Surface Activity of Surfactant–Polyelectrolyte Mixtures through Nanoplasmonic Sensing Technology

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Abstract: Deposition plays an important role in the active delivery and efficiency of hair and skin formulations since it allows active compounds to interact with surfaces in order to achieve the product’s desired performance characteristics. Therefore, it is essential to study the surface activity and behavior of certain compounds that are frequently used in cosmetic and pharmaceutical formulations in order to understand how they interact with relevant biological surfaces, such as hair and skin. We chose to study the surfactants and conditioning agents utilized in the formulation of conditioning shampoos, which are usually designed to be able to achieve the deposition of these substances on the hair and scalp to provide lubrication and better conditioning for hair fibers, facilitating detangling and providing a better feel. In this study, cationic polymer and salt fractions were varied to obtain eighteen different conditioning shampoo formulations in which the deposition was measured by utilizing a nanoplasmonic sensing technology instrument. Moreover, a wet combing test was performed for each of the formulations to investigate if there was any correlation between the combing force and the surface deposition. The complete study was performed using a sustainable anionic surfactant in order to compare the results with those obtained from the traditional formulations.

Keywords: cationic polymer; sustainability; surface deposition; lubrication; nanoplasmonic sensing technology; wet combing; electrolyte

1. Introduction

Hair is considered to be a complex, integrated system that shows peculiar physical and chemical properties [1]. Morphologically, it is divided into three differentiated regions: the cuticle, cortex, and medulla. The structure and characteristics of these regions provide the hair with some particular properties, such as its hydrophobicity, which can be reduced through chemical and physical treatments, causing a more hydrophilic state and, therefore, a negatively charged surface [2]. The correct use of hair cosmetics can lead to the minimization and repair of this damage. Conditioners are designed to decrease friction, detangle hair, minimize frizz, and improve combability by neutralizing the free negative charges on hair fibers and depositing positive charges that interact with them, aiming to reduce the hair’s static electricity [3] and to improve the lubrication of the cuticle that reduces fiber hydrophilicity [4,5]. Cationic ingredients, such as polymers, are commonly included in conditioning formulations as they can be very substantive to the hair and difficult to remove [6]. Moreover, the interaction of these cationic substances with anionic surfactants, which are mainly included in shampoo formulations, has gained popularity as it further contributes to enhancing the conditioning effect and also allows for the formulation of products with both cleansing and conditioning purposes [7–9].

The deposition of cationic polymers on hair fibers generally occurs through electrostatic interactions between the polymer and the hair’s surface, as it is negatively charged [10]. When cationic polymers are present in mixtures containing anionic and amphoteric surfactants, the deposition mechanism is different. The cationic polymer interacts...
with anionic and amphoteric surfactants through both electrostatic and hydrophobic interactions [11], leading to the formation of a complex or aggregate [12–15]. The aggregate was studied and described as a gel-like phase with a high level of cationic charge that is able to deposit the polymer on a negatively charged hair surface, leading to the formation of a clear film [16]. The association leading the assembly of polyelectrolyte–surfactant complexes and their potential adsorption on the hair surface are mainly governed by electrostatic interactions that are potentially influenced by characteristics of the polymer, such as charge density and molecular weight; characteristics of the surfactant, such as hydrophobic length and concentration; or the solution’s properties, such as pH, ionic strength, and temperature [3].

