Experimental report

29/11/2023

Proposal: **9-13-1052** **Council:** 10/2022

Title: Adsorption to hair-mimetic surfaces

Research area: Soft condensed matter

This proposal is a continuation of 9-13-1006

Main proposer: **Mark RUTLAND**

Experimental team: Serena COZZOLINO
Gustavo LUENGO

Local contacts: Alexei VOROBIEV
Philipp GUTFREUND

Samples: D2O
NaCl
Chitosan
Deuterated tetradecyltrimethylammonium bromide
Tetradecyltrimethylammonium bromide
Deuterated Sodium Dodecylsulfate
18-MEA thiol
poly(diallyl dimethylammonium chloride)
sodium 3-mercapto-1-propanesulfonate
N-(2-sulfanylethyl)icosanamide

Instrument	Requested days	Allocated days	From	To
SUPERADAM	4	0		
D17	4	0		
FIGARO	4	4	26/05/2023	30/05/2023

Abstract:

This is a continuation of the ILL proposal 9-13-1006. It supports Serena Cozzolino's InnovaXN PhD project, which uses biomimetic surfaces to gain insight into the interaction properties of hair surfaces, which are challenging to observe directly. This is fundamental knowledge for the industry partner: for improving product performance in restoring hair ¿function¿ and replacing existing ingredients with biosourced ones. NR is the primary technique for this project, as contrast variation is key to exposing the hierarchical adsorption on the hair-mimetic surface from complex mixtures of surfactants and polyelectrolytes. The biomimetic surfaces are produced by self-assembly of thiols on gold. L'Oreal recently synthesised the thiol analogue of 18-MEA, which is the most abundant lipid found on the hair surface and presents a characteristic methyl branch. This vastly improves the biomimetic characteristics of the produced model surfaces. The proposed experiments will reveal i) how the branched properties of the lipids affect adsorption, as well as ii) revealing the hierarchy in adsorption in z and iii) validate the biomimetic hair model.

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Cycle 232, May 26th to 30th – instrument: FIGARO

This was a continuation of the ILL proposal 9-13-1006. The aim of both is to study the interaction properties of hair at the molecular level, working on hair-mimetic surfaces and simplified formulations. The model surfaces are designed to reproduce either the hydrophilic, negatively charged surface of damaged hair, or the hydrophobic surface of healthy hair, which is characterized by the presence of a lipid layer. In the previous proposal we studied adsorption of model surfactants and polyelectrolytes on model hair surfaces produced by using commercially available thiols self-assembled on gold. In the meantime, we obtained some custom-made, long-chain thiols that can better mimic the chain packing of the hair lipid layer. The aim of experiment 9-13-1052 was then to complete the characterization of those new surfaces in the presence of selected surfactants and polyelectrolytes of cosmetic relevance.

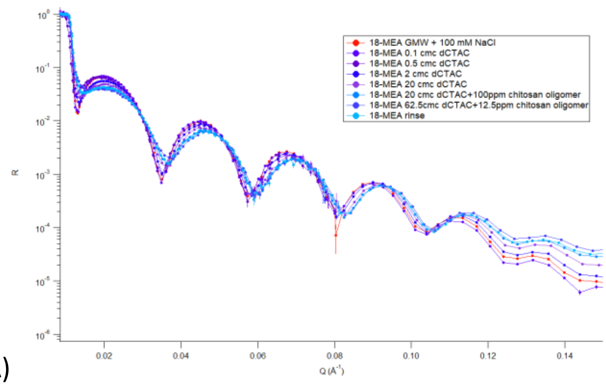
The produced surfaces specifically were:

- 18-MEA thiol (derivative of the most abundant hair lipid)
- EA thiol (to compare the effect of the antepenultimate branch of 18-MEA
- Mixed 18-MEA/sulfonate thiols (partly damaged hair model)
- Sulfonate thiol (fully damaged hair model)

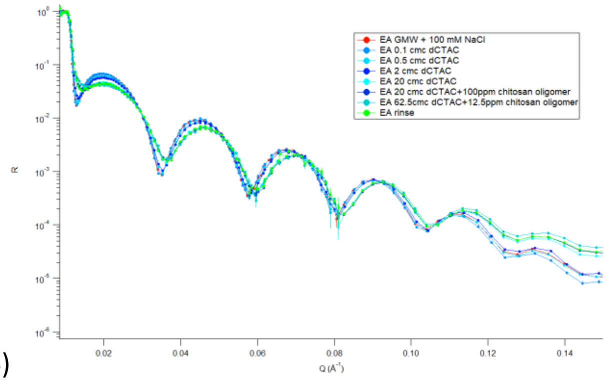
The adsorption sequence we applied after characterization of the surfaces in gold contrast-matched water (GCMW), was as follows:

