

1 Extended Abstract

2 Equilibration of polyelectrolyte-surfactant layers at fluid/fluid 3 interfaces: Different Scenarios [†]

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15 **Abstract:** This work addresses the main physico-chemical aspects related to the formation of
16 polyelectrolyte-surfactant layers at fluid interfaces, combining a careful examination of the
17 interfacial properties of the adsorbed films by using a pool of surface-sensitive technique.
18 Furthermore, the assembly of the mixtures will be correlated to the bulk association processes trying
19 to provide a comprehensive picture describing the interfacial behavior of polyelectrolyte-surfactant
20 mixtures at fluid interface. This requires the study of combinations of different polycations
21 (poly(diallyldimethylammonium chloride) and chitosan) with surfactants bearing different charge
22 (neutral, anionic and zwitterionic). Thus, it will be possible to obtain a whole perspective of the role
23 of the association processes on the structure and properties of the interfacial layers.

Keywords: polyelectrolytes; surfactants; fluid Interfaces; rheology.

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1. Introduction

The interaction of polyelectrolyte-surfactant mixtures with interfaces plays a very important role in many technological fields, including cosmetics, food science or drug delivery [1-3]. This has stimulated the research trying to shed light on the most fundamental aspects governing the adsorption processes of the complexes formed in the bulk, and the equilibration of the interfacial layers. The current knowledge related to the physico-chemistry of polyelectrolyte-surfactant systems has evidenced that, in most of the cases, the association process of polyelectrolyte and surfactant molecules in the bulk is guided by non-equilibrium effects, even though the control of the protocol used for mixing the component allows obtaining reproducible aggregates (kinetically trapped-aggregates), with these non-equilibrium effects impacting decisively on their interfacial properties of polyelectrolyte-surfactant systems [4,5]. Therefore, the understanding of the interfacial processes involving polyelectrolyte-surfactant mixtures makes necessary deepening on the mechanisms underlying the complexation process occurring in the bulk [6-8], i.e. the structural complexity of polyelectrolyte-surfactant mixtures and the richness of their phase behavior, which result from the formation of supramolecular aggregates [9-12].

Despite the large number of studies dealing with the polyelectrolyte – surfactant mixtures, it has not been possible yet to establish a framework enabling for the description of the association of polymers and surfactants in the bulk and at interfaces mainly due to the intricate balance of interactions involved in these systems, which emergence from

1 their multicomponent character [7-10,13]. The understanding of the complex physico-
2 chemical behavior of polymer-surfactant systems can be probably considered one of the
3 most important challenges of colloidal and interfacial sciences due to its recognized
4 interest in different fields of science and technology.

5 The main aim of this work is to unravel the different interfacial behavior appearing
6 in polycation-surfactant mixtures. The adsorption at the water/vapor interface is studied
7 by surface tension measurements. In addition to the steady state measurements of the
8 surface tension, we will follow the adsorption kinetics of the complexes at the water/vapor
9 interface by the time evolution of the surface tension (dynamic surface tension) and the
10 mechanical performance of the interfaces against dilation using oscillatory barrier
11 experiments in a Langmuir trough. The obtained results will be combined with the
12 information obtained from the study of the self-assembly phenomena taking place in
13 solution to provide a comprehensive description of the equilibration processes occurring
14 during the formation of interfacial layers in this type of systems.

15 2. Experimental Section

16 2.1. Chemicals

17 PDADMAC with an average molecular weight in the 100-200 kDa range and chitosan
18 (CHI) with an average molecular weight in the 50–190 kDa range and average
19 deacetylation degree in the 75-85 % range were purchased from Sigma-Aldrich (Saint
20 Louis, MO, USA) and used as received. The anionic surfactant SLES (sodium laureth
21 sulfate), with an average number of 2 oxyethylene, was supplied by Kao Chemical Europe
22 S.L. (Barcelona, Spain) as an aqueous solution of 70 wt% of surfactant concentration.
23 SLMT (sodium N-lauroyl-N-methyltaurate) was synthesized and purified following the
24 procedure described in our previous publication [14]. The zwitterionic surfactants CB
25 (coco-betaine) and CAPB (cocoamidopropyl-betaine) were supplied by Clariant
26 International Ltd. (Muttentz, Switzerland) and Solvay S.A. (Brussels, Belgium),
27 respectively. Both carboxybetaines were obtained as aqueous solutions with a surfactant
28 concentration of 31 wt% for CB and 38 wt% for CAPB.

