




Article

Adsorption of Mixtures of a Pegylated Lipid with Anionic and Zwitterionic Surfactants at Solid/Liquid

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Abstract: This work explores the association of a pegylated lipid (DSPE-PEG) with different anionic and zwitterionic surfactants (pseudo-binary and pseudo-ternary polymer+ surfactant mixtures), and the adsorption of the polymer + surfactant aggregates onto negatively charged surfaces, with a surface charge density similar to that existing on the damaged hair epicuticle. Dynamic light scattering and zeta potential measurements shows that, in solution, the polymer + surfactant association results from an intricate balance between electrostatic and hydrophobic interactions, which leads to the formation of at least two different types of micellar-like polymer + surfactant aggregates. The structure and physicochemical properties of such aggregates were found strongly dependent on the specific nature and concentration of the surfactant. The adsorption of the polymer + surfactant aggregates onto negatively charged surface was studied using a set of surface-sensitive techniques (quartz crystal microbalance with dissipation monitoring, ellipsometry and Atomic Force Microscopy), which allows obtaining information about the adsorbed amount, the water content of the layers and the topography of the obtained films. Ion-dipole interactions between the negative charges of the surface and the oxyethylene groups of the polymer + surfactant aggregates appear as the main driving force of the deposition process. This is strongly dependent on the surfactant nature and its concentration, with the impact of the latter on the adsorption being especially critical when anionic surfactant are incorporated within the aggregates. This study opens important perspectives for modulating the deposition of a poorly interacting polymer onto negatively charged surfaces, which can impact in the fabrication on different aspects with technological and industrial interest.

Keywords: adsorption; polymer; surfactants; pegylated lipid; solid surfaces; complexes

1. Introduction

Polyelectrolyte mixtures with surfactants bearing opposite charges self-associate to form complexes. Their structure, size and surface charge density usually depend on the protocol followed for mixing the two components, therefore, the mixtures usually are kinetically arrested non-equilibrium systems [1–9]. Despite of the above problem, this type of mixtures has a big impact on many industrial applications: cosmetics, pharmacy, food science, coagulation agents, etc. [10]. This is because these multicomponent complex fluids allow controlling the interfacial properties, phase behavior and gelling properties of the formulations [11,12]. In most of the mixtures reported in the literature polycations have been used, whose replacement is a requirement for future cosmetic formulations [13,14]. Moreover, the use of biocompatible and biodegradable polymers is also a goal for the future.

Most of the polycations used so far have no surfactant character, although they usually present a synergic effect with the surfactants leading to a strong decrease of the surface tension, γ , with

respect to the pure surfactant [1,3,5]. This is important because it allows one to reduce the amount of surfactant needed for reaching the same value of γ , which is important for detergency and foaming performances [15].

Even though a theoretical model has been presented that predicts reasonably well the dynamic and equilibrium surface tensions of protein + surfactant mixtures adsorbed at water/vapor interfaces, its ability to predict the interfacial dilational elasticity of the adsorbed layers is only qualitative [16,17]. Moreover, rigorously it cannot be applied to mixtures of polyelectrolyte + surfactant mixtures, in which both components bear opposite charges, because they contain a higher number of components: free polymer, polyelectrolyte + surfactant complexes, and in some cases free surfactant at the interface. Furthermore, polymer + surfactant aggregates can be out of equilibrium systems and therefore their interfacial behavior cannot be described in terms of conventional thermodynamic model defined by a set of parameters associated with the interactions occurring within the system and the area occupied by each specie at the interface [18–28]. It must be stressed that the situation is even worse in the case of the adsorption of this type of mixtures on the solid/liquid interface because only extensive experimental, theoretical and computational studies exist for polyelectrolyte solutions, and the studies dealing with the theoretical description of polymer + surfactant mixtures adsorbed onto solid surfaces are scarce yet [29–35]. This is because a rigorous description of these systems requires consider one the polydispersity of size and surface charge, the non-equilibrium character of the mixtures and the existence of several components [36–39].

In previous works, we have studied polyelectrolyte + surfactant mixtures, pointing towards their performance in capillary cosmetics applications [36,37,39]. One option that has been frequently study is the use of polyethylene glycol, PEG, mixtures with surfactants because PEG is neutral and biocompatible, although it is not obtained from natural sources nor it is biodegradable. An example is the mixture PEG + sodium dodecyl sulfate, SDS [40–44]. The interactions of the PEG chains, polyethers, with anionic and neutral surfactants are relatively well understood, whereas they are still controversial aspect when the study of the interaction with cationic surfactant is concerned [43]. In the present work, we simplify the system in order to decrease the importance of the problems arising from the formation of very large complexes. We have chosen a low molecular weight polymer (5 kDa molecular weight) and relatively monodisperse polymer on a poly(ethyleneglycol) chain linked to a phospholipid: sodium salt of *N*-carbonyl methoxy(polyethyleneglycol)-1,2-disteroyl-sn-glycero-3-phosphoethanolamine, hereinafter called DSPE-PEG. This polymer has formerly been used for building liposomes for drug delivery, as emulsifier and as foam stabilizer. Moreover, it is biocompatible and biodegradable, which makes it useful in the pharmaceutical and cosmetic areas. [45–48]. Finally, it is expected that it will not form very large complexes with most of the surfactants previously studied because of its anionic character. Three different surfactants have been studied: sodium laureth sulfate (SLES), sodium methylisetonate (SLMI), and coco betaine (CB). SLES and SLMI are anionic surfactants while CB is zwitterionic, and all of them are less irritant for skin than sodium dodecylsulfate, SDS, which is important in cosmetics [49]. It must be noted that SLMI is obtained from coconut oil.

We have evaluated the adsorption of the binary polymer-surfactant mixtures and of a ternary mixture formed by DSPE-PEG + (SLES + CB) at the solid/liquid, S/L, interface. Also information of the bulk properties, and the polymer + surfactant association process, have been obtained using dynamic light scattering, DLS and zeta potential, ζ , measurements.

2. Materials and Methods

DSPE-PEG was purchased from the NOF Corporation, Ltd. (Tokyo, Japan) and was used as received without further purification. SLES with 2 oxyethylene groups, was purchased from Kao Chemical Europe S.L. (Barcelona, Spain) and was purified by lyophilization followed for recrystallization of the obtained powder using acetone for HPLC (Acros Organics, Geel, Belgium). CB and SLMI were supplied by Clariant International Ltd. and were also purified by lyophilization, and then recrystallized in anhydrous ethanol (Waltham, MA, USA) and anhydrous methanol (Sigma-Aldrich,

Saint Louis, MO, USA), respectively. In all the cases, we have checked that for the pure compounds the surface tension vs. concentration curves do not present any minimum near the critical micelle concentration, c.m.c. Figure 1 shows the molecular structures of the DSPE-PEG and the three surfactants.

