


Review

Physicochemical Aspects of the Performance of Hair-Conditioning Formulations

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Abstract: Most of the currently used products for repairing and conditioning hair rely on the deposition of complex formulations, based on mixtures involving macromolecules and surfactants, onto the surface of hair fibers. This leads to the partial covering of the damaged areas appearing in the outermost region of capillary fibers, which enables the decrease of the friction between fibers, improving their manageability and hydration. The optimization of shampoo and conditioner formulations necessitates a careful examination of the different physicochemical parameters related to the conditioning mechanism, e.g., the thickness of the deposits, its water content, topography or frictional properties. This review discusses different physicochemical aspects which impact the understanding of the most fundamental bases of the conditioning process.

Keywords: hair conditioning; deposition; physico-chemical tools; shampoos; reparation; surfaces; surfactants; polymers

1. Introduction

Environmental exposure together with the thermal and chemical treatments may cause changes in the hair texture, leading to hair frizz and tangling as well as dryness. This is frequently associated with a significant removal of the covalent bonds between the external 18-methyl eicosanoic acid (18-MEA) and the epicuticle on the surface of the hair, which makes the hair more hydrophilic, leading to cuticle swelling and consequently to its shedding [1]. The reparation of the damaged cuticle cannot be done biologically as the hair fibers are mainly composed of dead cells, which prevents their replication. This means that the cuticle disappearance leads to the environmental exposure of the cortex and other damages which may cause the fracture of the hair fibers [2]. However, the outermost part of the capillary fibers may be partially repaired using hair-conditioning procedures, which are generally physical method enabling the temporal covering and filling of the damaged area of the cuticle, which leads to a reduction of the friction between fibers and an enhanced water absorption [3–5]. Furthermore, the application of hair-conditioning products may increase the hair volume, softness and glossiness, reduce frizz, improve hair manageability, and stimulate new hair growth as well as clean hair from detritus [2].

Among the currently used approaches for hair-conditioning, those involving the interaction of complex mixtures, including macromolecules (synthetic polymers, polyelectrolytes, proteins, etc.) and surfactants, with the surface of the hair fibers are probably the most commonly exploited [6–8]. This type of conditioning procedure involves the deposition of the formulations, containing mainly surfactants,

cationic polyelectrolytes and silicones, onto a surface with a relatively large area (typically $\sim 6 \text{ m}^2$ for a head with 20 cm long hairs) [9] which necessitates a careful examination of the physicochemical bases underlying such deposition processes [10–14].

Most of the currently used formulations are composed by supramolecular complexes formed by the interaction of cationic polyelectrolytes (namely polycations) and surfactants (mainly negatively charged and zwitterionic). Such supramolecular complexes may appear as soluble complexes or phase-separated systems [15–18], with the state in which the complexes are found depending on the concentration of compounds involved in the formulation, the temperature and/or the ionic strength. The correct choice of the composition and other variables provides the basis for preparing a one-phase formulation, which can undergo a phase-separation process as result of the dilution process occurring during their application onto the hair fiber under the shower. This leads to an enhanced deposition of the conditioning species onto the hair fibers. It is worth noting that only a small amount of the conditioning compounds present in the formulation remains deposited onto the surface of the hair fibers. However, the effects associated with the deposition of thin layers of conditioning species are strong and may be extended during several hours, or even days [19].

The formation of phase-separated complexes and their deposition onto the hair fibres are recognized as two of the most important aspects governing the performance of the formulations currently used for hair-conditioning [20,21]. However, the physicochemical bases underlying such performance still remain unclear. This review is aimed to disentangle the role of the interactions between polyelectrolyte, surfactant and the surface of the hair during the deposition of conditioning formulations, with this playing a central role for controlling and triggering the deposition process of the formulation onto the hair fibers [22,23]. The understanding of the above aspects is essential to ensure that shampoo/conditioner formulations fulfill the requirements associated with their role in washing and improving the sensorial effects of hair.

2. Fundamental Aspects of the Hair Structure

The understanding of the most fundamental bases governing the washing–conditioning processes requires a careful examination of the complex structure of hair fibers because they are the substrate for the conditioning. It is worth mentioning that shampoos and conditioner together with different damaging processes affect the maintenance and grooming process of hair fibers, altering many of their properties [24].

Hair is a biocomposite material formed mainly by proteins (65–95% of the total hair weight), mainly keratin, which is a fibrous and resistant α -helix protein containing tyrosine, glycine and cysteine as its most common amino acids [1,25,26]. Furthermore, other component such as lipids, water (up to the 32% of the total hair weight), pigments or other trace elements (melamine) are also found in hair fibers [1,4,27,28].

The average number of fibers on a human head is around 100,000, with each fiber presenting a diameter in the range 50–100 μm . An anatomical division of hair fibers allows one to distinguish three different regions [29]: (i) bulb, (ii) root, and (iii) stem. The bulb appears at the deepest end region of the hair, having an important role in the hair growth. The bulb is connected to the dermal papillae, which are deeply vascularized and innervated, allowing the supply of nutrients needed for hair growth. The root is strongly attached to the hair follicle, appearing located between the bulb and the surface of the epidermis, where the hair takes the form of the stem. As the cells move toward the surface of the skin, the amino acids that they contain start to bind, creating what is known as a hair shaft [3,27]. The roots and stem present a hierarchical multilayered structure formed by three concentric layers: (i) medulla, (ii) cortex, and (iii) cuticle. Figure 1 represents a sketch of the hierarchical structure of a hair fiber.

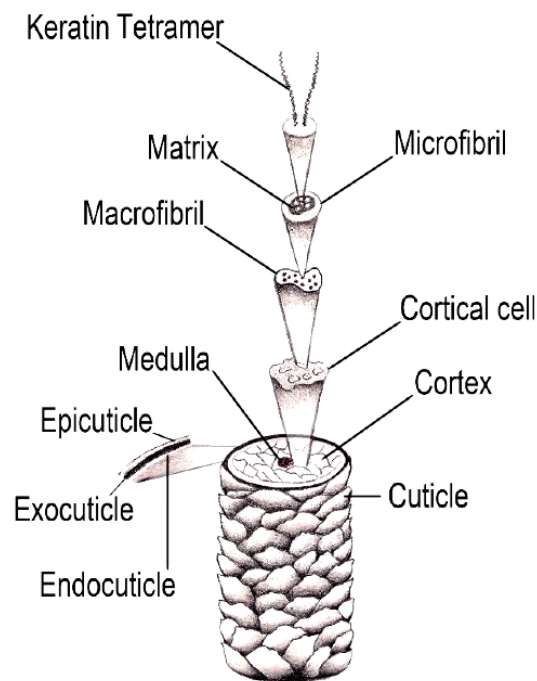


Figure 1. Sketch representing the hierarchical structure of a hair fiber. Reprinted from [3] under a Creative Commons Attribution 4.0 International License.