Finding a suitable measurement method has been one of the greatest challenges in the study of the deposition of these polyelectrolyte–surfactant complexes. Some efficient techniques, such as the dissipative quartz crystal microbalance (D-QCM), surface plasmon resonance (SPR) ellipsometry, and atomic force microscopy (AFM), were previously utilized in multiple studies comprising similar systems for investigating the adsorption of these complexes on the hair’s surface or on specifically modified surfaces that mimicked the hair’s properties [3,17,18]. In [19], mixtures formed by a cationic homopolymer, polyallyltrimethylammonium chloride, and two different surfactants, the negatively charged sodium laureth sulfate (SLES) and the zwitterionic coco betaine (CB) were studied to observe the adsorption of the formed aggregates onto solid surfaces, using two different methods. The thickness of the adsorbed layer was found using atomic force microscopy (AFM) and a dissipative quartz crystal microbalance (D-QCM) technique with quartz crystals containing negatively charged gold substrates as surfaces. Moreover, ellipsometry, with silica plates as the substrate, was applied to find the amount of polymer within the adsorbed layers. Likewise, these mentioned techniques were applied to study some other similar systems, including complexes formed by a highly charged cationic homopolymer (polyallyltrimethylammonium chloride) and a sulfate-free anionic surfactant, sodium methyl cocoyl taurate (SMCT), over silica substrates [20], as well as mixtures of cationic guar (cat-guar) or cationic hydroxyethylcellulose (cat-HEC) with the anionic surfactants sodium dodecyl sulfate or sodium laurel ether-3 sulfate on silica surfaces [21]. A different technique based on the minimization of a mean-field free-energy functional, SFC, was presented in [22] to describe the adsorption of mixtures formed by PDADMAC containing 100 monomers and different surfactants: (i) three anionic, namely, sodium laureth sulfate (SLES), di-rhamnolipid (di-RL), and mono-rhamnolipid (mono-RL); (ii) the zwitterionic coco betaine (CB); and (iii) alkyl polyglucoside (APG), under conditions in which the ionic strength was fixed by the addition of KCl.

The nanoplasmonic sensing technology is a novel method that exploits gold nanoparticles as local sensing elements, constituting a very versatile sensing platform that enables the detection and monitoring of a large variety of material and interface processes under in situ conditions [23]. Gold is among the most common surfaces used in adsorption studies that aim to mimic the adsorption on the hair’s surface [17]. This study aimed to utilize the nanoplasmonic sensing technology provided by Insplorion® to quantify the surface deposition of a cosmetic formulation, evaluating the effects of the cationic polymer and the salt addition in a basic conditioning shampoo formulation. In addition, we worked to identify any correlation between the deposition process and the wet combing force applied to hair after the application of the shampoo.

2. Materials and Methods

2.1. Materials

All the materials utilized were available in the cosmetics laboratory of Manhattan College. Sodium lauryl ether sulfate (SLES), the anionic surfactant, was obtained from Tri-K Surfactants. Cocamidopropyl betaine, the amphoteric surfactant, was obtained from Lubrizol (Clifton, NJ, USA). Polyquaternium-7 cationic polymer (Merquat), a non-ionic surfactant with chains of 12 to 16 monomers long, was obtained from Lubrizol®. Alkyl polyglucoside was selected as the sustainable surfactant to observe the surface deposition
phenomenon, mainly due to its natural origins of a sugar unit and a fatty alcohol [24,25]. Moreover, alkyl polyglucosides have been proven to be readily biodegradable in aerobic conditions, and they have shown low toxicity against several organisms [26]. Thus, they could potentially be desirable for developing sustainable cosmetics formulations. Alkyl polyglucoside C12-16 (APG, 53%), known as lauryl glucoside, was donated by BASF® (Florham Park, NJ, USA). Scheme 1 shows a diagram of its structure. Sodium chloride, purchased from Fisher Scientific®, was used as an electrolyte. DI water was used to turn samples into solutions, and citric acid (50%) was then added to adjust the pH of the samples.

![Scheme 1. APG C12-16 chemical structure [27].](image)

For the deposition analysis, a nanoplasmonic sensing technology instrument provided by Insplorion® (Insplorion Xnano, Göteborg, Sweden) was used. For the wet combing test, we used a tensile tester machine, provided by Dia-stron® (Clarksburg, NJ, USA).

2.2. Sample Preparation

The 30 g samples, which varied in polymer, salt, and water contents, were formulated in 100 mL glass beakers at room temperature. The samples were mixed on a stir plate at 1200 rpm for 2 h to ensure the complete dilution of the surfactants and other components. After mixing, the pH was adjusted to a target of 6.8–7.2, and the samples were then set to rest for 24 h at room temperature.