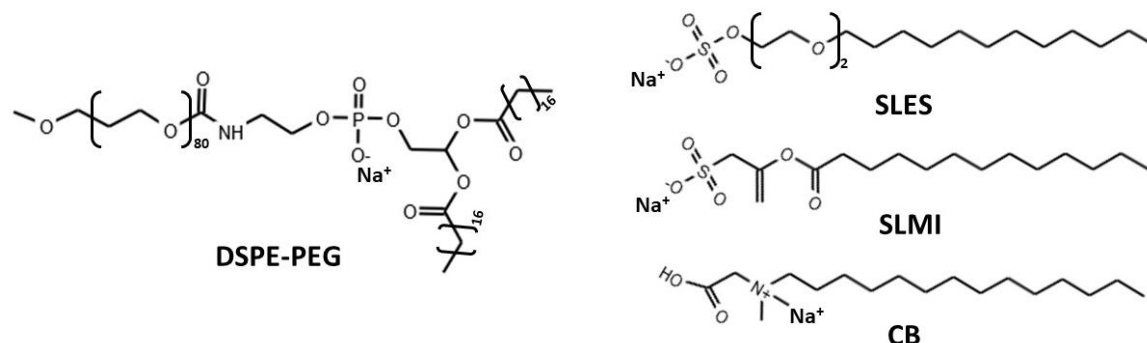


Figure 1. Molecular structures of the DSPE-PEG and the three surfactants.

Ultrapure deionized water used for cleaning and solution preparation was obtained by a multicartridge purification system AquaMAX™-Ultra 370 Series. (Young Lin Instrument Co., Ltd., Gyeonggi-do, Korea), presenting a resistivity higher than 18 MΩ·cm, and a total organic content lower than 6 ppm.

The polymer + surfactant solutions studied in this work containing a fixed DSPE-PEG concentration of 5 g/L, and different surfactant concentrations in the 2×10^{-6} –4 mM range. The pseudo-ternary mixtures containing DSPE-PEG, SLES and CB were prepared maintaining the concentration ratio between the anionic SLES and the zwitterionic CB in 3:2. All polymer + surfactant solutions were prepared by weighting following the procedure described in our previous publication [50]. Polymer + surfactant solutions contain a KCl (purity > 99%, Sigma-Aldrich, MO, USA) concentration of 40 mM, and a pH ~ 5.6 fixed with glacial acetic acid (purity > 99%, Sigma-Aldrich, MO, USA).

The association process between DSPE-PEG and the surfactant was studied by following the changes in ζ potential obtained by laser Doppler electrophoresis, and average apparent diffusion coefficient (D_{app}) of the polymer-surfactant aggregates, related to the average apparent radius of the aggregates by the Stokes–Einstein relationship, by Dynamic Light Scattering (DLS) using a Nanosizer ZS (Malvern instruments, Malvern, UK). Further experimental details can be found elsewhere [36,38,39,51–53].

Surface tensions measurements were performed for determining the critical micelle concentration (cmc) of the surfactant in solutions. For this purpose, the surface tension of the water/vapor interface was measured until a steady state was reached, i.e., changes of surface tension smaller than 0.1 mN m^{-1} during 30 min using a surface force tensiometer from Krüss K10 (Hamburg, Germany) fitted with a Pt Wilhelmy plate. Further experimental details can be found in our previous publication [50].

The adsorption of the polymer + surfactant solutions onto negatively charged surfaces was followed using two complementary techniques: quartz crystal microbalance with dissipation monitoring (QCM-D, QCM Z500 from KSV, Espoo, Finland) and ellipsometry (EP³ from Nanofilm, Göttingen, Germany). A detailed description of the physicochemical details of both techniques can be found in our previous publications [36,38,39,54], and here it has been only included the most relevant experimental aspects.

A QCM-D fitted with gold-coated AT-cut quartz crystals was used. These crystals were cleaned with piranha solution (70% sulfuric acid/30% hydrogen peroxide) over 30 min, and then thoroughly rinsed with pure water. Negatively charged thiol-decorated gold substrates, obtained by the deposition and covalent reaction of a self-assembled monolayer of the sodium salt of 3-mercaptopropylsulfonic acid (hereafter thiol) onto the electrode surface, were used as surfaces for studying the adsorption polymer + surfactant mixtures with surfactants in QCM-D experiments. These surfaces are known to be a good representation of the negatively charged cysteine-rich surface of weathered, damaged human

hair [55,56]. QCM-D measures the impedance spectra of a quartz crystal for the fundamental frequency ($f = 5$ MHz) and for the odd overtones up to the 11th. The impedance spectra were analyzed using a single layer model following the procedure described by Voinova et al. [57,58], which allows one to relate the changes in the resonant frequency Δf and dissipation factor ΔD of the different overtones (note that fundamental frequency is not considered for data analysis due to the noisy character of its signal) to the effective acoustic thickness, h_{ac} , and the shear viscoelastic modulus of the adsorbed layers $G^* = G' + iG''$, with G' and G'' being related to the storage (elastic modulus) and dissipation (viscous modulus) of energy during the oscillation, respectively.

An imaging null-ellipsometer was also used to determine the amount of material adsorbed onto the solid surfaces as the optical thickness, h_{op} . Ellipsometry experiments were carried out using a solid–liquid cell at a fixed angle of 60° using silica plates as substrate (Siltronix, Archamps, France). These substrates were treated with piranha solution for 30 min to create a surface with similar charge and water contact angle to those of the thiol-decorated gold surfaces, which allows the performing of a quantitative comparison between the results obtained by QCM-D and ellipsometry. The validity of this approach was proven in our previous work, where the adsorption of charged polyelectrolytes onto thiol-decorated gold electrodes, and electrodes coated with a silica layer similar to that of the plates used in ellipsometry, was found to be similar [59]. The thickness and the refractive index of the layers are obtained as the pair of values that minimize the differences between the experimental values of the ellipsometric angles, Δ and Ψ , and those obtained solving the Fresnel's equation using a suitable layer model [60–62].