The medulla is a loosely packed and disordered region representing the central core of the hair fibers and is composed of a nucleus of central cells, which appears different depending on the type of hair. The next stratum is the cortex, which corresponds to approximately 90% of the weight of the hair. This layer is the largest and thickest region of the hair fibers and governs their mechanical properties [1,25,29], which are determined by a structure formed by packed spindle-shaped cortical cells, filled with a series of keratin filaments following a direction parallel to the longitudinal axis of the hair shaft, and an amorphous matrix formed by proteins with a high sulfur content (mainly keratin). The latter appears as a strongly cross-linked network formed as result of the disulfide bonds between the cystine residues in adjacent keratin filaments, governing the stability, shape and texture of the hair [26]. The outermost layer of the hair is the cuticle, a very resistant stratum, that protects the fiber from the scalp to the ends. The cuticle presents a structure of overlapping scales, formed by dead cells (keratinocytes), which have a length of about 60 μm and a thickness in the range 0.3–0.5 μm , with their shape and orientation governing the frictional properties of the hair. The cuticle of native fibers presents a smooth appearance, which limits the friction between fibers [26].

The cuticle is the substrate of most of the cosmetic treatments, with each cuticle cell being divided into several sublamellar layers, as shown in Figure 2 (from the outer part to the inner region): F-layer, epicuticle, layer A, layer B or exocuticle, endocuticle and complex cell membrane (CMC) [25,30]. The epicuticle is covered by a thin layer (F-layer) of fatty acids, covalently linked through thioester bonds to the protein matrix, with the 18-MEA being the main fatty acid. The covalently grafted fatty acid layers may appear linked to the cuticle forming either an ordered structure or a disordered one [31,32].

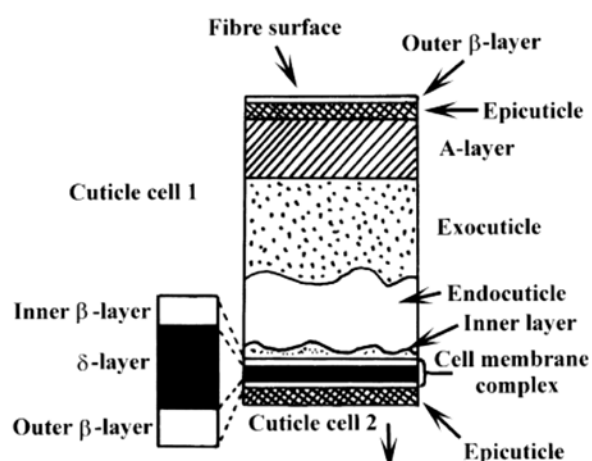


Figure 2. Scheme representing the hierarchical structure of the cuticle. Reprinted from [30], Copyright (2002), with permission from John Wiley and Sons.

Below the epicuticle, a cystine-rich highly cross-linked A-layer is found. The specific chemistry of this layer gives it a high mechanical and chemical resistance, as well as a high resistivity to swelling in water. The A-layer is followed by the exocuticle and endocuticle, with the former also being rich in cystine [4,24]. The complex cell membrane is the intercellular material in charge of joining the cell membranes between two cuticle cells, consisting of cell membranes and adhesive material that joins the cell membranes and cuticle–cortex cells. The most important layer of the CMC is called the β -layer, considered the intercellular cement.

It is worth mentioning that the shine and volume of native hair is the result of the combination of the hydrophobic character of the external region of the hair with the properties of the cortex. The existence of fatty acids at the outermost region of the hair fibers is critical in the control of the physicochemical properties of hair [33]. Thus, when hair fibers undergo certain physical or chemical processes, the lipid barrier, i.e., F-layer, can be damaged. This results in the removal of the first protection of the hair fibers, yielding into a worsening of the mechanical properties of the hair fibers [9].

3. Physicochemical Bases of the Hair-Conditioning Process

There are many factors which can influence the integrity of the hair surface, with the removal of the fatty acids covalently linked to the outermost surface of the cuticle or the oxidation of the disulfide bonds from the cystine residues to cysteic acid considered two of the most common alterations. This results in the formation of an excess of acidic groups on the hair surface, which undergo a dissociation process in aqueous medium, and hence the presence of many negatively charged residues on the fiber surface is found. The anionic residues on the fibers surface make them susceptible to interacting with the positively charged chemical species, generally polycations, existing in conditioners [1,9,19,24,34,35]. This interaction favors the deposition of the conditioning molecules onto the fibers, reducing their static electricity and improving the lubrication of hair fibers as well as the manageability and combing. This is because the deposition of the conditioner layer enables the flattening of the cuticle scales against each other. Figure 3 presents a scheme showing the aspect of the hair surface before the conditioning (virgin or damaged hair) and upon the deposition of a conditioner layer.

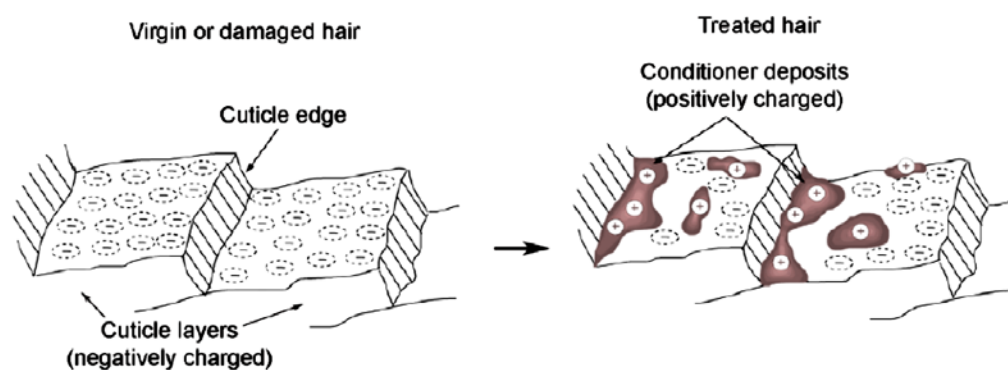


Figure 3. Scheme representing a damaged hair surface and the same surface upon the deposition of the conditioner layer. Reprinted from [24], Copyright (2008), with permission from Elsevier.

The understanding of the conditioning process requires taking into consideration the specific morphology and chemistry of the surface of the fibers. Its complex nature is also reflected in the deposition of the conditioning species, which are not homogeneously distributed within the fiber surface (see Figure 3). It is worth mentioning that the heterogeneity and biological richness of hair makes it difficult to unravel the physicochemical bases underlying the deposition of conditioner species onto hair fiber. The following sections will pay attention to some of the most fundamental aspects governing the interactions occurring between the conditioner formulations, mainly polyelectrolyte–surfactant mixtures, and the hair fibers.