2.2.1. Effect of the Cationic Polymer Fraction

The effect of the cationic polymer fraction in the formulation was observed by making ten different samples, all at 12 wt. % total surfactant, with a 10:2 proportion from the anionic (SLES) to the cationic surfactant (CPAB). Merquat was the polymer added between 0% and 1% for both systems. The mass fraction was set at 0%, 0.3%, 0.8%, and 1%. All the components were weighed and added one at a time to the water, which was stirred constantly. After pH adjustment and resting time, the samples were poured into 15 mL plastic vials, using two vials per sample.

2.2.2. Effect of the Electrolyte Fraction

To understand the effect of the electrolyte fraction, eight samples were created, with sodium chloride concentrations at 0%, 0.3%, 0.8%, and 1%. The total surfactant fraction was set at 12 wt. %, with a 10:2 proportion from the anionic (SLES) to the cationic surfactant (CPAB) and the polymer fraction at 0.5 wt. %. The surfactants and the polymer were added first to the water while it was stirred. After everything was properly dissolved, the salt was added to the samples, which were allowed to mix for additional 15 min. After pH adjustment and resting time, the samples were poured into 15 mL plastic vials, using two vials per sample.

2.3. Methods

2.3.1. Deposition

Nanoplasmonic sensing (NPS) is an optical technology that utilizes a sensor made of gold nanostructures on a glass support that is covered by a dielectric coating. The sensor is placed within a cell through which the samples and the light pass. NPS obtains information about the changes in the effective refractive index. The signal obtained by the instrument is the wavelength at which the sensors’ extinction exhibits a maximum, the $\lambda_{NPS}$. The change of this maximum signal over time contains information of the adsorbed mass, thickness,
and density. A general overview of the technology is presented in Scheme 2. For the analysis, water was utilized as an ambient solution, and the samples were not diluted before testing. For the test, the ambient solution was passed through the cell for 5 min and then through the sample for 15 min. This cycle was repeated three times, for a total duration of 60 min. The deposition was measured twice in each one of the samples to ensure reproducibility.

![Scheme 2](image1.png)

**Scheme 2.** (a) Insplorion® XNano instrument. (b) NPS technology data analysis [28]. NPS, Nano Plasmonic Sensing.

2.3.2. Wet Combing Force

The reduction in wet combing force was estimated by taking two measurements of the force needed to comb through a wet hair tress, using the Dia-stron MTT175 flexible miniature tensile tester (DIA-STRON, Clarksburg, NJ, USA), displayed in Scheme 3. The hair tress used for the measurement was 15 cm long, weighed approximately 2 g, and was sealed with a 1 in flex swatch. The first measurement was taken from a wet hair tress that was previously washed for 1 min with 1 mL of a 25 wt. % SLES solution and combed three times to eliminate any tangle. The second measurement was taken after 1 mL of sample was applied to the wet hair tress, was washed for 1 min, and then rinsed off and combed three times to eliminate any tangle. The combing force that was required pre- and post-treatment was compared to determine the percent reduction in wet combing force.

![Scheme 3](image2.png)

**Scheme 3.** Dia-stron® combing test instrument.
3. Results and Discussion

Since the objective of this study was to analyze the deposition process and to find out if there was any correlation with the wet combing force, this was the data that we explored. The study was done with SLES and a more sustainable surfactant as well.

3.1. Deposition

Nanoplasmonic sensing (NPS) technology is a method that tracks changes in the optical properties of materials. The instrument registers the wavelength at which the sensors’ extinction spectrum exhibits a maximum [28]. In order to convert the NPS response to obtain the optical mass adsorbed by the sensor, it is necessary to have some knowledge about the properties of the sensed material. In this case, with the available resources that we had for this study, it was not possible to measure these properties, and as the samples were mixtures of different surfactants and other compounds, it was not possible to find these properties tabulated, either. In a technology note provided by Insplorion® [29], the detailed procedure of converting the NPS response to a corresponding change in mass showed that the change in the wavelength measured by the instrument was quantitatively proportional to the change in optical mass. Therefore, the NPS response for all the samples can be compared to infer the factor that enhanced the deposition.

3.1.1. Effect of the Cationic Polymer

Figures 1 and 2 show the results of the NPS signal that corresponded to the change in the wavelength of each of the samples formulated with SLES and APG, respectively, when varying the cationic polymer content between 0 and 1.

