaces* **2020,** *4*, 33.

29.   Fernández-Peña, L.; Guzmán, E.; Leonforte, F.; Serrano-Pueyo, A.; Regulski, K.; Tournier-Couturier, L.; Ortega, F.; Rubio, R. G.; Luengo, G. S., Effect of molecular structure of eco-friendly glycolipid biosurfactants on the adsorption of hair-care conditioning polymers. *Colloids Surf. B* **2020,** *185*, 110578.

30.   Nunes, A.; Marques, P.; Marto, J.; Ascenso, A.; Gonçalves, L.; Fitas, M.; Pinto, P.; Sotomayor, J.; Ribeiro, H. M., Sugar Surfactant-Based Shampoos. *J. Surfact. Deterg.* **2020,** *23*, 809-819.

31.   Cornwell, P. A., A review of shampoo surfactant technology: consumer benefits, raw materials and recent developments. *Int. J. Cosmet. Sci.* **2018,** *40*, 16-30.

32.   Gubitosa, J.; Rizzi, V.; Fini, P.; Cosma, P., Hair Care Cosmetics: From Traditional Shampoo to Solid Clay and Herbal Shampoo, A Review. *Cosmetics* **2019,** *6*, 13.

33.   Tadros, T. F., *Applied surfactants: principles and applications*. John Wiley & Sons: Chichester, UK, 2006.

34.   Llamas, S.; Guzmán, E.; Baghdadli, N.; Ortega, F.; Cazeneuve, C.; Rubio, R. G.; Luengo, G. S., Adsorption of poly(diallyldimethylammonium chloride)—sodium methyl-cocoyl-taurate complexes onto solid surfaces. *Colloids Surf. A* **2016,** *505*, 150-157.

35.   Llamas, S.; Fernández-Peña, L.; Akanno, A.; Guzmán, E.; Ortega, V.; Ortega, F.; Csaky, A. G.; Campbell, R. A.; Rubio, R. G., Towards understanding the behavior of polyelectrolyte–surfactant mixtures at the water/vapor interface closer to technologically-relevant conditions. *Phys. Chem. Chem. Phys.* **2018,** *20*, 1395-1407.

36.   Llamas, S.; Guzman, E.; Akanno, A.; Fernandez-Pena, L.; Ortega, F.; Campbell, R. A.; Miller, R.; Rubio, R. G., Study of the Liquid/Vapor Interfacial Properties of Concentrated Polyelectrolyte-Surfactant Mixtures Using Surface Tensiometry and Neutron Reflectometry: Equilibrium, Adsorption Kinetics, and Dilational Rheology. *J. Phys. Chem. C* **2018,** *122*, 4419-4427.

37.   Guzmán, E.; Fernández-Peña, L.; Akanno, A.; Llamas, S.; Ortega, F.; G. Rubio, R., Two Different Scenarios for the Equilibration of Polycation—Anionic Solutions at Water–Vapor Interfaces. *Coatings* **2019,** *9*, 439.

38.   Guzmán, E.; Llamas, S.; Fernández-Peña, L.; Léonforte, F.; Baghdadli, N.; Cazeneuve, C.; Ortega, F.; Rubio, R. G.; Luengo, G. S., Effect of a natural amphoteric surfactant in the bulk and adsorption behavior of polyelectrolyte-surfactant mixtures. *Colloids Surf. A* **2020,** *585*, 124178.

39.   Guzmán, E.; Fernández-Peña, L.; S. Luengo, G.; Rubio, A. M.; Rey, A.; Léonforte, F., Self-Consistent Mean Field Calculations of Polyelectrolyte-Surfactant Mixtures in Solution and upon Adsorption onto Negatively Charged Surfaces. *Polymers* **2020,** *12*, 624.

40.   Kumar, N.; Tyagi, R., Dimeric Surfactants: Promising Ingredients of Cosmetics and Toiletries. *Cosmetics* **2013,** *1*, 3-13.

41.   Akanno, A.; Guzmán, E.; Fernández-Peña, L.; Ortega, F.; Rubio, R. G., Surfactant-Like Behavior for the Adsorption of Mixtures of a Polycation and Two Different Zwitterionic Surfactants at the Water/Vapor Interface. *Molecules* **2019,** *24*, 3442. doi:10.3390/molecules24193442.