4. Composition of Formulations for Hair Conditioning

It was stated above that conditioning agents are mainly used to reduce friction between fibers, detangle the hair, minimize frizz and improve styling ability. This is associated with two main aspects: (i) neutralization of the negative charge of the hair fiber by adding positive charges and (ii) lubrication of the cuticle, which is associated with the reduction of the hydrophilic character of the damaged fibers. Different antistatic and lubricant substances are used in conditioner products, which be classified into five main groups, namely polymers, oils, waxes, hydrolyzed amino acids and other cationic molecules [36], with polycations and silicones probably being the most widespread components in currently used products.

Polycations are water-soluble compounds; at low concentration (0.1 to 1 wt%), they are compatible with the rest of the ingredients existing in the formulation of a shampoo/conditioner. On the other hand, when the use of silicone is concerned, its compatibility with the rest of components of the formulations is relatively poor in most of the cases. Silicone appear generally dispersed as discrete droplets within the formulation, which is possible by the incorporation of thickener molecules, e.g., ethyleneglycol distearate and stearic monoethanolamide, into the formulation [37]. It is worth mentioning that most of the currently commercialized formulations combine polycations and silicones. Table 1 summarized the composition of a model conditioning formulation [38].

It is worth mentioning that the preparation of cosmetic formulations for hair-conditioning is not exempt to the current efforts to improve the protection of human health and the environment. This is even more important considering the Regulation (EC) No. 1223/2009 and their Annexes associated with the use of chemical compounds in cosmetics or the most general Regulation (EC) No. 1907/2006, the so-called REACH (Registration, Evaluation, and Authorization of CHemicals), which limit the number of ingredients available to the cosmetics industry for the development of new formulations and processes [39]. This requires the progressive substitution of many chemical compounds that have been frequently used in most of the products currently on the market by others that meet the specifications set by the regulations and that present similar or even better performance.

Table 1. Model composition of a hair conditioner according to [38]. q.s: quantum satis (the amount which is enough).

Phase ¹	INCI Name	wt%
A	Water	q.s
B	Hydroxyethyl cellulose	0.30
C	Quaternium-82	1.00
	cetyltrimethylammonium chloride	3.33
D	Cetyl alcohol	1.50
	Stearyl alcohol	2.00
	Pentaerythritol tetracaprylate/tetracaprate	2.50
E	Phenyl trimethicone	0.50
	Wheat amino acids	1.00
F	Hydrolyzed wheat protein PG-propyl silanetriol	1.00
F	Sodium hydroxide	q.s
G	Citric acid	q.s
H	Preservative, color, fragrance	q.s

¹ Procedure for preparing the conditioner: Disperse B into A. Add F to raise pH to 7.0–8.0. When solution is clear, adjust pH with G to a pH of 4.0–5.0. Add C and mix well. Start heating to 76–82 °C. Add D at 77 °C. Mix well for 20 min. Start cooling to room temperature. Add E at 38 °C. Mix well. Add F or G, if necessary, to adjust pH. Add H and mix well.

The new orientation of the cosmetic industry toward the manufacturing of more eco-sustainable formulations has led to the introduction of plant-derived proteins as conditioning agents. Some examples of these are those derived from quinoa, jojoba, baobab, soy or rice. Furthermore, a current practice in cosmetic industry is the use of plant-derived compounds, such as panthenol or squalene, to substitute those commonly used in formulations which may be originated from non-acceptable sources (animals or synthesis). In general, the performance of proteins as repairing agents of hair is the result of their penetration into the hair shaft, enabling moisture retention and making the fiber less susceptible to breakage [3].

The most frequently used formulations are complex mixtures involving several polymers and surfactants, together with other chemical compounds. This makes it necessary to reduce the number of components under study when seeking to determine the most fundamental bases underlying their performance. Following this approach, hair-conditioning formulations may be simplified to polyelectrolyte–surfactant mixtures. This is because many of the currently used formulations are multipurpose products, which include washing bases (mainly surfactants) to ensure the cleaning of the hair and conditioning agents (mainly cationic polyelectrolytes) to reduce interfiber friction, detangle hair, minimize frizz and improve styling performance.

4.1. Surfactants

Surfactants weaken the adhesion forces that bind dirt and dust to the hair and solubilize them in the hydrophobic interior of the micelles or suspend them in water [36]. For a long time, most of the formulations for cosmetic purposes used sodium dodecyl sulfate (SDS), which is an excellent detergent and foaming agent. However, its use is currently advised against as result of its irritant character for skin and mucosa. Nowadays, mixtures involving several surfactants of different nature for are generally used improving the performance of the formulations and for eco-sustainability purposes. Examples of surfactants appearing in commercial formulations are as follows [3,36,40]:

- Anionic surfactants. These surfactants are characterized by the presence of a negatively charged polar group (carboxylates, sulfates, sulfonates or phosphates) bound to a hydrophobic chain, in most cases an alkyl one. These surfactants are considered to be the most efficient in the cleaning of sebum fats and dirt in general. However, an excessive deposition of this surfactant onto the surface of the hair fibers during the washing process may increase the number of negative charges, which would be detrimental for the conditioning process as result of the increase in the friction

between fibers. Some examples of anionic surfactants found in commercial shampoos are sodium laureth sulfate (SLES), sodium lauroyl methyl isethionate (SLMI) or sodium methyl lauroyl taurate (SLMT) [7,41–46].

- Cationic surfactants. These surfactants are characterized by their positively charged polar group (generally quaternary ammonium), playing a central role in the neutralization of the negative charge existing on the damaged hair surface and minimizing frizz. They may be also used as softeners. Examples of cosmetically acceptable cationic surfactants for hair-conditioning products are benzalkonium chloride, trimethylalkylammonium chloride or cetylpyridinium cetrimonium chloride [3,47].
- Nonionic surfactants. These surfactants do not exhibit a net electrical charge in aqueous solutions due to the absence of hydrophilic dissociable groups. These surfactants are less aggressive than other surfactants, and they are widely used as emulsifiers and solubilizers in cosmetic formulations. The most common among this type of surfactants are those based on ethylene oxides, the so-called ethoxylated surfactants. Another important class of nonionic surfactants are “multihydroxy” molecules, such as glycol esters, glycerol and polyglycerol esters, glycosides and polyglycosides and sucrose esters [7,46].
- Zwitterionic surfactants. These surfactants contain both cationic and anionic groups in their hydrophilic heads and are characterized by the possibility of controlling their net charge by tuning the pH. They have good foaming, detergent and wetting properties and are very mild, presenting excellent dermatological properties; therefore, they are used to reduce the aggressiveness of anionic surfactants. The most common are N-alkyl betaines, derived from trimethylglycine (betaine) [45,46,48].