29 Glacial acetic acid, hydrochloric acid (HCl, aqueous solution at 35 wt%) and sodium
30 hydroxide (NaOH, purity 99%) for fixing the pH, and sodium chloride (NaCl, purity
31 >99.9%) were supplied for Sigma-Aldrich (Saint Louis, MO, USA).

32 Ultrapure deionized water used for cleaning and solution preparation was obtained
33 by a multicartridge purification system aquaMAX™-Ultra 370 Series (Young Lin
34 Instrument, Co., Anyang, Korea). The water used had a resistivity higher than 18 MΩ-cm,
35 and a total organic content lower than 6 ppm.

36 2.3. Characterization techniques

37 The binding of the anionic surfactants to the polycation chains was evaluated by
38 potentiometric titration using a surfactant selective electrode model 6.0507.120 from
39 Metrohm AG (Herisau, Switzerland) connected to a pH-meter (model CG842-Schott
40 Instruments GmbH, Mainz, Germany). The binding degree of surfactant β is estimated
41 from the potentiometric measurements as [15]

$$42 \beta = \frac{c_s^{bound}}{c_{monomer}}, \quad (1)$$

43 where c_s^{bound} is the concentration of surfactant bound to the polymer chains and
44 $c_{monomer}$ the concentration of charged monomers on the polyelectrolyte chain. The
45 determination of the binding isotherm using surfactant selective electrodes requires firstly
46 to obtain a calibration curve using surfactant solutions in the same concentration range
47 used for the preparation of the polyelectrolyte-surfactant mixtures. For this purpose, the

1 electromotive force (EMF) of surfactant solutions is recorded, which allows constructing
2 a calibration curve by plotting the recorded EMF against the surfactant concentration. The
3 comparison of the calibration curve with the EMF dependence on the surfactant
4 concentration obtained for polyelectrolyte-surfactant mixtures provides an evaluation of
5 the number of free surfactant molecules remaining in solution when the mixture is
6 analyzing.

7 The turbidity of the solutions was evaluated from their transmittance at 400 nm
8 obtained using a UV-Visible spectrophotometer (HP-UV 8452). The turbidity of the
9 samples was determined by the optical density at 400 nm ($OD_{400}=[100 - T(\%)]/100$,
10 where T is the transmittance). It is worth mentioning that neither the polyelectrolyte nor
11 the surfactant present any absorption band above 350 nm.

12 The changes on the surface pressure Π occurring during the adsorption of
13 polyelectrolyte-surfactant aqueous solutions with different surfactant concentrations to
14 the water/vapor interface was followed using a home-made profile analysis tensiometer
15 in pendant drop configuration (for further details see reference [14]). The adsorption at
16 the water/vapor interface was measured until steady state was reached, i.e., changes of
17 surface pressure smaller than $0.1 \text{ mN}\cdot\text{m}^{-1}$ during 30 min.