Figure 1. NPS signal as a function of time for samples formulated with SLES/CAPB 12 wt. % and different levels of the cationic polymer at room temperature and pH ~7. NPS, Nano Plasmonic Sensing.

Figure 2. NPS signal as a function of time for samples formulated with APG/CAPB 12 wt. % and different levels of the cationic polymer at room temperature and pH ~7.

Figures 1 and 2 show the signal, which was measured for 60 min, of five samples containing different levels of cationic polymer and formulated with two different surfac-
tant, SLES and APG. As it was described previously, each of the tests comprised three consecutive cycles in which the ambient solution (water) was passed through the optical cell for 5 min and then the sample was passed for 15 min. It was easily observed that all of the samples, no matter the nature of the surfactant or the level of cationic polymer, exhibited the same behavior. After the first 5 min in which the ambient solution was read, there was a significant increment in the signal that corresponded to the injection of the sample into the optical cell, followed by a stabilization period while the sample was read. After the 15 min reading of the sample, the ambient solution was passed again, which corresponded to the drop in the signal at 20 min. This pattern was repeated twice throughout the complete test.

As mentioned before and explained with further detail in [26], the maximum change in the NPS signal between the starting and final points of the measurement has proportional relation with the adsorbed mass on the surface of the sensor. Therefore, although the information of the parameters required to calculate the amount of mass adsorbed is not available, it is possible to use the $\Delta \lambda$ maximum values to compare the deposition between all the samples and have an insight of the effect of the cationic polymer over this phenomenon.

Figures 3 and 4 show the comparison of the $\Delta \lambda$ maximum for the set of samples in which the fraction of cationic polymer was varied for both surfactants evaluated. As the figures show, the change in the signal measured had a clear tendency to increment as the fraction of cationic polymer increased within the formulation, which means that the amount of mass adsorbed by the surface was greater with the increment of cationic polymer. Thus, the data illustrate that the addition of the cationic polymer to the conditioning shampoo formulation enhanced the surface deposition. It can be seen that the level of deposition achieved with APG was a little higher than that of SLES for the same amount of polymer within the formulation. This was not expected, due to the non-ionic nature of the APG surfactant. However, the interactions between the surfactant and the surface seemed to govern the deposition phenomenon in this case.

![Figure 3](image1.png)

**Figure 3.** $\Delta \lambda$ maximum for samples formulated with SLES/CAPB 12 wt. % and different levels of the cationic polymer at room temperature and pH ~7.

![Figure 4](image2.png)

**Figure 4.** $\Delta \lambda$ maximum for samples formulated with APG/CAPB 12 wt. % and different levels of the cationic polymer at room temperature and pH ~7.
3.1.2. Effect of Salt Addition

Figures 5 and 6 show the measured NPS signal for the samples containing different levels of salt and formulated with SLES and APG, respectively. The results show a similar pattern as the results showing the effect of the amount of cationic polymer. There was an increment of the signal upon every injection of the sample, which implied a change in the mass on the surface of the sensor.

Figure 5. NPS signal as a function of time for samples formulated with SLES/CAPB 12 wt. % and different levels of salt at room temperature and pH ~7.

Figure 6. NPS signal as a function of time for samples formulated with APG/CAPB 12 wt. %, cationic polymer 0.5 wt. %, and different levels of salt at room temperature and pH ~7.

In addition, the $\Delta \lambda$ maximum for the same set of samples is shown in Figures 7 and 8, which show that there was a decrease in the signal as the amount of salt increased. Thus, it can be inferred that the adhesion to the surface was being suppressed by the presence of salt within the formulation.

Figure 7. $\Delta \lambda$ maximum for samples formulated with SLES/CAPB 12 wt. %, cationic polymer 0.5 wt. %, and different levels of salt at room temperature and pH ~7.
3.2. Wet Combing Force

The reduction in wet combing force can illustrate how effective each formulation is at lubricating and therefore how well it can provide better sensory attributes to the hair. The combing force was evaluated for the initial, middle, and last points of each set of samples evaluated for each variable in order to elucidate the effects of each of the variables studied and whether there was any correlation with the deposition results.