4.2. Polymers

The correct choice of the polymers in the preparation of formulations for conditioning purpose depends on several aspects: (i) ability of the polymer to bind to the hair fiber, (ii) chemical nature of the polymers, (iii) rheological properties of the solutions and (iv) ability for the formation of film and adhesion properties of such layers [1].

As stated above, polycations considered the most common polymers contained in formulations for hair-conditioning purposes. However, other types of polymers can be found in such formulations. These polymers are generally classified in terms of their chemical nature or their role in the formulation (fixative, thickeners, etc.).

The most common polycations in formulations for conditioning purposes are those presenting quaternary ammonium as charged groups (polyquaternium) [49]. These polymers present a good adhesion to the keratinous structure of the hair fibers, which favors their role in conditioning. Furthermore, these polymers can interact with the surfactants existing in the formulations, which results in the formation of polyelectrolyte–surfactant complexes. The rich phase behavior of such complexes is essential for the performance of conditioners [9,50–53]. Some common polyquaternium polymers used in cosmetic products for hair care and conditioning are reported in Table 2 [20].

Different hydrophilic neutral polymers may be also contained in hair care formulations [53], e.g., poly[(meth)acrylic acid] (PMA), poly(acrylamide) (PAM), poly(ethylene oxide) (PEO), block and random copolymers of poly(ethylene oxide) and (propylene oxide), poly(vinyl alcohol) (PVA) and poly(vinylpyrrolidone) (PVP). The role of such polymers is generally to increase the viscosity of the formulations (thickeners). However, in some cases neutral polymers can be also used for conditioning purposes.

It is worth mentioning that cosmetic formulations can present several polymers fulfilling different performance requirements, e.g., shampoos combining polyquaternium 10 (0.1 wt%) and PEO (0.75 wt%), with the first one being the conditioning agent and the second one playing a role of thickener [54].

Table 2. Summary of some of the most common polycations found in conditioners.

Name	Composition
<i>polyquaternium 2</i>	poly[bis(2-chloroethyl) ether-alt-1,3-bis [3-(dimethylamino)propyl]urea] quaternized
<i>polyquaternium 6</i>	homopolymer of poly(diallyl-dimethyl-ammonium chloride)
<i>polyquaternium 7</i>	copolymer containing 50 wt% diallyl-dimethylammonium chloride and 50 wt% acrylamide
<i>polyquaternium 10</i>	hydroxyethyl cellulose quaternized with 2,3-epoxypropyl-trimethyl-ammonium chloride
<i>polyquaternium 17</i>	poly[oxy-1,2-ethanediyldimethyliminio)-1,3-propanediyldimino-(1,6-dioxo-1,6-hexanediyldimino-1,3-propanediyldimethyliminio)-1,2-ethanediyldichloride]
<i>polyquaternium 18</i>	poly[oxy-1,2-ethanediyldimethyliminio)-1,3-propanediyldimino-(1,6-dioxo-1,6-heptanediyldimino-1,3-propanediyldimethyliminio)-1,2-ethanediyldichloride]
<i>polyquaternium 22</i>	copolymer containing 50 wt% diallyl-dimethylammonium chloride and 50 wt% acrylic acid
<i>polyquaternium 39</i>	copolymer containing 50 wt% diallyl-dimethylammonium chloride, 25 wt% acrylamide and 25 wt% acrylic acid
<i>polyquaternium 53</i>	copolymer containing 40 wt% methacrylamidopropyltrimonium chloride, 50 wt% acrylamide and 10 wt% acrylic acid
<i>polyquaternium 67</i>	hydroxyethyl cellulose quaternized and polymerized with n-propyl-2-hydroxy-3-trimethyl ammonium and n-propyl-2-hydroxy-3-dimethyl dodecyl ammonium monomers
<i>polyquaternium 86</i>	copolymer of vinyl pyrrolidone, vinyl imidazole, vinyl imidazole quaternized with methyl chloride and methacrylic acid (25 wt% of each type of monomer)

5. Model Surfaces

One of the current challenges in understanding the performance of formulations for hair-conditioning is the evaluation of their interaction with hair and tissues. This is rather difficult and makes it necessary to use model surfaces. Such model surfaces should mimic one or several of the most relevant aspects of the biological complexity of real hair fibers (complex mixtures of lipids, proteins and other compounds) [55,56]. Thus, even though the biological complexity is an important aspect of the final result of conditioning formulations, it is possible to assume that the adsorption processes are mainly determined by the surface charge of the surface and the existence of hydrophilic and hydrophobic groups on their surface [8]. This leads to a situation in which the use of model surfaces is a powerful tool for deepening the understanding of the physicochemical bases underlying the interaction of cosmetic formulations and hair fibers [50,53].

Different surfaces are commonly used for representing the hair, or more in particular, some of its main characteristics, which include the negative charge of damaged hair fibers, their contact angle or their hydrophobic/hydrophilic character [57]. The use of such simple representations provides a helpful description of the impact of different physicochemical parameters on the conditioning process, which is also correlated to the origin of the hair and the degree of damage of the fibers (native or oxidized) [57]. However, a deeper understanding of the performance of the conditioning formulations requires introducing lipids and chemical groups which resembles the keratin surface to the model [8]. Furthermore, the particular mechanical properties of hair fibers represent another level of complexity which may need to be introduced when model surfaces are concerned. This is particularly important because it is known that the mechanical properties of the fibers may be modified upon damaging processes and that different cosmetic treatments may decisively impact the rheological properties of hair fibers [33,58,59]. It is worth mentioning that surfaces presenting a negative charge similar to that existing in damaged hair are among the most used, with surfaces decorated with a thiol layer may enable a better mimicking of the high cystine content on the external surface of the cuticle [20]. However, other functional groups can be used when the only controlled parameter is the charge of the hair fiber. It is worth mentioning that surfaces similar to those commonly used in the study of the adsorption of polymer or surfactant onto solid surfaces (gold, silica or mica) [60–62] are widespread for studying the performance of conditioning formulations.

6. Quantitative Evaluation of the Adsorption of Cosmetic Ingredients

The use of quantitative parameters for evaluating the performance of cosmetic ingredients for conditioning purposes may be done taking advantage of different physicochemical techniques. This approach provides information about different parameters of interest in conditioning: adsorbed amount or thickness of the layer, morphology of the deposits, mechanical properties or water content. The use of the techniques for determining such parameters may be applied in some cases using real fibers as substrate, even though in most of the cases they are only applicable to studies on model surfaces. This necessitates careful extrapolation of the obtained results to the real situation [63].