18 3. Results and discussion

19 3.1. Polymer-surfactant association in solution

20 The binding isotherms for the surfactants to the polymer chains deduced from
21 electromotive force (EMF) measurements for the association of SLES and SLMT to
22 PDADMAC chains shown in Figure 1a evidences a high efficiency of PDADMAC for
23 binding anionic surfactant as has been previously reported in the literature [16], with an
24 amount of free surfactant in solution remaining below 10% even for the highest surfactant
25 concentrations. The low concentration of free surfactant in solution allows us to make the
26 assumption that for the interaction of PDADMAC and anionic surfactant, the bulk has
27 approximately zero free-surfactant concentration. On the contrary, when the interaction
28 of chitosan chains with anionic surfactant is concerned (see inset in Figure 1a), the
29 situation changes and even though it occurs from the lowest surfactant concentrations, a
30 very high fraction of the charged monomers remain uncompensated. This appears clear
31 considering that for concentrations close to $2.6 \times 10^{-2} \text{ mM}$, where big aggregates are already
32 detected in the solution, only the 0.2 % of the charged monomers are compensated by
33 SLES binding. Furthermore, the amount of free surfactant at the highest surfactant
34 concentrations remains around the 25 % of the initial surfactant concentration. Therefore,
35 the results suggest that the chitosan-SLES solutions contain both chitosan-SLES complexes
36 and a non-negligible concentration of free SLES molecules [17]. The low binding of the
37 anionic surfactant to the chitosan can be understood considering a strong screening of the
38 electrostatic interactions due to the relatively high ionic strength (100 mM). Furthermore,
39 the strong contribution of the charge screening justify the formation of insoluble
40 complexes for surfactant concentrations far from the corresponding to the saturation of
41 all the charges [18]. Therefore, the interaction of polycation and oppositely charged
42 systems can lead to two different systems: strongly interacting systems (PDADMAC-
43 anionic surfactant) and weakly interacting systems (chitosan-anionic surfactant). This is
44 clear from the dependence of ratio between the number of free surfactant molecules and
45 the total number of surfactant molecules on the ration between the number of charges
46 monomers and the number of surfactant molecules for mixtures of PDADMAC and
47 chitosan with SLES (see Figure 1b).

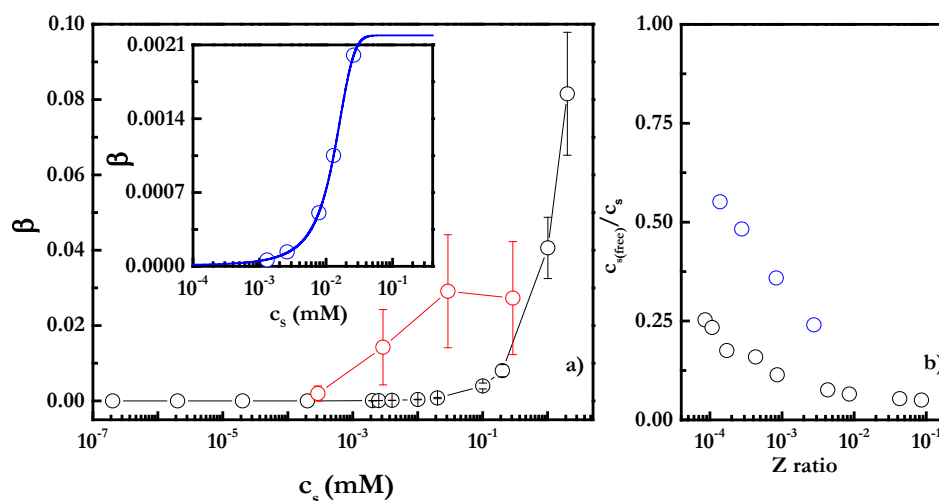


Figure 1. (a) Binding isotherms for PDADMAC-SLMT (○) and (○) PDADMAC-SLES complexes (polymer concentration 5 g/L, pH=5.6 and NaCl concentration 40 mM) as function of the initial concentration of surfactant in bulk, c_s . The inset shows the binding isotherm for chitosan-SLES complexes (polymer concentration 2 g/L, pH=4.6 and NaCl concentration 100 mM) as function of the initial concentration of surfactant in bulk, c_s . The lines are guides for the eyes. (b) Z ratio dependences of the ratio between the concentration of free SLES molecules remaining in the solution ($c_{s(\text{free})}$) and the total SLES concentration (c_s) for mixtures of SLES with chitosan (○) and PDADMAC (○). Notice that the concentration of NaCl was fixed in 100 mM.

The association of zwitterionic surfactant with polycations cannot be followed by measuring the changes of the EMF. However, turbidity and electrophoretic mobility measurements can provide important insights in the association process when zwitterionic surfactant are involved, where the the presence of anionic and cationic groups in the hydrophilic head of the zwitterionic molecule may modify the aggregation pattern in relation to that what is found in mixtures of polyelectrolytes and surfactant bearing opposite charges. Figure 2 shows the dependences of the electrophoretic mobility and turbidity on the surfactant concentration for the association of PDADMAC with CB and CAPB.