3.2.1. Effect of Cationic Polymer

The calculated reduction percentages for the samples formulated with both surfactants evaluated and containing 0%, 0.5%, and 1% of cationic polymer are shown in Figure 9. The addition of the cationic polymer to the formulation clearly generated a greater decrease in the grooming forces of the hair, which is one of the main targets of conditioning formulations.

3.2.2. Effect of Salt Addition

Figure 10 shows the reduction percentage for the samples containing different levels of cationic polymer formulated with both SLES/CAPB and APG/CAPB at 12 wt. % at room temperature and pH ~7.

As it was established, the addition of cationic polymers to conditioning shampoo formulations contributes to the surface deposition of substances that aim to provide lubrication, easy detangling, and a better-feeling sensation to the hair, among some other desired characteristics. The results obtained in this study using nanoplasmonic sensing technology are in accordance with multiple studies previously published [17,30,31], as they confirm the effect of the cationic polymer on the surface deposition of conditioning
shampoo formulations containing anionic surfactants. Therefore, this study demonstrates the effectiveness of nanoplasmonic sensing technology for measuring the surface deposition by aiming to mimic surface deposition on the hair. Gold, silica, and mica are the frequently used surfaces for modeling and studying the adsorption processes of cosmetic formulations [17,32]. The Insplorion® sensors utilized in this study comprise a gold disk covered with a SiO₂ coating that makes them suitable for studying the deposition process of this type of cosmetic formulations. The sensors did not have a negative charge, like the hair’s surface, and within the scope of this study, it was not contemplated to modify them to obtain a negatively charged surface. Our main goal was to ascertain the effectiveness of the NPS technique in order to study the deposition from polyelectrolyte and surfactant mixtures. Similar technologies, by which the amount of mass deposited on the surface was calculated, were used to evaluate the adsorption of surfactants onto specific surfaces, including the wet and dry mass adsorbed [33]. In the case of the nanoplasmonic sensing method, the technique measures the dry mass on the surface and does not provide information about the solvent coupled mass. In addition, the instrument is very surface-sensitive, losing sensitivity around 30–50 nm from the surface, which allows for a more sensitive analysis of the initial steps of the deposition process but might not be the best fit for an analysis of thicker layers. Consequently, this technique enables the study of the deposition process, although the measurement of deposited mass using the nanoplasmonic sensing technology provides less than that of the total mass potentially adsorbed on the surface.

The sustainable surfactant exhibited the same behavior as that of the SLES (Figures 6 and 8); but the maximum ∆λ was slightly higher, and so was the amount of mass deposited on the sensor. Since the APG surfactant utilized in this study has a non-ionic nature, it would be expected to lead to a lower deposition caused by poor interaction with the charged polymer. The higher deposition achieved with this system may be explained by the electrostatic interaction between the polymer and the surface, which was mainly governed by the difference in the charges [34]. Despite the weak interaction between the surfactant and polymer and the consequent low formation of conditioning complexes, the adsorption

![Figure 10. Wet combing reduction percentage for samples with different levels of salt, formulated with both SLES/CAPB and APG/CAPB at 12 wt. % and cationic polymer 0.5 wt. % at room temperature and pH ~7.](image-url)
in this case was governed by the strong interaction between the polymer and surface. Scheme 4 below shows a schematical representation of how the polymer interacted with the anionic surfactant and how it was deposited on the surface. The scheme also shows how the deposition of the polymer occurred from the mixture with the non-ionic surfactant.

Scheme 4. Adsorption of polyelectrolyte–surfactant mixtures onto a solid surface.

The ionic strength is another important parameter that influences the surface deposition from polyelectrolyte–surfactant mixtures [35]. NaCl is considered a strong electrolyte as it is a salt that dissociates completely in water, releasing Na\(^+\) and Cl\(^-\) ions, and therefore conferring a strong ionic nature to the solution. The increment of this electrolyte led to the suppression of the deposition [36], as illustrated in Figures 7 and 8. The addition of salt substantially reduced the binding affinity, causing less interaction of the polymer with the surfactant [37]. Moreover, the presence of cations and anions inhibited the adsorption [30] of the polymer and the polymer–surfactant complexes as they interacted with the surface and competed for the available sites. Thus, the chains and molecules were loosely attached due to a smaller number of contact points and weak interactions [17].