It is worth noting that both h_{ac} and h_{op} should be considered as effective thicknesses due to the heterogeneity of most of the polyelectrolyte layers, thus they provide different information about the adsorbed amount within the layer due to their different sensitivities to the water associated with the adsorbed layer [38]. QCM-D gives information regarding the mass of the adsorbed layer which includes the amount polymer, surfactant and water included within the adsorbed layer, whereas ellipsometry, which is based in the differences between the refractive indexes of the layer and the medium, only gives information of the amount of polymer and surfactant included within the adsorbed layer. Therefore, $h_{op} \leq h_{ac}$, and the comparison of experiments performed using both techniques gives an estimate of the water content of the layers x_w as [63,64]

$$x_w = \frac{h_{ac} - h_{op}}{h_{ac}} \quad (1)$$

Topographical images in air of dry adsorbed layers onto modified silica plates were obtained by Atomic Force Microscopy (AFM) in tapping mode using a Nanoscope III (Bruker, Billerica, MA, USA) fitted with a silicon tip, model RTESP (Veeco Instrument Inc, Plainview, NY, USA). It is worth mentioning that even though it would be probable the emergence of some morphological changes in the layers as result of the drying, it is expected that the general conclusions obtained from the analysis of wet and dry samples should not be significantly different as was discussed in our previous publications [37,39].

3. Results and Discussion

3.1. Polymer-Surfactant Association in Aqueous Solutions

The DLS results allow obtaining information about the possible association between DSPE-PEG and the surfactants. DSPE-PEG is an amphiphilic polymer, thus it can form micelles at concentrations high enough as the ones used in this work. Indeed, Arleth et al. [45] reported the existence of micelles of hydrodynamic radius $R_h \sim 12$ nm. However, Figure 2a shows that under our experimental conditions the formation of micelles is almost hindered. Notice that for solutions of DSPE-PEG at pH = 5.6, the appearance of a second population on the hydrodynamic radius distribution with dimensions comparable to the polymer micelles was observed. However, this contribution may be considered

negligible considering that the scattered intensity increase by a factor 10^6 with the size of the scatters, and hence it is possible to disregard the formation of micelles for the pure polymers under the conditions used in this work. A main difference with respect to the work of Arleth et al. [45] is that we have worked at pH = 5.6 whereas they worked at pH = 7.4. Figure 2 shows that the here studied sample also forms micelles with $R_h = 13.4 \pm 0.7$ nm at the same pH used by Arleth et al. [45]. Also the increase of ionic strength at constant pH favors the formation of micellar aggregates, which is reasonable considering the charge screening effects. All our measurements have been done at [KCl] = 0.3 wt%, that is equivalent to an ionic strength $I \approx 40$ mM, whereas Arleth et al. [45] worked at $I = 150$ mM.

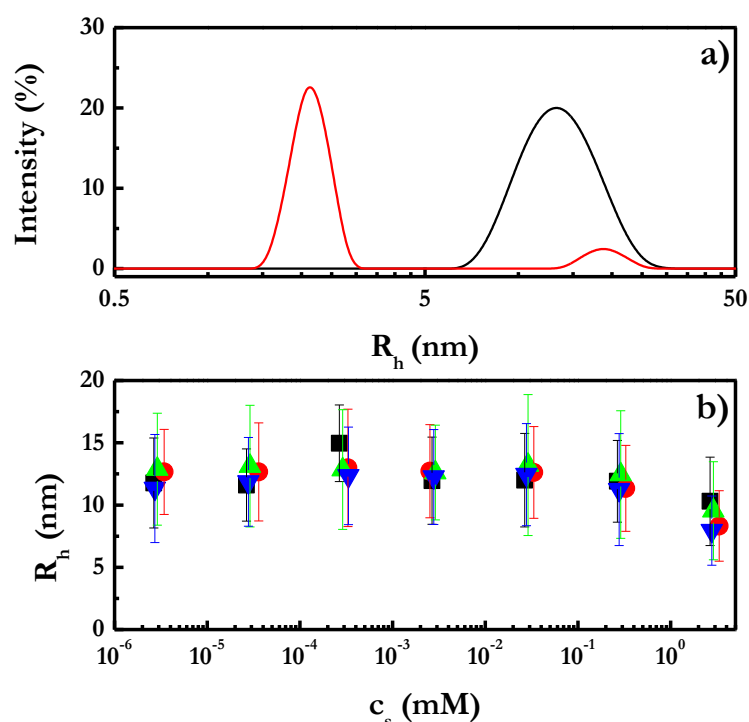


Figure 2. (a) Hydrodynamic radius distribution determined as the scattered intensity by DSPE-PEG for polymer solutions with a concentration of 0.5 wt% and KCl concentration of 0.3 wt% measured at two different pH values: (—) 7.4 and (—) 5.6. (b) Dependence of R_h on the surfactant concentration, c_s , for the different DSPE-PEG+surfactant mixtures studied in this work: (■) SLES, (●) CB, (▲) SLES+CB (molar ratio 3:2) and (▼) SLMI. All the mixtures contain a fixed DSPE-PEG concentration of 5 g/L, and their ionic strength and pH were fixed a 40 mM (KCl) and 5.6, respectively.

Figure 2b shows that the apparent hydrodynamic radius, R_h , for the polymer + surfactant mixtures is almost independent of the surfactant nature and its concentration, and very close to the values obtained by Arleth et al. [45] at pH = 7.4 for micelles of DSPE-PEG. One can speculate about two contributions for the formation of aggregates: (i) the formation of polymer + surfactant complexes, and (ii) the change of the ionic strength associated with the addition of surfactant. In any case, it is expected that the effect of the change of ionic strength associated with the surfactant will be very small, or even negligible, due to the relatively high value of inert salt concentration used. However, since the aggregates are already observed for a surfactant concentration as low as 2×10^{-6} mM one can easily discard the increase of ionic strength as the driving force for the aggregate formation (about three orders of magnitude less than that corresponding to the change of pH from 7.4 to 5.6), and the addition of surfactant induces the formation of micellar-like aggregates from the lowest surfactant concentrations. The slight decrease of the hydrodynamic radius as the surfactant concentration is approached to the highest surfactant concentrations may be the result of a transition on the conformation of the polymer + surfactant micellar-like aggregates.

Further details on the polymer + surfactant association can be obtained from the measurement of the ζ potential (in the following ζ). Figure 3 shows the values of ζ obtained for all the mixtures studied as function of the surfactant concentration, c_s . The value of ζ for DSPE-PEG appears close to zero. This seems to be reasonable considering that the main component of this pegylated lipid is a neutral chain of PEG, with the negative charge provided by the phosphate group being negligible on the average behavior of the molecules, and hence the net charge of the DSPE-PEG molecules remains close to the electroneutrality. On the other side, for all the mixtures the values of ζ are much lower than the value obtained for the pure polymer, which suggests the formation of polymer + surfactant aggregates. This may be possible considering two different interactions: (i) hydrophobic interactions between the PEG backbone and the hydrophobic tail of the surfactant molecules; and (ii) ion–dipole interactions between the negatively charged head group of the surfactant molecules and the partially positive oxygens of the PEG chains [65]. Furthermore, ζ remains almost independent of the surfactant concentration until the highest surfactant concentrations at which increases. It should be noted that it was impossible to get closer to the electroneutrality point because the mixtures undergo a sedimentation process.