The results from turbidity and electrophoretic mobility measurements did not evidence any signature of complexation between PDADMAC and the zwitterionic surfactants for low surfactant concentrations, with the values of both electrophoretic mobility and turbidity being very close to that what found for PDADMAC solutions. This bulk behavior might be a result of the weak interaction between the species in the solution for the diluted surfactant concentration range. However, the increase of surfactant concentrations leads to a decrease of the electrophoretic mobility from the value corresponding to PDADMAC solutions down to values close to the isoelectric point at the highest surfactant concentrations, which is accompanied by an increase of the turbidity. These results are compatible with the existence of polyelectrolyte–zwitterionic surfactant complexation. Therefore, it may be expected that the surfactant binding occurs through surfactant micelles. This makes possible an effective compensation of the PDADMAC charges, which was hindered at the lowest surfactant concentrations as result of the presence of a positive charge on the polar head of the zwitterionic surfactant.

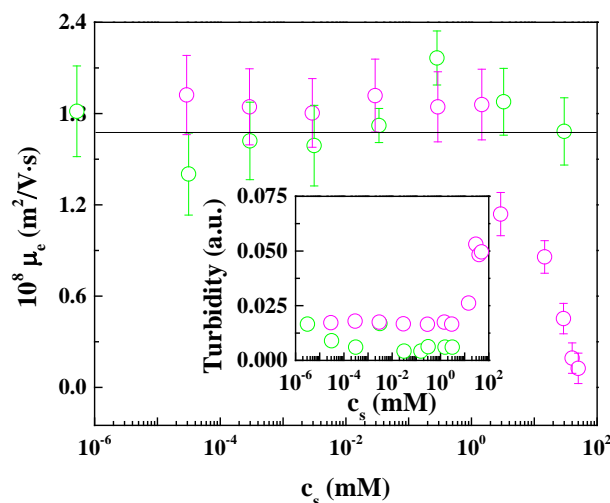


Figure 2. Surfactant concentration dependences of the electrophoretic mobility for mixtures of PDADMAC with CB (●) and CAPB (●). The line shows the electrophoretic mobility of pure PDADMAC solution. The inset represents the surfactant concentration dependence of the solution turbidity for mixtures of PDADMAC with CB (●) and CAPB (●). The composition of the mixtures is polymer concentration 5 g/L, pH=5.6 and NaCl concentration 40 mM.

3.2. Surface pressure isotherms for polymer-surfactant mixtures

The study of the surfactant concentration dependences of the surface pressure Π of solutions of surface active compounds provides important information on the mechanisms involved in the equilibration of the fluid interface. Figures 3a and 3b shows the surfactant concentration dependences of the surface pressure for mixtures of PDADMAC and the two anionic surfactants. For the sake of comparison, the data corresponding to the pure surfactant are also shown. It should be stressed that PDADMAC alone does not undergo any adsorption at the fluid interface.