As it has been demonstrated, the nanoplasmonic sensing technology is effective for studying the surface deposition phenomenon from formulations containing surfactant–polyelectrolyte mixtures. However, within the scope of this investigation, this method was still insufficient for identifying and differentiating the nature of the mass being deposited. Thus, the wet combing force measurement was used to evaluate the efficiency of the formulations on the hair conditioning target [3]. Moreover, as stated previously, the deposition evaluation on the NPS surface generated positive results, even though the sensors were not negatively charged, like the hair’s surface. Therefore, the evaluation of the combing test with real hair was expected to show positive results. In addition, it allowed us to investigate whether there was any correlation between the results obtained with the NPS and the combing test. Figures 9 and 10 illustrate the reduction percentage of the combing force upon the application of formulations with different levels of polymer and salt, respectively. The effect of the polymer leading to lower frictional forces during the combing and detangling of the hair confirmed the behavior reported in several studies of hair conditioning formulations [17,30]. The complexes and cationic polymer being deposited formed a thin layer over the surface that reduced friction and provided lubrication, thus easing detangling and improving combability [4]. The results exhibit a reduction in the wet combing force after the application of the formulations containing different levels of both polymer and salt; while the polymer increased the reduction, the salt lowered it. This coincided with the results found for deposition, considering that, as the increase of the polymer led to a higher deposition, it was expected to obtain a better conditioning effect on the hair as the amount of polymer was increased in the formulation. Conversely, the increase of the salt suppressed the deposition as it interfered with the electrostatic interactions of the polymer with the hair surface and the surfactant, leading to a lower amount of mass adsorbed. Thus, the conditioning effect was expected to be minor with the increment of the salt within the formulation. The correlation found here is illustrated
in Figures 11 and 12, which show that both variables studied, there was a proportional relationship between the deposition and the reduction of the combing force.

Figure 11. Correlation between the deposition and wet combing reduction percentage for samples with different levels of polymer, formulated with both SLES/CAPB and APG/CAPB at 12 wt. % at room temperature and pH ~7.

Figure 12. Correlation between the deposition and wet combing reduction percentage for samples with different levels of salt, formulated with both SLES/CAPB and APG/CAPB at 12 wt. % and cationic polymer 0.5 wt. % at room temperature and pH ~7.

4. Conclusions

The effectiveness of the nanoplasmonic sensing technology as a method for testing and evaluating the deposition process from formulations containing mixtures of surfactants and polyelectrolytes was demonstrated by the evaluation of eight different samples with different amounts of cationic polymer and salt. The instrument allowed us to obtain a qualitative overview of the deposition over time and to compare the results between samples, which constituted a rapid technique for addressing formulations’ direction in relation to deposition goals. The method could potentially turn into a quantitative evaluation of the adsorption of cosmetic formulations if the available resources allowed the determination of the parameters required for the model; they are not easily determined as the samples utilized here are complex mixtures of various substances. However, despite this limitation...
found in this study, the method turned out to be an effective fast-evaluation technique, considering that a quick screen for the deposition of cosmetics is critical.

We demonstrated that the deposition of conditioning agents is enhanced by the addition of a cationic polymer that undergoes an electrostatic interaction with the hair’s surface and surfactants within the formulation. Conversely, we found that the addition of strong electrolytes such as NaCl, which is commonly used as a viscosity builder in shampoo formulations, suppresses the deposition of conditioning agents as they weaken the interactions of the cationic polymer with the hair and the surfactants. In addition, the free cations and anions are forced to compete for the available contact sites in the surface, making the adsorption considerably lower.

Finally, we found a correlation between the deposition from conditioning cleansing formulations and the reduction of the wet combing force, showing that more mass deposits led to a higher reduction percentage of friction force when combing wet hair, and thus easing the detangling and lubrication of hair. The correlation found met the expected behavior, and the technology can be used as a formulation screen for the deposition process within the cosmetic field.

Recommendations for future work could include evaluating the effect of some other variables that may potentially affect the interactions of the cationic polymer within the conditioning formulation and the surface deposition, such as pH, the charge density of the polymer, and the ratio between the surfactant and the polymer, in order to further corroborate the efficacy of the method. In addition, future studies could include a sustainable polymer as well as sustainable surfactants, with the purpose of contributing to sustainability in cosmetic science using the application of this method.