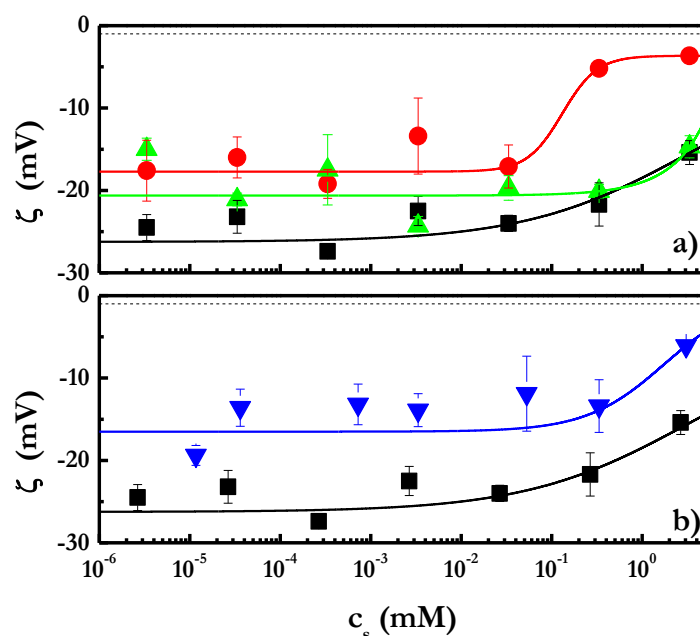


Figure 3. Dependence of the ζ potential on the surfactant concentration, c_s , for the different polymer + surfactant mixtures studied in this work: (a) ζ values for pseudo-binary and pseudo-ternary mixtures of DSPE-PEG containing SLES and/or CB. (■) SLES, (●) CB and (▲) SLES+CB (molar ratio 3:2); (b) ζ values for pseudo-binary of DSPE-PEG containing SLES or SLMI. (■) SLES and (▼) SLMI. All the mixtures contain a fixed DSPE-PEG concentration of 5 g/L, and their ionic strength and pH were fixed a 40 mM (KCl) and 5.6, respectively. The dashed line corresponds to the value of ζ for a DSPE-PEG aqueous solution with concentration 5 g/L and the same ionic strength and pH than the mixtures.

Taking into consideration the polymer + surfactant association, it is not strange that for the mixtures containing SLES the zeta potential becomes more negative than for the pure polymer because the anionic character of this surfactant, the same is true for mixtures containing SLMI as surfactant. At the lowest surfactant concentrations, the association of the surfactant molecules and polymer chains is driven through hydrophobic interactions, which results in polymer-surfactant aggregates in which surfactant molecules bound through hydrophobic interactions to the external PEG layer of DSPE-PEG micellar-like aggregates. This leads to a situation in which the hydrophilic charged head groups of the surfactant appear exposed to the aqueous phase, which may be considered similar to that what happens for the interaction of the cationic polymer poly(diallyl-dimethylammonium chloride), PDADMAC, and

a neutral alkyl polyglucoside. This agrees with the findings by Heydari et al. [66] for the interaction of PEG and SDS. At the highest surfactant concentrations, the micellization of the surfactant can be expected, which probably results in the formation of mixed DSPE-PEG + surfactant micelles with the PEG chains protruding to the solution. This leads to a decrease of the negatively charged groups exposed to the aqueous solutions, driving the system close to the isoelectric point. This is in agreement with the precipitation found for the polymer-surfactant aggregates when the surfactant concentration overcomes a value about 5 mM. This conformational transition in DSPE-PEG + surfactant aggregates may be correlated to transition from an association controlled by hydrophobic interactions at low surfactant concentration to an association controlled by ion-dipole interactions at the highest surfactant concentrations reported by Dai and Tam [67] in mixtures of PEG and SDS. Thus, the modification on the DSPE-PEG + surfactant interactions is translated in a transition from a conformation in which DSPE-PEG micellar-like aggregates decorated with surfactant molecules are formed to a second one in which surfactant micelles with inclusions of DSPE-PEG chains are formed [68]. It should be noted that the zeta potential of mixtures containing SLMI is slightly higher than that of mixtures containing SLES. This may be explained considering that the oxyethylene groups existing in the hydrophobic tail of SLES favors the association between SLES and the PEG chains contained in the DSPE-PEG.

It seems to be reasonable that for DSPE-PEG + CB mixtures the values of ζ appear higher than for mixtures containing anionic surfactant. Furthermore, mixtures belonging to the high concentration region the values of ζ are closer to the isoelectric point than for the two other pseudo-binary mixtures. This may be explained considering the zwitterionic character of CB, which results in a smaller negative net charge of the micellar-like aggregates, and consequently ζ assumes values closer to that of the pure polymer. This seems to favor the transition between the two association regimes. For the pseudo-ternary mixture, the zeta potential is close to those for DSPE-PEG + CB mixture at very low surfactant concentrations, whereas at high surfactant concentrations the values are closer to those of the DSPE-PEG + SLES system. Similar behavior was reported for the interaction of the SLES+CB mixtures with PDADMAC [37,38]. The formation of different types of micellar-like aggregates provides a justification to the invariability of the apparent hydrodynamic diameter of the polymer + surfactant aggregates [69]. It is worth mentioning that the transition from an association in which surfactant molecules (SDS) are bound to aggregates of an amphiphilic copolymers of the Pluronic family (triblock copolymers of poly(ethylene oxide) and poly(propylene oxide)) to a situation in which micellar aggregates of the surfactant interacts with the copolymer molecules was reported by Kancharla et al. [70]. They found that the threshold concentration for the transition between the two conformations was smaller than the corresponding to the critical micellar concentration (cmc) of the pure surfactant. This picture combined with the values of the cmc of the surfactants obtained by surface tension measurements (see Table 1), allows confirming the lift-off point of the dependences of the ζ on the surfactant concentration (see Figure 3) as the threshold concentration where the transition between the two types of micellar-like aggregates occurs.

Table 1. Critical micellar concentration values obtained from surface tension measurements.

Surfactant	c_s (mM)
SLES	0.14
SLMI	5.0
CB	1.00
SLES + CB	0.29

The mixture of SLES+CB presents a molar ratio 3:3.

Figure 4 shows a sketch of the two most probable configurations of the DSPE-PEG + surfactant aggregates in the different surfactant concentration regime. The existence of two types of micellar-like aggregates was suggested by Bernazzani et al. [71] for mixtures of PEG and SDS. A qualitative similar

picture was obtained from the self-consistent mean field calculations performed by Banerjee et al. [72] for mixtures of DSPE-PEG and SLES. It is worth mentioning that even though the association process of DSPE-PEG with the surfactants follows a cooperative pathway; this cooperativity presents a different origin to that found in the association of oppositely charged polyelectrolyte-surfactant systems. In the latter, the increase of the surfactant binding to the polymer chains leads to the formation of micelles associated with the polymer, commonly forming a pearl-necklace structure, for surfactant concentrations well below the cmc [73,74]. However, for DSPE-PEG mixtures the presence of the polymer results in a micellization from the initial stages of the association, leading to the formation of core-shell structures at the highest surfactant concentrations [67,71].