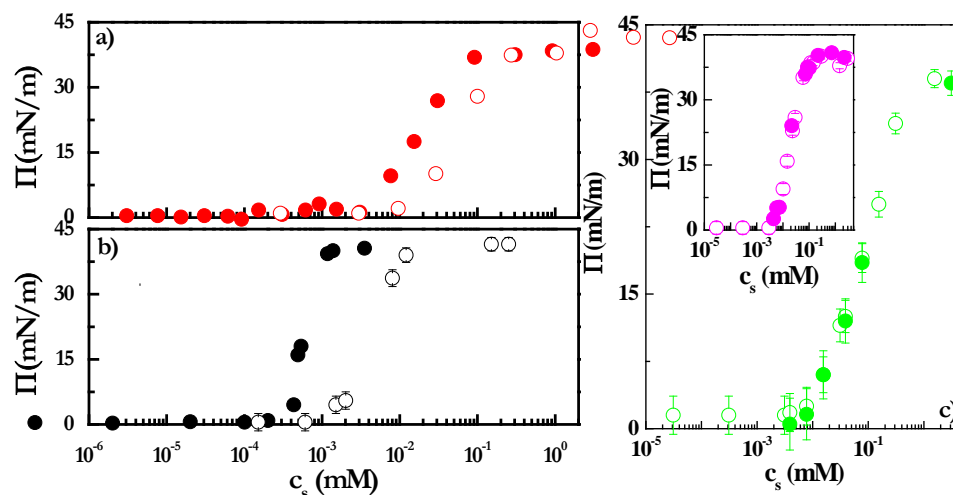


Figure 3. Surface pressure dependences on the surfactant concentration: (a) SLMT (●) and PDADMAC – SLMT (○). (b) SLES (●) and PDADMAC – SLES (○) solutions. (c) CB (●) and PDADMAC-CB (○). The inset presents the data for CAPB (○) and PDADMAC-CAPB (●). The composition of the mixtures is polymer concentration 5 g/L, pH=5.6 and NaCl concentration 40 mM.

The adsorption behavior of the anionic surfactant is the typical for surfactant solutions, where Π increases with the bulk concentration up to the surfactant concentration overcomes the threshold defined by the critical micellar concentration (cmc). Afterwards, Π remains constant with further increases of c_s (surfactant). On the other

side, the adsorption of PDADMAC-surfactant solutions show that the surface pressure values for pure surfactant and polyelectrolyte-surfactant solutions are similar at the lowest surfactant concentrations due to the low coverage of the interface. The increase of the surfactant concentration leads to the increase of Π for both surfactant and polyelectrolyte-surfactant solutions. This increase starts for surfactant concentrations around one order of magnitude lower when polyelectrolyte-surfactant solutions are considered, which is signature of the existence of a synergetic effect for the increase of the surface pressure as result of the interaction in solution of the polyelectrolyte and the surfactant. This type of synergetic effects do not influence the adsorption behavior of solutions formed by PDADMAC and zwitterionic surfactants derived of the betaines, which may be explained by the aforementioned differences in the aggregation process occurring in the bulk (see Figure 3c) [19].

The surface pressure isotherms of both pure surfactant solutions and PDADMAC-zwitterionic surfactant mixtures present a monotonous increase from the quasi-null value corresponding the bare water/vapor interface up to to values close to 40 mN/m in the vicinity of the cmc of the pure surfactant. The differences of surface tension of the pure surfactant solutions and PDADMAC-surfactant solutions are smaller than the combined error bars both mixtures. This together with the results previously discussed for the bulk properties seems to confirm the absence of real complexation below the cmc of the surfactant. This can be explained considering that the presence of the positive charge within the hydrophilic head of the surfactant introduces an electrostatic barrier which may prevent the complexation process between the carboxylic acid group of the surfactants ($pK \sim 2-4$), which is expected to be deprotonated under the pH conditions in the present study (slightly acid, $pH \sim 5.5$) [20], and the quaternarium ammonium of the PDADMAC.

The scenario is even more complex when the adsorption of mixtures of chitosan and SLES is considered, which may be ascribed to the weak association of chitosan and the anionic surfactant. Furthermore, on the contrary that PDADMAC, chitosan is a surface active polymer under the here considered conditions. Figure 4 shows the surface pressure-surfactant concentration isotherms for the adsorption of pure SLES and chitosan-SLES mixtures at the water/vapor interface.