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References
1. Robbins, C.R. Chemical and Physical Behavior of Human Hair, 4th ed.; Springer: New York, NY, USA, 2013.
2. Dawber, R. Hair: Its structure and response to cosmetic preparations. Clin. Dermatol. 1996, 14, 105–112. [CrossRef]
3. Fernández-Peña, L.; Guzmán, E. Physicochemical Aspects of the Performance of Hair-Conditioning Formulations. Cosmetics 2020, 7, 26. [CrossRef]
4. Dias, M.F.R.G. Hair Cosmetics: An Overview. Int. J. Trichology 2015, 7, 2–15. [CrossRef] [PubMed]
5. Draelos, Z.D. Hair Care. An Illustrated Dermatologic Handbook; Taylor & Francis: London, UK, 2004.
6. Lee, W.; Idson, B. Update on hair conditioner ingredients. Cosmet. Toilet. 1983, 98, 42–46.
7. O’Lenick, T. Anionic/cationic complexes in hair care. J. Cosmet. Sci. 2011, 62, 209–228. [PubMed]
8. Harusawa, F.; Nakama, Y.; Muneo, T. Anionic-cationic ion-pairs: As conditioning agents in shampoos. Cosmet. Toilet. 1991, 106, 35–39.
9. Hunting, A.L. Can there be cleaning and conditioning in the same product? Cosmet. Toilet. 1988, 103, 73–82.
10. Andreas, P.; Peter, H.; Sabine, V.; Ralf, S.; Wolfgang, S. The interaction of cationic polymers with human hair. *Macromol. Symp.* 1997, 126, 241–252.

11. Bain, C.D.; Claesson, P.M.; Langevin, D.; Meszaros, R.; Nylander, T.; Stubenrauch, C.; Titzmuss, S.; Klitzin, R. Complexes of surfactants with oppositely charged polymers at surfaces and in bulk. *Adv. Colloid Interface Sci.* 2010, 155, 32–49. [CrossRef] [PubMed]

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

13. Somasundaran, P.; Chakraborty, S.; Qiang, Q.; Deo, P.; Wang, J.; Zhang, R.; Chakraborty, S. Surfactants, polymers and their nanoparticles for personal care applications. *J. Cosmet. Sci.* 2004, 55, 1–17.

14. Carole, L.; Mullay, J.; Kyer, C.; McCalister, P.; Cliftord, T. Use of statistical modeling to predict the effect silicone deposition, and conditioning sensory performance of cationic cassia polymers. *J. Cosmet. Sci.* 2011, 62, 161–177.

15. Stanimirova, R.D.; Kralchevsky, P.A.; Danov, K.D.; Xu, H.; Ung, Y.W.; Petkov, J.T. Oil drop deposition on solid surfaces in mixed polymer-surfactant solutions in relation to hair- and skin-care applications. *Colloids Surf. A Physicochem. Eng. Asp.* 2019, 577, 53–61. [CrossRef]

16. Hössel, P.; Diering, 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. [CrossRef]

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

18. Banerjee, S.; Cazeneuve, C.; Baghdadli, N.; Ringeissen, S.; Léonforte, F.; Leermakers, F.A.M.; Luengo, G.S. Modeling of Polyelectrolyte Adsorption from Micellar Solutions onto Biomimetic Substrates. *J. Phys. Chem.* 2017, 121, 8368–8651. [CrossRef]

19. Guzmán, E.; Llamas, S.; Fernández- Peña, L.; Léonforte, F.; Baghdadli, N.; Cazeneuve, C.; Ortega, F.; Rubbio, A.G.; Luengo, G.S. Effect of a natural amphoteric surfactant in the bulk and adsorption behavior of polyelectrolyte-surfactant mixtures. *Colloids Surf. A* 2019, 585, 124178. [CrossRef]