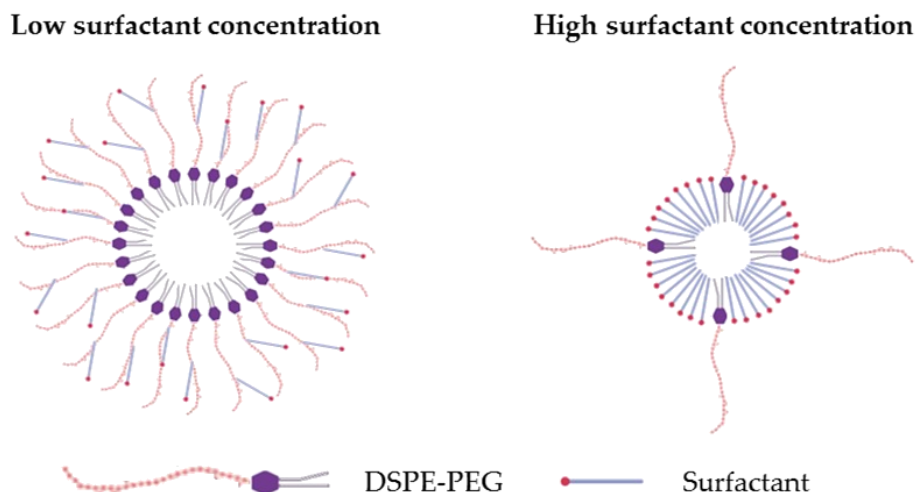


Figure 4. Sketch of the different types of aggregates obtained as function of the surfactant concentration.

3.2. Adsorption onto Negatively Charged Surfaces

The study of the adsorption process of polymer + surfactant aggregates onto negatively charged surfaces with similar surface properties (charge density and wetting properties) that the the damaged hair epicuticle were performed using two complementary techniques: QCM-D and ellipsometry, whereas the topography of the deposited layers was analyzed by AFM. QCM-D provides the total amount of material adsorbed, i.e., polymer + surfactant + hydration water and the complex viscoelastic shear modulus of the adsorbed film. On the other hand, ellipsometry measures only the amount of polymer + surfactant adsorbed. The combination of both techniques have allowed us to calculate the amount of hydration water adsorbed within the film using the Equation (1) [63,75]. In this work, the adsorbed amount will be discussed in terms of the thickness of the film, h_{ac} and h_{op} for the results obtained using QCM-D and ellipsometry, respectively. Figure 5 shows the dependences of both thicknesses on the surfactant concentration for all the three pseudo-binary and the pseudo-ternary mixtures studied. It has to be underlined that both the polymer + surfactant aggregates and the substrate are negatively charged. Despite adsorption in this situation might be counter intuitive, this behavior has been known for many years [11], and in the present case can be explained through an acid-base reaction between the oxygen of the oxyethylene groups of the DSPE-PEG and the negatively charged groups along the surface [76]. Nevertheless, the adsorption of the polymer is relatively small ($h_{ac} = 2.8$ nm and $h_{op} = 0.1$ nm), which give indication that the layer is highly hydrated ($x_w = 0.95$). This suggests that the adsorption of DSPE-PEG results in the formation of a very heterogeneous layer attached to the surface by a very limited number of segments and with many segments protruding to the aqueous environment.

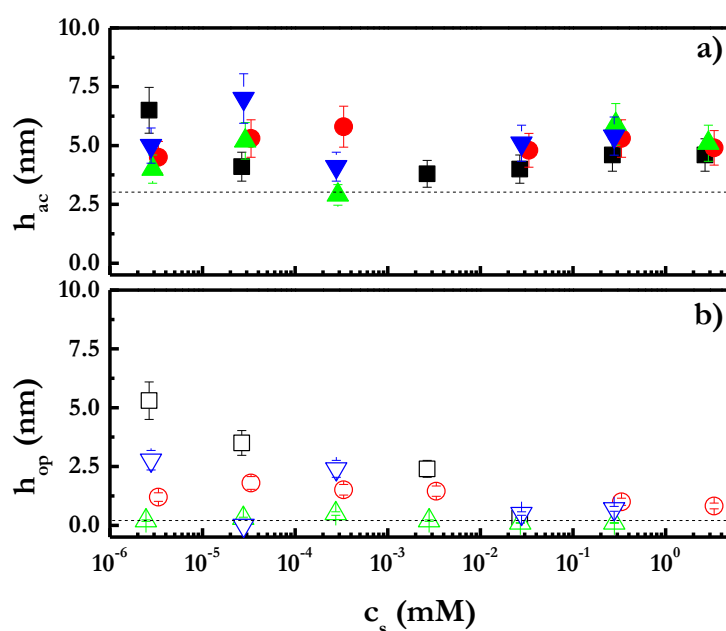


Figure 5. Dependence of h_{ac} (a) and h_{op} (b) on the surfactant concentration, c_s , for the different DSPE-PEG+surfactant mixtures studied in this work: (■, □) SLES, (●, ○) CB, (▲, △) SLES+CB (molar ratio 3:2) and (▼, ▽) SLMI. All the mixtures contain a fixed DSPE-PEG concentration of 5 g/L, and their ionic strength and pH were fixed a 40 mM (KCl) and 5.6, respectively. The dashed lines correspond to the values of acoustical and optical thicknesses for the adsorption of a DSPE-PEG layer from a solution with concentration 5 g/L and the same ionic strength and pH than the mixtures.