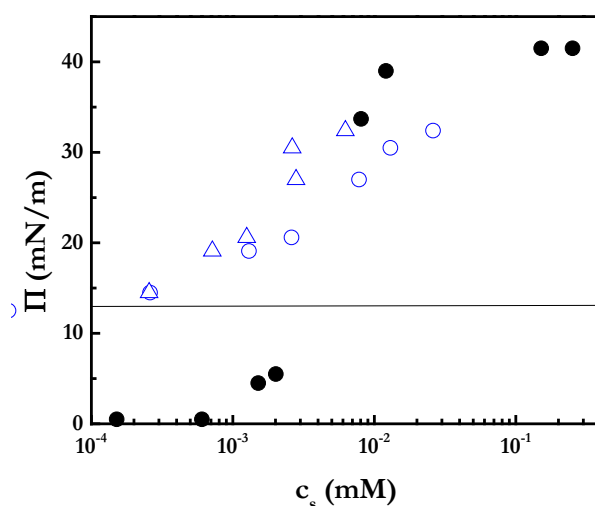


Figure 2. Surfactant concentration dependences of the surface pressure for SLES (●), chitosan-SLES mixture (polymer concentration 2 g/L, $pH=4.6$ and NaCl concentration 100 mM) (○) and chitosan-SLES mixtures with the surfactant concentration re-scaled to the free surfactant concentration remaining in solution (polymer concentration 2 g/L, $pH=4.6$ and NaCl concentration 100 mM) (△). The solid line represents the surface pressure value of a chitosan solution.

1 The surface pressure of both pure SLES solutions and chitosan-SLES mixtures
2 increases with the surfactant concentration. However, for chitosan-SLES mixtures, the
3 surface pressure appears different to that corresponding to the pure surfactant from the
4 lowest value of the surface tension (chitosan-SLES mixtures present higher values of the
5 surface pressure for the lowest SLES concentrations). This indicates, similarly than in
6 mixtures of PDADMAC and anionic surfactant, the existence of a synergetic effect of
7 chitosan and SLES. However, for a SLES concentration around 5×10^{-3} mM, it was found a
8 crossover between the surface pressure curves corresponding to the mixture and to the
9 pure, which leads to a situation in which the surface pressure of the mixture becomes
10 lower to that of the SLES solution with the same concentration. This unexpected behavior
11 can be explained in terms of that discussed for mixtures of proteins and ionic surfactants
12 [21]. A first regime of adsorption, appearing at the lowest SLES concentration, where
13 higher values of surface pressure are found for chitosan-SLES mixtures with respects to
14 those corresponding to pure SLES solutions. This may be due to the surface activity of
15 bare chitosan at the water/vapor interface, and the synergism of the interaction of the
16 chitosan and SLES on the increase of the surface pressure. Thus, the increase of the surface
17 pressure with the surfactant concentration before the crossover of the surface pressure
18 curves may be due to a co-adsorption of chitosan-complexes and free surfactant
19 molecules, with the concentration of complexes at the interface being reduced at the
20 highest surfactant concentrations. The latter may be explained considering the role of the
21 hydrophobic interactions between the SLES hydrophobic tails, and probably between the
22 SLES hydrophobic tails and the hydrophobic domains of chitosan (deacetylated
23 monomers). This leads to the formation of hydrophilic chitosan-SLES aggregates with a
24 lower surface activity, in agreement with the picture proposed by Petrovic et al. [22] for
25 mixtures similar to that studied in the current work.

26 The above scenario may be confirmed by the re-scaling the surface pressure isotherm
27 of chitosan-SLES mixtures considering only the concentration of free surfactant remaining
28 in solution as was obtained from the binding isotherm (see Figure 1). The re-scaled surface
29 tension curve for chitosan-SLES mixtures tends to overlap with the surface tension
30 isotherm obtained for SLES solutions at the highest surfactant concentrations. Thus,
31 according to the above description three different regions can be differentiated in the
32 adsorption isotherm: (i) in absence SLES, chitosan is adsorbed at the interface leading to
33 a surface pressure higher than that expected for the bare fluid interface (ii) at the lowest
34 SLES concentrations ($< 5 \times 10^{-3}$ mM), chitosan and SLES are co-adsorbed at the interface and
35 the surface pressure is higher than that corresponding to SLES solutions, and (iii) at the
36 highest SLES concentration ($> 5 \times 10^{-3}$ mM), the amount of chitosan at the interface is
37 relatively low, and the behavior of the monolayer is reminiscent from that corresponding
38 to pure SLES layer. This leads to a situation in which the interfacial behavior is governed
39 by the concentration of SLES free in solution, and the surface pressure is slightly lower
40 than the corresponding to SLES solutions with the same concentration.