42.   Im, S. H., Shampoo compositions. In *Handbook of hair in health and disease*, Preedy, V. R., Ed. Wageningen Academic Publishers: Wageningen, The Netherlands, 2012; pp 433-476.

43.   Guzmán, E.; Ortega, F.; Baghdadli, N.; Luengo, G. S.; Rubio, R. G., Effect of the molecular structure on the adsorption of conditioning polyelectrolytes on solid substrates. *Colloids Surf. A* **2011,** *375*, 209-218.

44.   Goddard, E. D.; Gruber, J. V., *Principles of Polymer Science and Technology in Cosmetics and Personal Care.* Marcel Dekker, Inc.: Basel, Switzerland, 1999.

45.   Kleinschmidt, F.; Stutbenrauch, C.; Delacotte, J.; von Klitzing, R.; Langevin, D., Stratification of foam films containing polyelectrolytes. Influence of the polymer backbone's rigidity. *J. Phys. Chem. B* **2009,** *113*, 3972-3980.

46. Guzmán, E.; Ortega, F.; Baghdadli, N.; Cazeneuve, C.; Luengo, G. S.; Rubio, R. G., Adsorption of Conditioning Polymers on Solid Substrates with Different Charge Density. *ACS Appl. Mat. Interfaces* **2011,** *3*, 3181-3188.

47. Luengo, G.; Galliano, A.; Dubief, C., Aqueous Lubrication in Cosmetics. In *Aqueous Lubrication: Natural and Biomimetic Approaches*, Spencer, N., Ed. World Scientific Publishing Ltd.: London, United Kingdom, 2014.

48. Yong-jian, L.; Jordan, S. L. P., Cationic cellulosic polymers with multifunctional and outstanding performances for personal care. *Cosmet. Toiletr. Manufac. Worldwide,* **2003,** *1*, 1-4.

49. Ajayi, O.; Davies, A.; Amin, S., Impact of Processing Conditions on Rheology, Tribology and Wet Lubrication Performance of a Novel Amino Lipid Hair Conditioner. *Cosmetics* **2021,** *8*, 77.

50. Langevin, D., Complexation of oppositely charged polyelectrolytes and surfactants in aqueous solutions. A review. *Adv. Colloid Interface Sci.* **2009,** *147-148*, 170-177.

51. Tam, K. C.; Wyn-Jones, E., Insights on polymer surfactant complex structures during the binding of surfactants to polymers as measured by equilibrium and structural techniques. *Chem. Soc. Rev.* **2006,** *35*, 693-709.

52. Szczepanowicz, K.; Bazylińska, U.; Pietkiewicz, J.; Szyk-Warszyńska, L.; Wilk, K. A.; Warszyński, P., Biocompatible long-sustained release oil-core polyelectrolyte nanocarriers: From controlling physical state and stability to biological impact. *Adv. Colloid Interface Sci.* **2015,** *222*, 678-691.

53. Kabanov, V. A.; Zezin, A. B., Soluble interpolymeric complexes as a new class of synthetic polyelectrolytes. *Pure Appl. Chem.* **1984,** *56*, 343-354.

54. Guzmán, E.; Ritacco, H.; Rubio, J. E. F.; Rubio, R. G.; Ortega, F., Salt-induced changes in the growth of polyelectrolyte layers of poly(diallyl-dimethylammonium chloride) and poly(4-styrene sulfonate of sodium). *Soft Matter* **2009,** *5*, 2130-2142.

55. Guzmán, E.; Fernández-Peña, L.; Ortega, F.; Rubio, R. G., Equilibrium and kinetically-trapped aggregates in polyelectrolyte-oppositely charged surfactant mixtures. *Curr. Opin. Colloid Interface Sci.* **2020,** *48*, 91-108.

56. Wallin, T.; Linse, P., Monte Carlo Simulations of Polyelectrolytes at Charged Micelles. 1. Effects of Chain Flexibility. *Langmuir* **1996,** *12*, 305-314.