The results show that the addition of surfactant enhances the deposition of DSPE-PEG onto the solid surface, with $h_{ac} > h_{op}$. Furthermore, h_{ac} remains close to 5 nm independently of the chemical nature of the surfactant and the surfactant concentration. This suggests that polymer + surfactant aggregates upon adsorption does not retain their bulk conformation, and undergo some reorganization once they interact with the surface. On the other side, h_{op} appears dependent on the specific characteristics of the surfactant mixed with the polymer. This may explained considering the differences on the sensitivity of QCM-D and ellipsometry to the water associated with the adsorbed layers. Furthermore, the differences between h_{ac} and h_{op} evidence that the reorganization of the aggregates should be different depending on the nature of the surfactant. Focusing the interest on the mass of polymer + surfactant deposited onto the negatively charged surface (h_{op} , see Figure 5b), the adsorption of pseudo-binary DSPE-PEG + surfactant mixtures containing anionic surfactants decrease with the surfactant concentration. This may be understood considering that at the lowest surfactant concentration assuming that the conformation of the polymer + surfactant aggregates may favor both the interaction of the ion–dipole interactions between the oxyethylene groups of PEG chains and the surface, and the interaction of the oxyethylene of the SLES tails or the ether group of the SLMI tails. It is expected that this type of interactions can be favored in SLES in relation to that occurring in SLMI because its higher number of available interacting group (two oxyethylene groups in SLES vs. one ether group in SLMI). This may result in an enhancement of the deposition of the aggregates containing anionic surfactant within the lowest surfactant concentration. This type of interactions are hindered with the increase of the surfactant concentration due to the change on the conformation of the complexes. This reduces the number of points of the aggregates which can interact with the surface, and consequently hinders the adsorption. The differences on the deposition with the surfactant concentration in mixtures of DSPE-PEG with SLES or SLMI are evidenced from the AFM images shown in Figure 6.

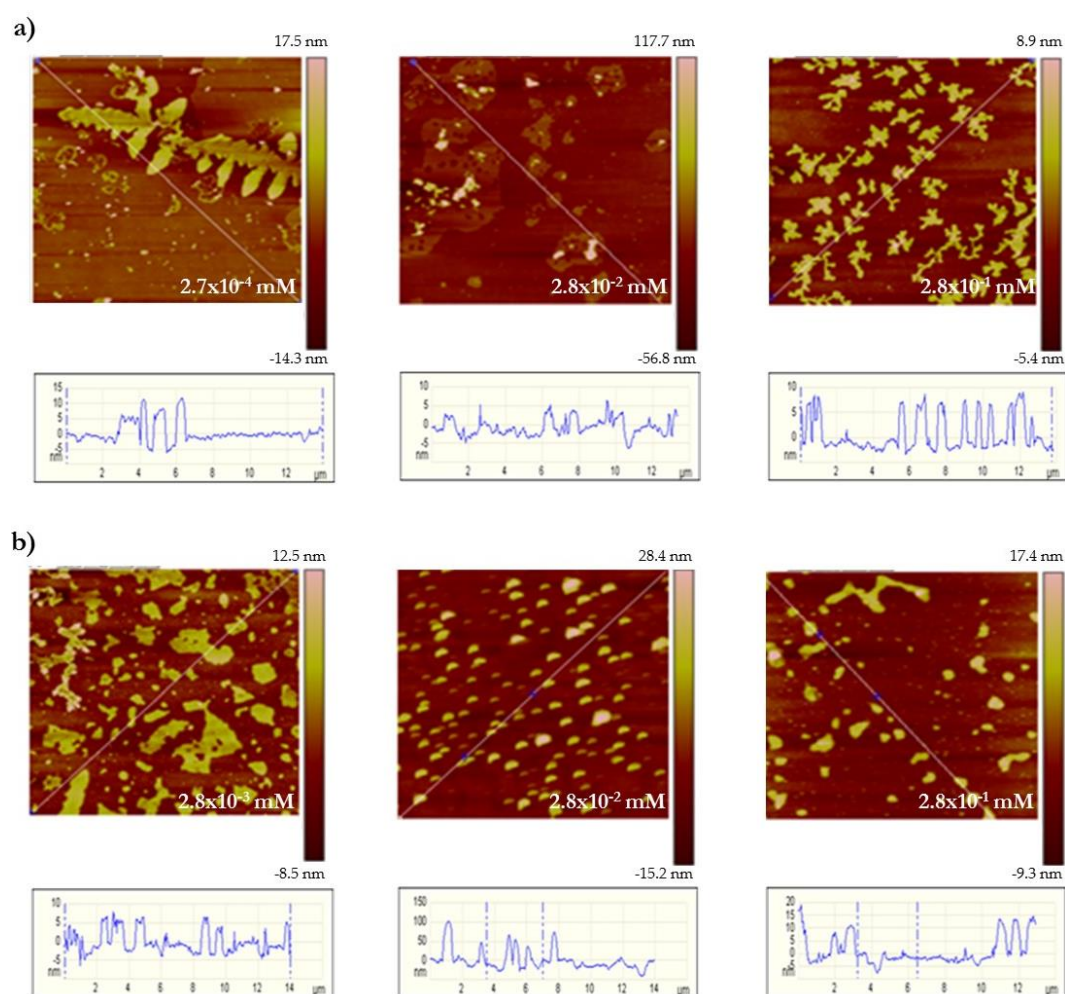


Figure 6. AFM images (tapping mode, $10 \times 10 \mu\text{m}^2$) obtained for layers obtained for the deposition of DSPE-PEG+surfactant mixtures containing different surfactant and solution concentration: (a) SLES and (b) SLMI. All the mixtures contain a fixed DSPE-PEG concentration of 5 g/L, and their ionic strength and pH were fixed at 40 mM (KCl) and 5.6, respectively.

The AFM images show that independently on the surfactant concentration, the obtained layers for mixtures of DSPE-PEG with anionic surfactant are rather inhomogeneous. This may be explained considering the important contribution of the lateral repulsions between the adsorbed negatively charged surfactant molecules. Furthermore, the increase of the surfactant concentration leads to the reduction of the coverage of the surface as result of the deposition of the polymer + surfactant aggregates as is expected from the adsorption results. This is clear from the formation of isolated islands of deposited material randomly distributed along the surface. Therefore, the decrease of the surface coverage with the increase of the surfactant concentration, and consequently, the increase of the heterogeneity of the layers results from two effects which may be associated with the changes in the conformation of the micellar-like aggregates: (i) the decrease of the number of PEG chains in the aggregates reduce the possibility of their deposition onto the surface through ion–dipole interactions, and (ii) the increase of the number of surfactant molecules in the aggregates increase the lateral repulsions between the aggregates, and between them and the surface, which hinders the adsorption and results on the formation of heterogeneous layers. It should be expected that the heterogeneity of the deposited impact on the water content of the layers reported in Figure 7. In the case of mixtures of DSPE-PEG+SLES, the deposit shows a dendritic structure whose motives decrease in size as the surfactant concentration increases, as well as the size of the deposits. It is

worth mentioning that the driving force for the formation of dendritic or leaf-like structures upon the adsorption of polymer + surfactant mixtures onto solid surface is unclear. However, it is possible that the formation of this type of patterns may be associated with the existence of weak interactions between the polymer + surfactant aggregates and the solid surface [77].