41 4. Conclusions

42 The adsorption of mixtures formed by polycations and surfactants at the water
43 vapor/interface results in a complex picture which depends on both the chemical nature
44 of the polymer and the surfactant. This results from the differences on the association
45 mechanism in the bulk that leads to the existence of different species in the solution. These
46 species present different affinity for the interface, with their preferential segregation at the
47 fluid interface determining their equilibration.

48 **Author Contributions:** Conceptualization, R.G.R. and E.G.; methodology, E.G., L.F.P., I.A.N. and
49 L.F.P.; software, E.G.; validation, F.O., R.G.R. and E.G.; formal analysis, L.F.P. and I.A.N.;
50 investigation, E.G., L.F.P., I.A.N., A.M. F.O. and R.G.R.; resources, E.G., F.O. and R.G.R.; data
51 curation, E.G.; writing—original draft preparation, E.G.; writing—review and editing, E.G., L.F.P.,
52 I.A.N., A.M. F.O. and R.G.R.; visualization, E.G.; supervision, R.G.R. and E.G.; project

administration, E.G., F.O and R.G.R.; funding acquisition, F.O., R.G.R. and E.G. All authors have read and agreed to the published version of the manuscript.

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References

1. Llamas, S.; Guzmán, E.; Ortega, F.; Baghdadli, N.; Cazeneuve, C.; Rubio, R.G.; Luengo, G.S. Adsorption of polyelectrolytes and polyelectrolytes-surfactant mixtures at surfaces: a physico-chemical approach to a cosmetic challenge. *Adv. Colloid Interface Sci.* **2015**, *222*, 461-487, doi:10.1016/j.cis.2014.05.007.
2. Fernández-Peña, L.; Guzmán, E. Physicochemical Aspects of the Performance of Hair-Conditioning Formulations. *Cosmetics* **2020**, *7*, 26, doi:10.3390/cosmetics7020026.
3. Lindman, B.; Antunes, F.; Aidarova, S.; Miguel, M.; Nylander, T. Polyelectrolyte-surfactant association—from fundamentals to applications. *Colloid J.* **2014**, *76*, 585-594, doi:10.1134/S1061933X14050111.
4. Guzmán, E.; Fernández-Peña, L.; Ortega, F.; Rubio, R.G. Equilibrium and kinetically trapped aggregates in polyelectrolyte-oppositely charged surfactant mixtures. *Curr. Opin. Colloid Interface Sci.* **2020**, *48*, 91-108, doi:10.1016/j.cocis.2020.04.002.
5. Varga, I.; Campbell, R.A. General Physical Description of the Behavior of Oppositely Charged Polyelectrolyte/Surfactant Mixtures at the Air/Water Interface. *Langmuir* **2017**, *33*, 5915-5924, doi:10.1021/acs.langmuir.7b01288.
6. Varga, I.; Campbell, R.A. General Physical Description of the Behavior of Oppositely Charged Polyelectrolyte/Surfactant Mixtures at the Air/Water Interface. *Langmuir* **2017**, *33*, 5915-5924, doi: 5910.1021/acs.langmuir.5917b01288.
7. Guzmán, E.; Llamas, S.; Maestro, A.; Fernández-Peña, L.; Akanno, A.; Miller, R.; Ortega, F.; Rubio, R.G. Polymer-surfactant systems in bulk and at fluid interfaces. *Adv. Colloid Interface Sci.* **2016**, *233*, 38-64, doi:10.1016/j.cis.2015.11.001.
8. Gradzielski, M.; Hoffmann, I. Polyelectrolyte-surfactant complexes (PESCs) composed of oppositely charged components. *Curr. Opin. Colloid Interface Sci.* **2018**, *35*, 124-141, doi:10.1016/j.cocis.2018.01.017.
9. Bain, C.D.; Claesson, P.M.; Langevin, D.; Meszaros, R.; Nylander, T.; Stubenrauch, C.; Titmuss, S.; Klitzing, R.v. Complexes of surfactants with oppositely charged polymers at surfaces and in bulk. *Adv. Colloid Interface Sci.* **2010**, *155*, 32-49, doi:10.1016/j.cis.2010.01.007.
10. Nylander, T.; Samoshina, Y.; Lindman, B. Formation of polyelectrolyte-surfactant complexes on surfaces. *Adv. Colloid Interface Sci.* **2006**, *123-126*, 105-123, doi:10.1016/j.cis.2010.01.004.
11. Thalberg, K.; Lindman, B. Polymer-surfactant interactions recent developments. In *Interactions of Surfactants with Polymers and Proteins*, Goddard, E.D., Ananthapadmanabhan, K.P., Eds. CRC Press: Boca Raton, FL, USA, 1993.
12. Miyake, M. Recent progress of the characterization of oppositely charged polymer/surfactant complex in dilution deposition system. *Adv. Colloid Interface Sci.* **2017**, *239*, 146-157, doi:10.1016/j.cis.2016.04.007.
13. Goddard, E.D. Polymer/Surfactant Interaction: Interfacial Aspects. *J. Colloid Interface Sci.* **2002**, *256*, 228-235, doi:10.1006/jcis.2001.8066.
14. Llamas, S.; Fernández-Peña, L.; Akanno, A.; Guzmán, E.; Ortega, V.; Ortega, F.; Csaky, A.G.; Campbell, R.A.; Rubio, R.G. Towards understanding the behavior of polyelectrolyte-surfactant mixtures at the water/vapor interface closer to technologically-relevant conditions. *Phys. Chem. Chem. Phys.* **2018**, *20*, 1395-1407, doi:10.1039/c7cp05528e.
15. Mezei, A.; Mezaros, R. Novel Method for the Estimation of the Binding Isotherms of Ionic Surfactants on Oppositely Charged Polyelectrolytes. *Langmuir* **2006**, *22*, 7148-7151, doi:10.1021/la0612670.
16. Campbell, R.A.; Angus-Smyth, A.; Yanez-Arteta, M.; Tonigold, K.; Nylander, T.; Varga, I. New Perspective on the Cliff Edge Peak in the Surface Tension of Oppositely Charged Polyelectrolyte/Surfactant Mixtures. *J. Phys. Chem. Lett.* **2010**, *1*, 3021-3026, doi:10.1021/jz101179f.
17. Hernández-Rivas, M.; Guzmán, E.; Fernández-Peña, L.; Akanno, A.; Greaves, A.; Léonforte, F.; Ortega, F.; G. Rubio, R.; Luengo, G.S. Deposition of Synthetic and Bio-Based Polycations onto Negatively Charged Solid Surfaces: Effect of the Polymer Cationicity, Ionic Strength, and the Addition of an Anionic Surfactant. *Colloids and Interfaces* **2020**, *4*, 33, doi:10.3390/colloids4030033.