57. Wallin, T.; Linse, P., Polyelectrolyte-Induced Micellization of Charged Surfactants. Calculations Based on a Self-Consistent Field Lattice Model. *Langmuir* **1998,** *14*, 2940-2949.

58. Guzmán, E.; Llamas, S.; Maestro, A.; Fernández-Peña, L.; Akanno, A.; Miller, R.; Ortega, F.; Rubio, R. G., Polymer–surfactant systems in bulk and at fluid interfaces. *Adv. Colloid Interface Sci.* **2016,** *233*, 38-64.

59. Khan, N.; Brettmann, B., Intermolecular Interactions in Polyelectrolyte and Surfactant Complexes in Solution. *Polymers* **2019,** *11*, 51.

60. Varga, I.; Campbell, R. A., General Physical Description of the Behavior of Oppositely Charged Polyelectrolyte/Surfactant Mixtures at the Air/Water Interface. *Langmuir* **2017,** *33*, 5915-5924.

61. Chiappisi, L.; Hoffmann, I.; Gradzielski, M., Complexes of oppositely charged polyelectrolytes and surfactants – recent developments in the field of biologically derived polyelectrolytes. *Soft Matter* **2013,** *9*, 3896-3909.

62. Liu, Z. H.; Lv, W. J.; Zhao, S. L.; Shang, Y. Z.; Peng, C. J.; Wang, H. L.; Liu, H. L., Effects of the hydrophilicity or hydrophobicity of the neutral block on the structural formation of a block polyelectrolyte/surfactant complex: A molecular dynamics simulation study. *Comput. Cond. Matt.* **2015,** *2*, 16-24.

63. Li, D.; Wagner, N. J., Universal Binding Behavior for Ionic Alkyl Surfactants with Oppositely Charged Polyelectrolytes. *J. Am. Chem. Soc.* **2013,** *135*, 17547-17555.

64.   Korte, M.; Akari, S.; Kühn, H.; Baghdadli, N.; Möhwald, H.; Luengo, G. S., Distribution and Localization of Hydrophobic and Ionic Chemical Groups at the Surface of Bleached Human Hair Fibers. *Langmuir* **2014,** *30*, 12124-12129.

65.   Baghdadli, N.; Luengo, G. S., A Closer Look at the Complex Hydrophilic / Hydrophobic Interactions Forces at the Human Hair Surface. *J. Phys.: Conference Series* **2008,** *100*, 052034.

66.   Nylander, T.; Samoshina, Y.; Lindman, B., Formation of polyelectrolyte–surfactant complexes on surfaces. *Adv. Colloid Interface Sci.* **2006,** *123-126*, 105-123.

67.   Goddard, E. D., Polymer—surfactant interaction part II. Polymer and surfactant of opposite charge. *Colloids Surf.* **1986,** *19*, 301-329.

68.   Dedinaite, A.; Claesson, P. M., Interfacial Properties of Aggregates Formed by Cationic Polyelectrolyte and Anionic Surfactant. *Langmuir* **2000,** *16*, 1951-1959.

69.   Mohr, A.; Nylander, T.; Piculell, L.; Lindman, B.; Boyko, V.; Bartels, F. W.; Liu, Y.; Kurkal-Siebert, V., Mixtures of Cationic Copolymers and Oppositely Charged Surfactants: Effect of Polymer Charge Density and Ionic Strength on the Adsorption Behavior at the Silica–Aqueous Interface. *ACS App. Mat. Interfaces* **2012,** *4*, 1500-1511.

70.   Terada, E.; Samoshina, Y.; Nylander, T.; Lindman, B., Adsorption of Cationic Cellulose Derivative/Anionic Surfactant Complexes onto Solid Surfaces. II. Hydrophobized Silica Surfaces. *Langmuir* **2004,** *20*, 6692-6701.

71.   Clauzel, M.; Johnson, E. S.; Nylander, T.; Panandiker, R. K.; Sivik, M. R.; Piculell, L., Surface Deposition and Phase Behavior of Oppositely Charged Polyion–Surfactant Ion Complexes. Delivery of Silicone Oil Emulsions to Hydrophobic and Hydrophilic Surfaces. *ACS Appl. Mat. Interfaces* **2011,** *3*, 2451-2462.