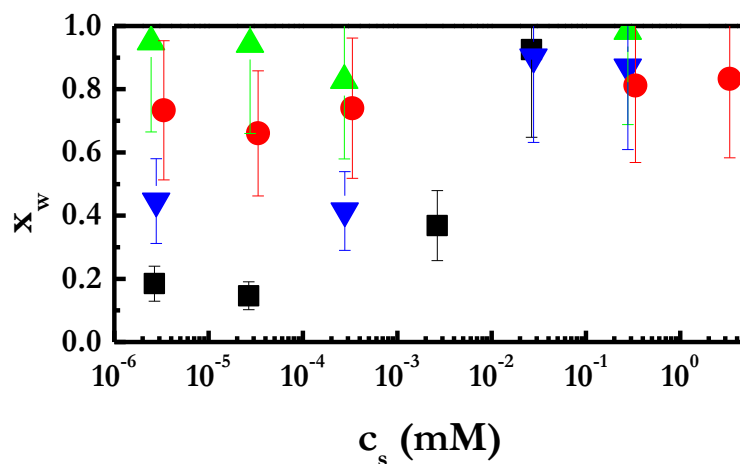


Figure 7. Dependence of water content, x_w , on the surfactant concentration, c_s , for the different DSPE-PEG+surfactant mixtures studied in this work: (■) SLES, (●) CB, (▲) SLES+CB (molar ratio 3:2) and (▼) SLMI. All the mixtures contain a fixed DSPE-PEG concentration of 5 g/L, and their ionic strength and pH were fixed a 40 mM (KCl) and 5.6, respectively. The dashed lines correspond to the values of acoustical and optical thicknesses for the adsorption of a DSPE-PEG layer from a solution with concentration 5 g/L and the same ionic strength and pH than the mixtures.

The water content of the layers obtained upon deposition of the mixtures of DSPE-PEG with the anionic surfactants increases from values about 0.2 and 0.4 at the lowest surfactant concentrations for mixtures with SLES and SLMI, respectively, up to values close to the 0.9. This agrees with the increase of the heterogeneity of the layers reported above. Furthermore, the lower values of the water content of the layers containing SLES at the lowest surfactant concentrations seem to confirm the role of the chemical nature of the surfactant and their interactions with the surface on the deposition and structure of the obtained layers.

The adsorption of the pseudo-binary mixture of DSPE-PEG with CB (see Figure 5) is poorer than that found for mixtures containing anionic surfactants, remaining almost unchanged with the surfactant concentration. This suggests that together with the surfactant concentration, the role of the surfactant nature in the deposition of the complexes is very important. This is confirmed on the heterogeneity of the AFM images obtained for layers of DSPE-PEG+CB mixtures (see Figure 8a) and the high water content (see Figure 6), around 0.9, found for such layers from the lowest surfactant concentrations. The AFM images show clearly that the layers of DSPE-PEG+CB are formed, independently of the surfactant concentration, by isolated aggregates distributed within the entire surface. The adsorption of the pseudo-ternary DSPE-PEG + (SLES + CB) mixture results in a behavior intermediate between those of the pseudo-binary mixtures containing SLES and CB, with the behavior being closer to the mixtures containing CB for the lowest surfactant concentration whereas the behavior becomes closer to the mixtures DSPE-PEG + SLES for the highest surfactant concentrations. This results in the formation of heterogeneous DSPE-PEG + (SLES + CB) layers (see Figure 8b for AFM images), with a high water content (see Figure 6), within the entire surfactant concentration range. It should be noted that the situation found for mixtures DSPE-PEG with different surfactants is very different to that found for the adsorption of mixtures of the polycation PDADMAC and similar surfactants [36,38]. The deposition of the latter mixtures is enhanced as the surfactant concentration increases, resulting in the formation of more homogeneous films with a lower hydration. Therefore, it should be expected that the deposition

and structure of the adsorbed layers can be easily controlled by tuning the nature and strength of the aggregate-surface interactions, which on the basis of the obtained results requires to control the composition of the polymer + surfactant mixture and the chemical nature of both polymer and surfactant.