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- 1 18. Chiappisi, L.; Hoffmann, I.; Gradzielski, M. Complexes of oppositely charged polyelectrolytes and surfactants – recent
2 developments in the field of biologically derived polyelectrolytes. *Soft Matter* **2013**, *9*, 3896–3909, doi:10.1039/c3sm27698h.
- 3 19. Akanno, A. Bulk and Surface Properties of Polyelectrolyte Surfactant Mixtures. Universidad Complutense de Madrid, Madrid,
4 2018.
- 5 20. Laschewsky, A. Structures and Synthesis of Zwitterionic Polymers. *Polymers* **2014**, *6*, 1544–1601, doi:10.3390/polym6051544.
- 6 21. Kotsmar, C.; Pradines, V.; Alahverdjieva, V.S.; Aksenenko, E.V.; Fainerman, V.B.; Kovalchuk, V.I.; Krägel, J.; Leser, M.E.;
7 Noskov, B.A.; Miller, R. Thermodynamics, adsorption kinetics and rheology of mixed protein–surfactant interfacial layers. *Adv.*
8 *Colloid Interface Sci.* **2009**, *150*, 41–54, doi:10.1016/j.cis.2009.05.002.
- 9 22. Petrović, L.; Milinković, J.; Fraj, J.; Bučko, S.; Katona, J.; Spasojević, L. Study of interaction between chitosan and sodium lauryl
10 ether sulfate. *Colloid Polym. Sci.* **2017**, *295*, 2279–2285, doi:10.1007/s00396-017-4205-7.
- 11