Information related to the adsorbed amount can be obtained using the dissipative quartz crystal microbalance (D-QCM), ellipsometry or surface plasmon resonance (SPR) [63]. These techniques allow obtaining information both on the deposition mechanism and on the steady-state adsorbed amounts. Furthermore, they help to obtain in vitro information under conditions which mimic the conditioning process [64]. It is worth mentioning that the surface densities obtained using D-QCM present a different meaning than those obtained using ellipsometry or SPR. D-QCM measurements provide information of the so-called acoustical thickness, h_{ac} , which gives information on both the adsorbed amount of the layers and the water associated with such layers. However, because the contributions of the deposited materials and the water associated with the layer cannot be separated from the D-QCM measurements, the use of ellipsometry and SPR can help with this task. These techniques provide information on the so-called optical thickness, h_{op} , which is a real estimation of the real surface density associated with the deposition of the conditioning ingredients. The determination of the optical thickness is based on the differences between the refractive indexes of the deposited films and those corresponding to the surrounding solvent. The above discussion makes it clear that sensitivities to the adsorbed material of the D-QCM and ellipsometry or SPR are different, with $h_{ac} > h_{op}$. The differences between the nature of sensed mass obtained by the different type of techniques allows an evaluation of the hydration degree of the deposited layer, $X_w = 1 - (h_{op}/h_{ac})$ [65]. The determination of the water content of the adsorbed layers using the abovementioned approach give results which are consistent with those obtained using other techniques such as neutron reflectometry [66].

D-QCM measurements give also an evaluation of the rheological properties of the adsorbed films, such as the viscoelastic shear modulus $G = G' + iG''$, with G' and G'' being the elastic and the viscous components, respectively. Scattering techniques, including neutron or X-ray reflectometry, may help in the evaluation of the adsorption process onto model surfaces in terms of the distribution of the adsorbed material within the layer (density profiles), the thickness and hydration degree [63].

The frictional properties of the adsorbed layers present a critical impact on the performance of the deposits of conditioning species. For such purpose, the surface force apparatus (SFA) is a powerful tool. The use of spectroscopy techniques, such as X-ray photoelectron spectroscopy (XPS) or infrared and Raman spectroscopy, can help in the evaluation of the chemical composition of the deposit. Furthermore, spectroscopy techniques allow mapping the distribution of the different components within the adsorbed layers, even directly onto hair fibers [67,68].

Another technique that has been also used for studying deposits on both hair fibers and model surfaces is atomic force microscopy (AFM). This technique helps in evaluating the topography and morphology of the adsorbed films as well as the interactions occurring within the adsorbed films [8]. One of the main advantages of AFM with respect to conventional electron microscopies is the absence of any pretreatment of the samples. AFM also avoids the use of high-voltage electron currents. Thus, the use of AFM minimizes the possible damage to the samples [8]. AFM can be used as an alternative to the SFA for evaluating the tribological properties of the layers, which is critical considering that the frictional properties of hair directly impact the consumer perception of the conditioned fibers [8,31]. AFM also helps in the evaluation of the adhesivity of the surfaces or in the disruption of the structure of the surface (force–distance curves). The latter is critical for distinguishing fibers with different health levels [69]. The use of electron microscopies, even though more complex to implement,

can help the evaluation of the performance of cosmetic formulations, as was recently shown by Fernández-Peña et al. [7] (see Figure 4).

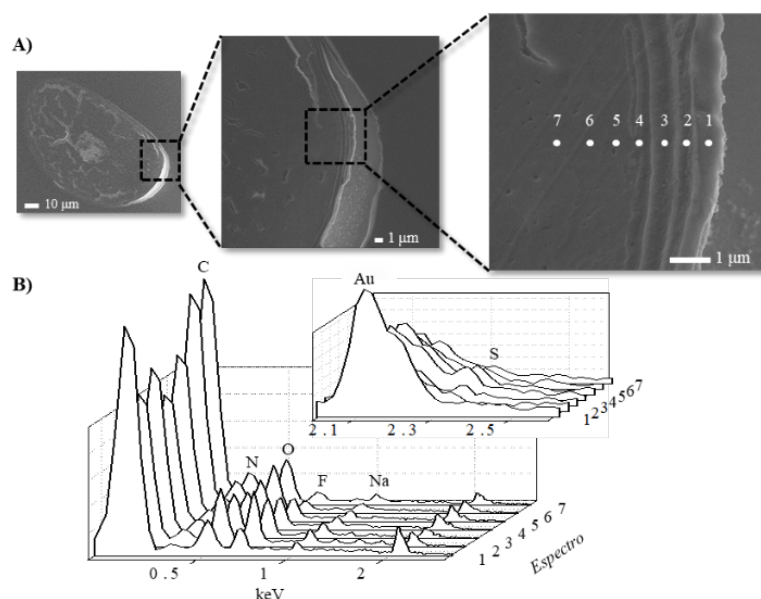


Figure 4. (A) Scanning electron microscopy images of a transversal cut of a hair fiber treated with a model conditioning formulation and two enlargements of the most external regions of the deposit. The numbers indicate the region in which electron dispersive spectroscopy analysis was performed. (B) Electron dispersive spectroscopy spectra for the different regions in panel a. Reprinted from [7], Copyright (2020), with permission from Elsevier.

The images of electron microscopy allow evaluating the efficiency of the deposition of the conditioning agents, which is clearly focused on the most external region of the fibers. However, electron microscopy does not provide information related to the penetration and absorption of the conditioning species to the inner regions of the fibers. The combination of electron microscopy images with electron dispersive spectroscopy helps to determine the role of the penetration of the conditioning species into the fiber. The spectra shown in Figure 4 show that the penetration is limited, as evidenced by the existence of S in the inner regions of the hair.

A last experimental technique applied to the study of hair fibers is differential scanning calorimetry (DSC) [70]. DSC has become a powerful tool for evaluating hair damage, especially when cosmetic treatments involving the heating of the hair, and, as a matter of fact, its damage, are concerned. The evaluation of the impact of the cosmetic treatments on hair using DSC may be done following two type of approaches, dry-DSC and wet-DSC, with the used approach being chosen depending on the required information. The evaluation of the efficacy of cosmetic products in hair fibers is generally performed using wet-DSC. On the other side, the evaluation of the modifications occurring in hair fibers as result of thermal hair-styling tools is generally performed using dry-DSC. This provides information about the impact of the thermal treatment on the properties of the hair fibers. However, the information of DSC should be generally combined with mechanical performance tests and/or information obtained using spectroscopic and scattering techniques to ensure robust and reliable conclusions.

Nowadays, different theoretical approaches, mainly based on the use of mean-field self-consistent calculations, have been used for the *in silico* prediction of the performance of different model conditioning formulations [11,71–74]. The results obtained following the abovementioned theoretical approaches are generally in good accordance with the experimental findings [7,45,46].