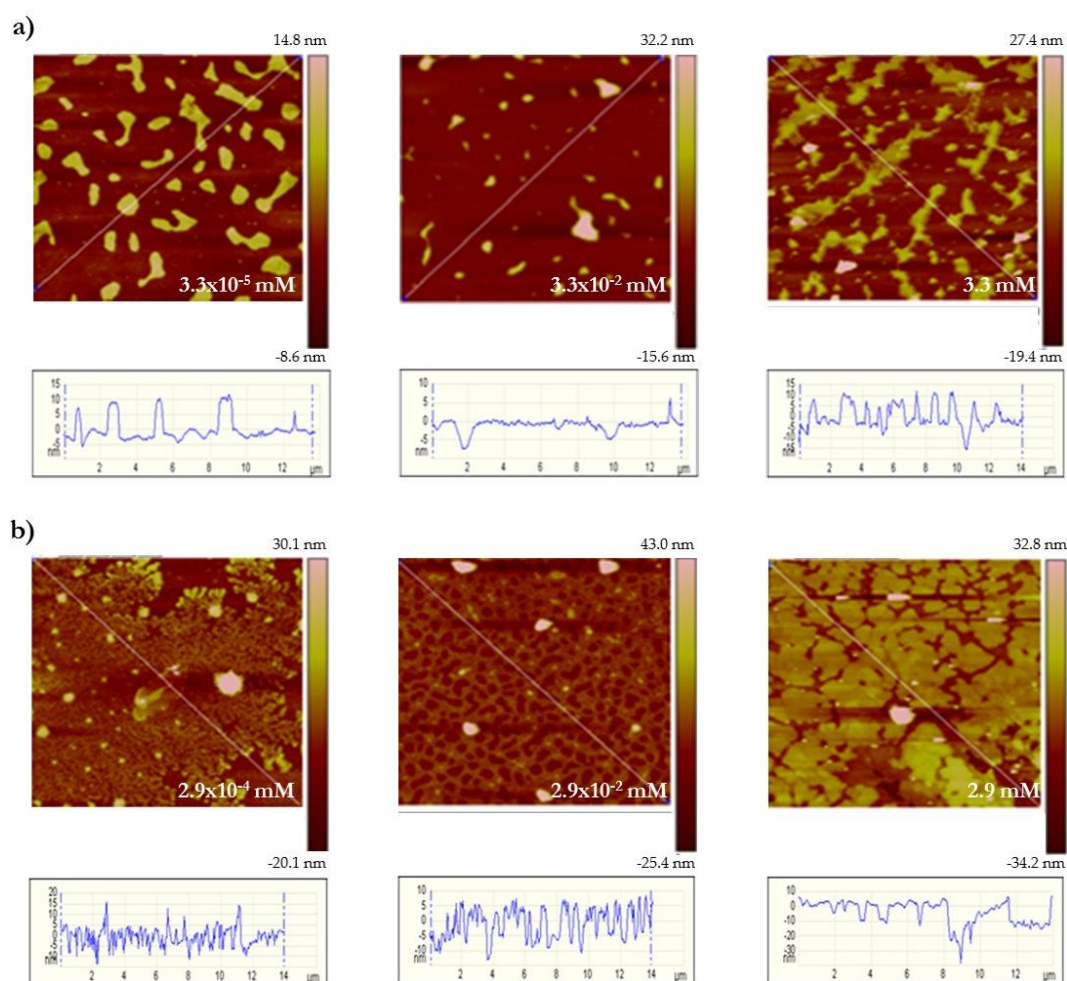


Figure 8. AFM images (tapping mode, $10 \times 10 \mu\text{m}^2$) obtained for layers obtained for the deposition of DSPE-PEG+surfactant mixtures containing different surfactant and solution concentration: (a) CB and (b) SLES + CB (molar ratio 3:2). All the mixtures contain a fixed DSPE-PEG concentration of 5 g/L, and their ionic strength and pH were fixed a 40 mM (KCl) and 5.6, respectively.

As already mentioned the QCM-D allows one to estimate the complex shear modulus of the adsorbed film. Figure 9 shows that the real and imaginary components, G' and G'' , for the DSPE-PEG + LESS mixture are equal within the experimental uncertainty, that is the typical situation for gels [78]. The values for the other mixtures are qualitatively and quantitatively the same within the experimental uncertainty. The values already reported for layers of PEG, PDADMAC or mixtures of PDADMAC with sodium lauroyl methyl taurate and SDS have led to the same conclusion, i.e., the adsorbed films had a gel-like character [36,59,79].

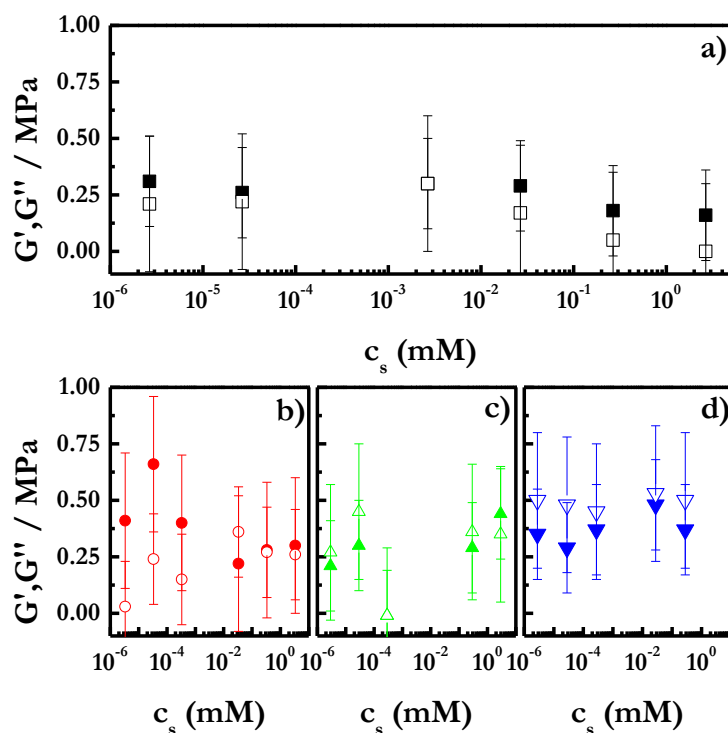


Figure 9. Dependence of G' (solid symbols) and G'' (open symbols) on the surfactant concentration, c_s , for the different DSPE-PEG+surfactant mixtures studied in this work: (a) DSPE-PEG + SLES, (b) DSPE-PEG + CB, (c) DSPE-PEG + (SLES + CB) (molar ratio 3:2) and (d) DSPE-PEG + SLMI. All the mixtures contain a fixed DSPE-PEG concentration of 5 g/L, and their ionic strength and pH were fixed a 40 mM (KCl) and 5.6, respectively.

Since the tribological behavior of the adsorbed film is a key variable for applications such as hair conditioning, the similar values of G' and G'' of the systems with DSPE-PEG and those with PDADMAC is a good indication that the new polymer could be a reasonably good substitute of PDADMAC, which is the polycation most frequently used in hair cosmetics. However, the remarkably heterogeneity of the layers obtained upon deposition of mixtures of DSPE-PEG and different surfactant is detrimental for the tribological properties of the films, and consequently a careful examination of the composition of the mixtures and adsorption conditions should be required before trying a substitution of the PDADMAC for DSPE-PEG. It is reasonable to expect that the increase of the molecular weight of the PEG chain grafted to the phospholipid might increase the adsorption on the model surface [66].

4. Conclusions

This work was focused on the study of the interaction in bulk of a pegylated lipid (DSPE-PEG) with three different surfactants, two anionic (SLES and SLMI) and one zwitterionic (CB), and the adsorption of such pseudo-binary mixtures onto a negatively charged. Furthermore, the association occurring in bulk and the adsorption of the pseudo-ternary mixture obtained by mixing DSPE-PEG with SLES and CB was also explored. The results showed the formation of micellar-like DSPE-PEG + surfactant aggregates independently of the chemical nature of the surfactant. However, the aggregation pathway was found to be strongly dependent on the composition of the mixtures, with the formation of different types of aggregates as result of the complex interplay of hydrophobic and electrostatic interactions occurring in the polymer + surfactant association. The adsorption of DSPE-PEG + surfactant aggregates onto negatively charged surfaces (thiol-decorated gold surfaces and silicon wafers) with a surface charge density similar to the damaged hair epicuticle, even counter-intuitive, was found to be possible through the ion–dipole interactions occurring between the oxyethylene groups of the PEG chains, and

when it was possible of the surfactant molecules, and the negative charges of the surface. Thus, the adsorption of the complexes onto the negatively charged surface was found to be strongly dependent on the specific nature of the surfactant associated with the DSPE-PEG molecules, with those surfactants interacting with the surface through the ion–dipole interactions allowing an enhancement of the deposition. Furthermore, a decrease of the adsorbed amount was found as the surfactant concentration decreases, which may be the result of the conformational change of the micellar-like aggregates existing in solution from a conformation in which many oxyethylene groups can interact with the solid surface to a conformation in which the possibility of effective interactions with the surface is reduced. This shows that the adsorption process mirrors the association process between the polymer chains and the surfactant molecules occurring in solution. It should be noted that the deposition process results in heterogeneous gel-like film with a high level hydration, which is expected to provide non-suitable tribological properties of the obtained layers. Therefore, even though pegylated lipids appear to be a promising alternative to replace conventional polyelectrolytes from consumer products, e.g., shampoos or conditioners, further studies are required for optimizing its deposition onto solid surfaces.

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