20. Llamas, S.; Guzmán, E.; Baghdadli, N.; Ortega, F.; Cazeneuve, C.; Rubio, R.; Luengo, G. Adsorption of poly(diallyldimethylammonium chloride)—Sodium methyl-cocoyl-taurate complexes on solid surfaces. *Colloids Surf. A Physicochem. Eng. Asp.* 2020, 505, 150–157. [CrossRef]

21. Svensson, A.V.; Huang, L.; Johnson, E.S.; Nylander, T.; Piculell, L. Surface Deposition and Phase Behavior of Oppositely Charged Polyelectrolyte-Surfactant Ion Complexes. 1. Cationic Guar versus Cationic Hydroxyethylcellulose in Mixtures with Anionic Surfactants. *Appl. Mater. Interfaces* 2009, 1, 2431–2442. [CrossRef]

22. Guzmán, E.; Fernández- Peña, L.; Sluengo, 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, 3, 624. [CrossRef]

23. Insplorium. NanoPlasmonic Sensing. s.f. [Online]. Available online: https://www.insplorion.com/app/uploads/NPS-Technology-1.pdf (accessed on 3 July 2022).

24. Savic, S.; Luic, M.; Jaksic, I.; Reichl, S.; Tamburic, S.; Müller-Goymann, C. An alkyl polyglucoside-mixed emulsifier as stabilizer and clean tech. 2022; (Application notes obtained from Insplorion company).

25. Rios, F.; Fernández-Artega, A.; Lechuga, M.; Jurado, E.; Fernández-Serrano, M. Kinetic study of the anaerobic biodegradation of alkyl polyglucosides and the influence of their structural parameters. *Environ. Sci. Pollut. Res.* 2016, 23, 8286–8293. [CrossRef]

26. Wikipedia. Available online: https://en.wikipedia.org/wiki/Lauryl_glucoside#media/File:Lauryl_glucoside.png (accessed on 25 September 2022).

27. Insplorium. Sensor technology for cleaner air, accelerated transition to fossil-free energy and advancing research in life science and clean tech. 2022; (Application notes obtained from Insplorion company).

28. Insplorium. Quantitative interpretation of the NPS signal. 2017; (Application notes obtained from Insplorion company).

29. McMullen, R.L.; Laura, D.; Zhang, G.; Kroon, B. Investigation of the interactions of cationic guar with human hair by electrokinetic analysis. *Int. J. Cosmet. Sci.* 2021, 43, 375–390. [CrossRef]

30. Shokri, J.; Shamseddini Lori, M.; Monajjemzadeh, F. Examining polyquaternium polymers deposition on human excised hair fibers. *J. Cosmet. Dermatol.* 2017, 17, 1225–1232. [CrossRef]

31. Luengo, G.S.; Guzman, E.; Fernández- Peña, L.; Leonforte, F.; Ortega, F.; Rubbio, R.G. Interaction of polyelectrolytes and surfactants on hair surfaces. Despositos and their characterization. In *Surface Science and Adhesion in Cosmetics*; Wiley: Hoboken, NJ, USA, 2021.

32. Sigal, G.B.; Mrksich, M.; Whitesides, G.M. Using Surface Plasmon Resonance Spectroscopy To Measure the Association of Detergents with Self-Assembled Monolayers of Hexadecanethiolate on Gold. *Langmuir* 1999, 13, 2749–2755. [CrossRef]

33. Petkova, R.; Tcholakova, S.; Denkov, N.D. Foaming and Foam Stability for Mixed Polymer-Surfactant Solutions: Effects of Surfactant Type and Polymer Charge. *Langmuir* 2012, 28, 4996–5009. [CrossRef]

34. Lochhead, R.Y.; Huisinga, L.R. A Brief Review of Polymer/Surfactant Interaction. *Cosmet. Toilet.* 2004, 119, 37–45.
36. Faucher, J.A.; Goddard, E.D.; Hannan, R.B. Sorption and Desorption of a Cationic Polymer by Human Hair: Effects of salt solutions. *Text. Res. J.*, **2015**, *47*, 616–620. [CrossRef]

37. Goddard, E.D. Polymer-surfactant interaction. Part II: Polymer and surfactant of opposite charge. In *Interactions of Surfactants with Polymers and Proteins*; Taylor & Francis Group: Abingdon, UK, 1993.