7. Physicochemical Aspects Involved in the Conditioning Process

The complex phenomenology involved in the interaction between conditioners and the hair surface makes it necessary to deepen on different physicochemical aspects playing an essential role in the performance of the formulations. It was stated above that the deposition of polycations onto the surface of the hair fibers is the driving force guiding the performance of most conditioning formulation, with this being strongly modified when the presence of anionic surfactants, as in two-in-one shampoos, is considered. Thus, the impact in the conditioning process of the interactions occurring between polyelectrolytes and anionic surfactants, and their adsorption onto the surface of the fibers, makes it essential to deepen the understanding of the behavior of these mixtures [34,75], as this is critical for an optimal development of cosmetic formulations [76]. The full potential of a conditioning formulation can only be developed by a careful examination of the different possible polymer–surfactant combinations and of the different interactions existing in the system during the conditioning process (surface–polymer, surface–surfactant and surface–polymer/surfactant) [77,78].

7.1. Mixtures of Oppositely Charged Polyelectrolytes and Surfactants in Solution

The study of the behavior of solutions containing polymer–surfactant mixtures is relevant for understanding their interactions with interfaces, both fluid/fluid and liquid/solid ones [79,80], with the association of polyelectrolyte–surfactant complexes being governed by both electrostatic interactions, where two components attract or repel each other due to the presence of charges, and hydrophobic interactions, where molecules are attracted due to the existence of domains in the molecules that have low affinity for water [81]. It is worth mentioning that as a first approach, the association of polyelectrolytes and surfactants may be analyzed in analogy to an ion-exchange process, where the electrostatic interactions are reinforced for the hydrophobic interactions between the alkyl chains of the surfactant molecules and the role of the entropy associated with the release of counterions presents a relatively important role [82]. This means that the ionic strength becomes a critical parameter in the association, impacting both the charge screening and counterions release [66].

The interactions involved in the assembly of polyelectrolyte–surfactant complexes may be exploited by varying the characteristics of the polyelectrolytes (such as charge density, molecular weight or functional groups) and surfactants (nature of the hydrophilic head, hydrophobic chain length and concentration) [80,81] or the solution properties (pH, ionic strength and temperature). Such interactions decisively impact the rich phase behavior of polyelectrolyte–surfactant mixtures, in which one- or multiphase mixtures are obtained depending on the composition and the nature of the components [6,44,83]. The existence of multiphase regions, the so-called phase-separation regions, has a central role in the hair-conditioning process. Figure 5 shows the different steps occurring during the assembly of polyelectrolyte–surfactant mixtures as the concentration of the surfactant increases.

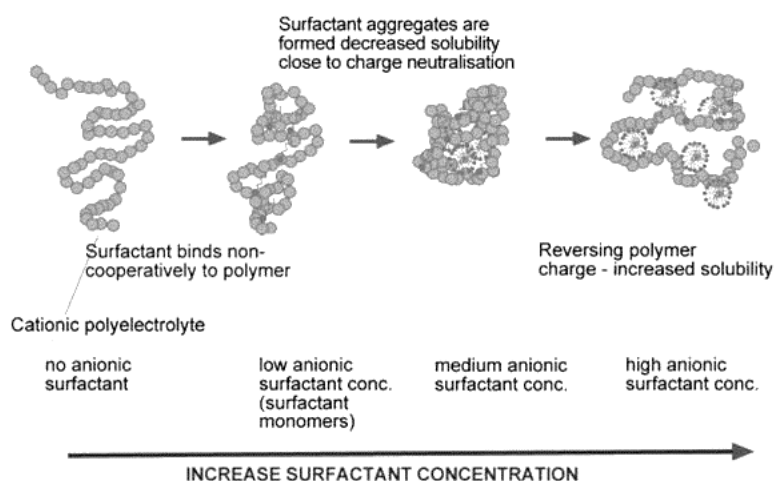


Figure 5. Different steps of the complexation process for polyelectrolyte–surfactant mixtures as result of the surfactant concentration increase. Adapted from [84], Copyright (2010), with permission from Elsevier.

A closer look to the complexation process evidences the existence of up to four different regions in the phase diagram of polyelectrolyte–surfactant mixtures [85]. Assuming that the ionic strength and the temperature are fixed parameters, the ratio between the surfactant and monomer concentrations allows defining the boundaries between different regions appearing in the phase diagram [86]. At low surfactant concentration, the system is in a regime in which the excess of polymer governs the properties of the mixtures, even though indirect evidence of the surfactant binding to the polyelectrolyte chains can be found. However, no evidence of a true neutralization of the charge of the polymer chain as result of the binding is found until a critical value for the concentration is overcome, the so-called critical aggregation concentration (CAC). Once the concentration is above the CAC, further increases of the amounts of surfactant lead to a progressive neutralization of the net charge of the complexes up to the isoelectric point, where neutral complexes are formed [87]. The complexes obtained in the vicinity of the isoelectric point have a poor colloidal stability, thus driving the system to the onset of a phase-separation region (2ϕ). The emergence of the phase separation is evidenced by the formation of precipitates, gels or other ordered structures enriched in polyelectrolyte–surfactant complexes [88–90]. It is worth mentioning that the stoichiometry of the complexes formed within the phase-separation region can be highly variable and depends on the specific nature of the considered mixture and the solution properties [87], even though the stronger effect associated with the phase separation occurs when 1:1 complexes are formed [91,92]. Once the isoelectric point is overcome, the addition of further amounts of surfactant results in an inversion of the charge of the formed complexes, i.e., overcompensated complexes, in which the excess of surfactant charges enables the dissolution and restabilization of the phase-separated complexes, driving again to a one-phase-region (1ϕ) [79,84,93,94]. There are several parameters that influence the phase separation–resolubilization of the polyelectrolyte–surfactant complexes, with the charge density of the polyelectrolyte chains and the ionic strength probably being the most important one. Figure 6 shows a schematic representation of the phase diagram for an arbitrary polyelectrolyte–surfactant mixture, in which the different phases are represented in terms of the Z ratio (ratio between the number of monomers and surfactant molecules).

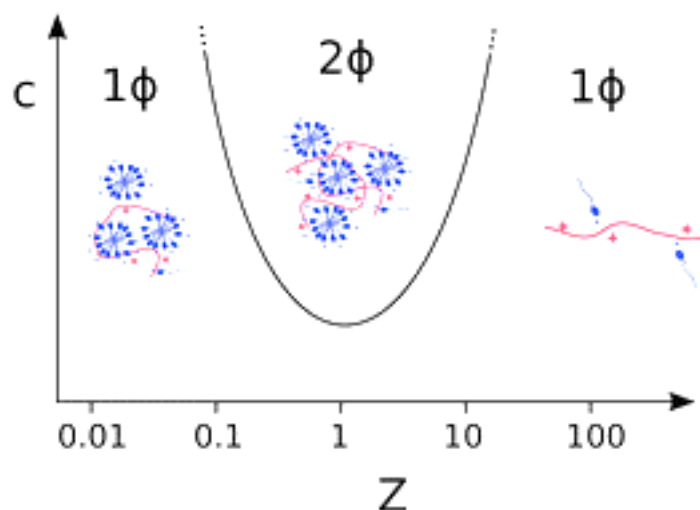


Figure 6. Scheme of the phase diagram for an arbitrary polyelectrolyte–surfactant mixture where the different phases are shown as function of the Z ratio. Reprinted from [94], Copyright (2013), with permission from the Royal Chemical Society.

The binding of the surfactant to the polyelectrolyte chains plays a main role in different physicochemical properties of polyelectrolyte–surfactant mixtures, and, as matter of fact, in the conditioning formulations. This is especially critical when the system is close to the CAC [94]. Different degrees of cooperativity can be found in the complexation process, which impact the association process and the considered mixtures on the phase diagram [81]. At low surfactant concentrations, a clear non-cooperative binding is generally found. This means that the surfactant molecules start to attach to monomers where there are no previously attached surfactant molecules, which results in a decrease of the intrachain repulsions. The presence of non-cooperative binding is generally found up to the CAC. Once the CAC is overcome, the binding starts to be cooperative, which means that, together with the binding by electrostatic interactions between the surfactant molecules and the polyelectrolyte chains, the interactions between the hydrophobic tails of the surfactants allows the binding to monomers in which there are already surfactant molecules. It is worth noting the important role of the cooperative binding on the redissolution of the phase-separated aggregates. There is a third binding type, the so-called anti-cooperative one. This is characterized by the binding through interactions of specific nature [80,81,94].

7.2. Adsorption of Polyelectrolyte–Surfactant Mixtures onto Solid Surfaces

The study of the adsorption processes of polymer–surfactant systems onto solid substrates is of interest for the cosmetic industry. This is because the performance of shampoo and conditioners is related to the deposition of polymer–surfactant complexes onto the surface of hair fibers, with the latter being a relatively large effective surface with an extraordinary chemical and topographic complexity [8,95]. The adsorption of the polymer–surfactant complexes onto solid surfaces depends on various factors such as the properties of the polymer (charge, molecular weight, concentration), the surface (charge, surface energy) and the solution (pH, temperature, solvent quality, ionic strength) as well as the nature and concentration of the surfactant [9,79,96–98]. Furthermore, the proximity of the phase-separation region plays an important role in the adsorption and its efficiency. It is worth noting that the adsorption of polyelectrolyte–surfactant mixtures is a rather complex process in which the simultaneous adsorption of free surfactant molecules and polymer chains together with the adsorption of the complexes may be expected [99]. Figure 7 shows the different regions for the adsorption of polyelectrolyte–surfactant mixtures as function of the surfactant concentration.

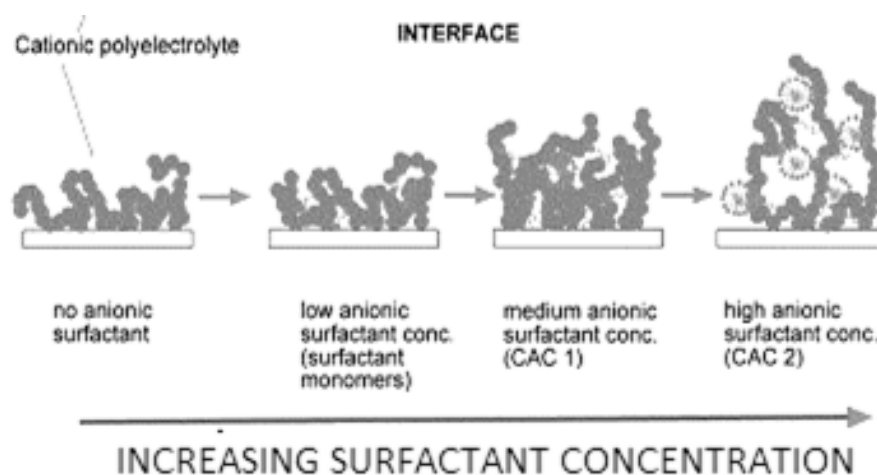


Figure 7. Different regions for the adsorption of polyelectrolyte–surfactant mixtures onto a solid surface as result of increasing surfactant concentration. Adapted from [84], Copyright (2010), with permission from Elsevier.

At low surfactant concentration, the adsorption of the polymer–surfactant complexes is governed by the polymer, with the polymer–surface interactions driving the deposition of the complexes. The compositional analysis of the layers obtained for the low surfactant concentration range evidences a rather limited incorporation of surfactant molecules within the obtained layer [100,101]. This is reasonable considering the high excess of monomers in the complexes and the low surfactant binding. The increase of the surfactant concentration enhances the average adsorbed amount, with an increasing incorporation of surfactant molecules within the adsorbed layer. Imminent phase separation is evidenced by a sharp increase of the adsorption [102]. At the onset of the phase separation, the maximum adsorption is found. The increase of the surfactant concentration in the complexes drives the formation of real mixed layers as the neutralization point becomes closer. Once the phase-separation region is overcome, a decrease in the adsorption should be expected as result of the re-hydrophilization of the resolubilized complexes, which limits their deposition onto the surfaces, especially onto hydrophilic surfaces such as those expected for damaged hair fibers [103,104]. Therefore, it can be stated that as the solubility of the complexes formed in solution worsens, adsorption on solid surfaces increases.

The ionic strength plays a very important role in the adsorption, with the charge screening of the polyelectrolyte governing the electrostatic interactions between the polymer and the surfactant molecules and between the formed complexes and the surface. This affects the adsorption process because the aggregation of the complexes in solution is modified. Furthermore, when the adsorption onto charged surfaces is considered, this can also lead to the screening of the binding sites, which would again modify the adsorption equilibrium [9,101].

It is worth noting that the adsorption process of polyelectrolyte–surfactant complexes onto negatively charged surfaces, such as the hair fibers, under conditions presenting relevance for the conditioning process, is a process with relatively high complexity, as evidenced by the AFM images obtained for deposition of a model conditioning formulation onto a negatively charged model surface shown in Figure 8. The AFM images evidence that, together with the layer deposited by the direct interaction of the complexes with the surface, some aggregates due to the gravitational sedimentation of the complexes are found on the surface.

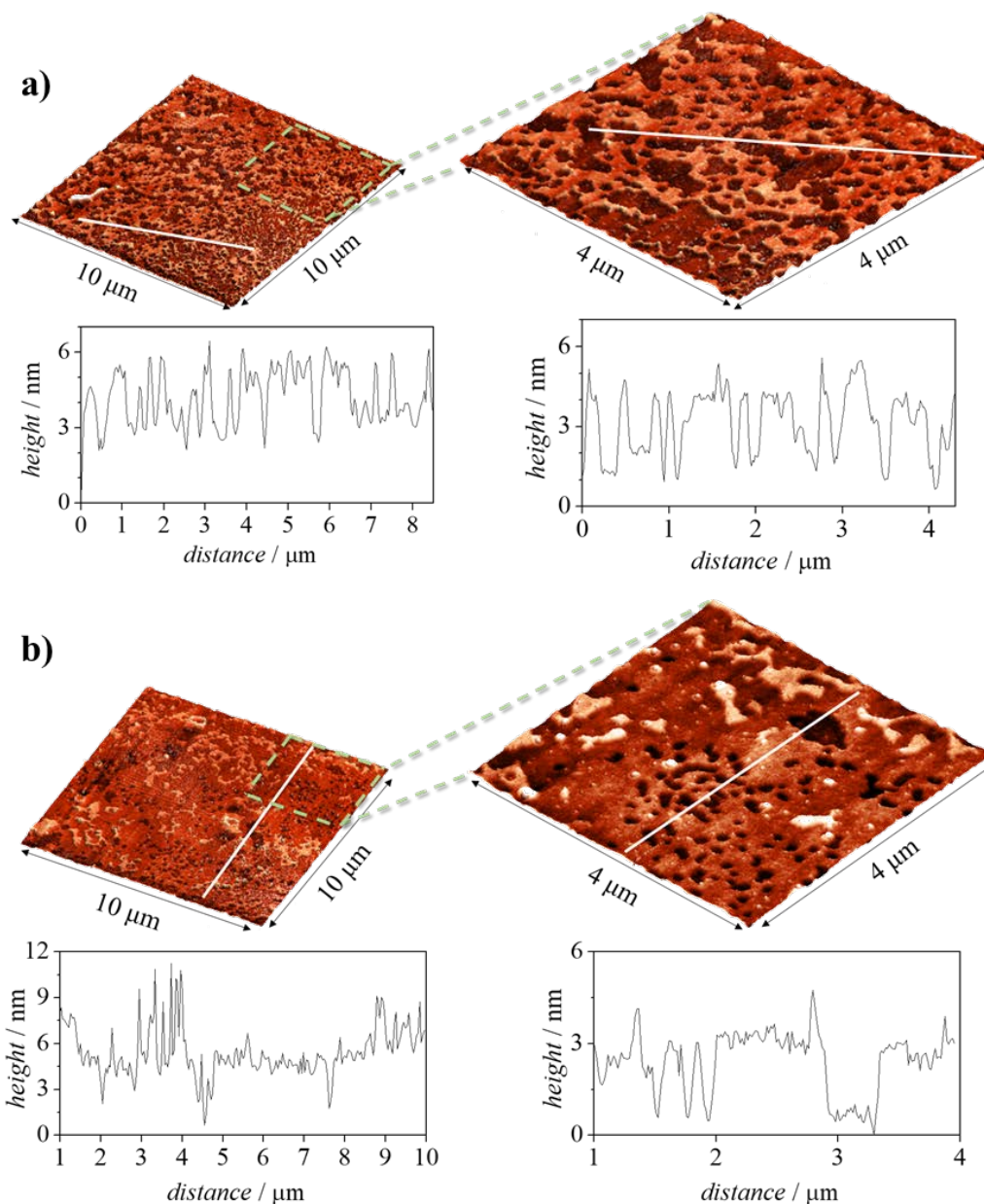


Figure 8. AFM images for the deposition of a model conditioning formulation onto a negatively charged surface: (a) obtained in the border of the phase-separation region; (b) obtained in the phase-separation region. Reprinted from [7], Copyright (2020), with permission from Elsevier.

7.3. Deposition Enhanced by Dilution

Shampoo and conditioner formulations contain a wide variety of surfactants (anionic, neutral and zwitterionic) and polymers which lead to a transparent single-phase mixture. This single phase character is associated with the high concentration of surfactant, which ensures the solubilization of the polymer due to its interaction with surfactant micelles.

The application process of the commercial product is governed by the phenomenon called precipitation-enhanced deposition as a consequence of the dilution process occurring during washing, with this being known as the Lochhead effect [21]. The washing and subsequent rinsing of the hair drives the system into the phase-separation region, which results in an enhanced deposition of the conditioning material onto the fiber surfaces. Such deposition is the result of the precipitation of the complexes which favors foaming and enhances the lubrication property of fibers and the adsorption of colloidal

materials such as silicone emulsions, impacting consumer satisfaction [105,106]. Figure 9 shows the two approaches commonly used for studying the behavior of polyelectrolyte–surfactant mixtures.

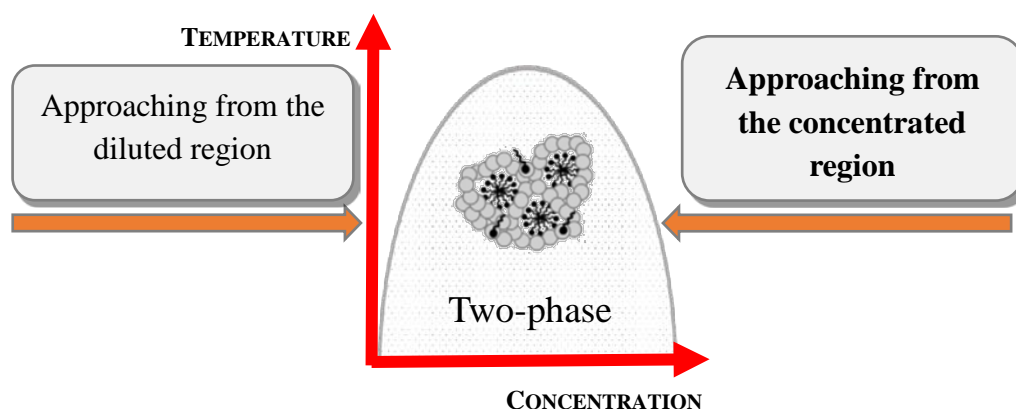


Figure 9. Two different approaches for studying the behavior and deposition of polyelectrolyte–surfactant mixtures onto solid surfaces.

It is worth mentioning that there is not a clear relationship between the amount of deposited complexes upon the precipitation process and the performance of the cosmetic formulations, with small changes in the composition of the mixtures leading to strong modifications in their behavior. This may be ascribed to the multicomponent nature of shampoos and conditioners, which can lead to a partial depletion of some of the components during the precipitation. This makes it so that a small change in the composition of the formulations completely modifies the region in which precipitation occurs and the composition of the deposited layer, with this impacting the performance of conditioners and shampoos.

8. Conclusions

Cosmetic products for hair-conditioning are multicomponent mixtures, and their design, manufacture and stability make it necessary to understand the physicochemical bases that govern their behavior. Despite the biological richness of the substrate of interest for the cosmetic conditioning process, i.e., capillary fiber, and the chemical complexity of the formulations, the use of the tools provided by the science and technology of colloids and interfaces can provide important insights on the most fundamental bases underlying the performance of cosmetic formulations for hair-conditioning purposes.

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