- Deuterated cationic surfactant d-CTAC, at concentrations of 0.1, 0.5, 2 and 20 cmc (critical micellar concentration). Cationic surfactants are used in shampoos to improve the properties of the formulations.
- Mixtures of d-CTAC with chitosan oligomer, at two different ratios to mimic in one case the same ratio in terms of cmc used in 9-13-1006, and in the second case to mimic a cosmetically relevant surfactant/polyelectrolyte ratio. This step aims at understanding whether the two cationic species compete or cooperate in adsorption.
- Rinsing step followed by 100 ppm chitosan oligomer, to check adsorption of the polyelectrolyte alone after exposure of the surface to the surfactant/polyelectrolyte mixture.
- Rinsing step followed by 100 ppm chitosan polymer, to check effect of the molecular weight.
- 20 cmc d-SDS, to check adsorption of the anionic surfactant after surface exposure to cationic species, followed by rinsing. Anionic surfactants are the main component of shampoos, so defining its action on pre-treated surfaces is of interest.
- 100 ppm pDADMAC, to compare adsorption of the natural polymer chitosan to a synthetic one, followed by rinsing.
- Hydrogenous SDS at the concentrations of 0.5 and 20 cmc, to add information by contrast variation, followed by a final rinsing step.

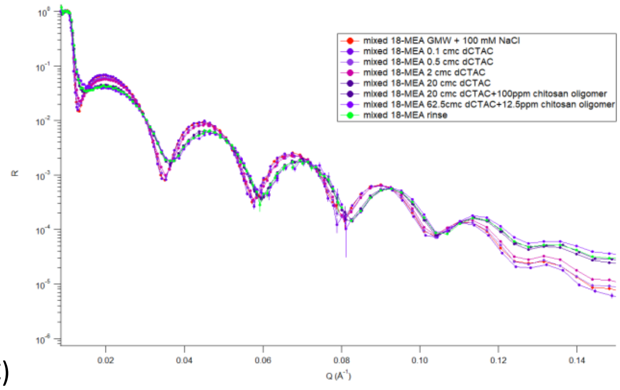
Data analysis is still ongoing, but qualitative results are presented below.



A)



B)



C) D)

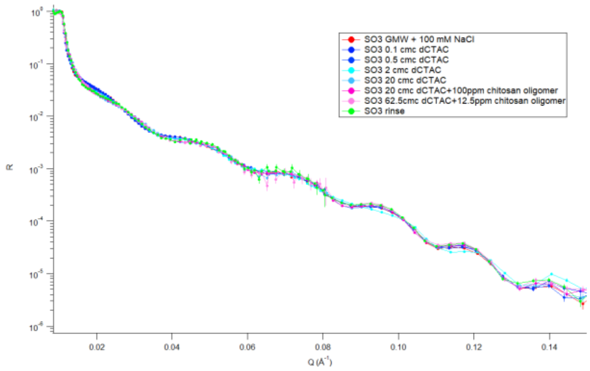
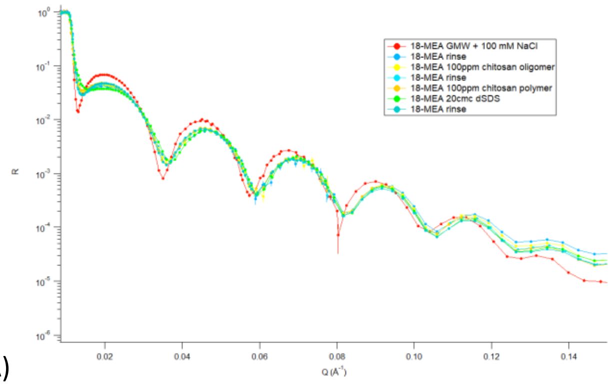
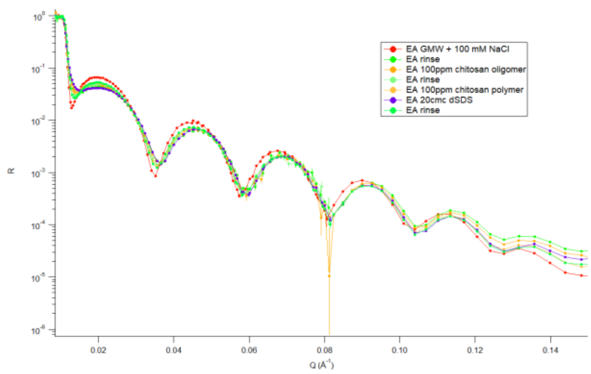


Figure 1. NR curves of A) 18-MEA thiol, B) EA thiol, C) mixed 18-MEA/sulfonate thiols, D) sulfonate thiol, in the presence of d-CTAC and d-CTAC/chitosan solutions. Signal variations for surfaces A to C are in the same range but they look more gradual in the case of A. Rinsing mostly does not remove adsorbed layers. Variations in D) look smaller due to the thinner thiol layer. To understand whether the adsorbed layer, in the case of the mixture, is composed of only one or both species and describe it fully, data fitting is needed.

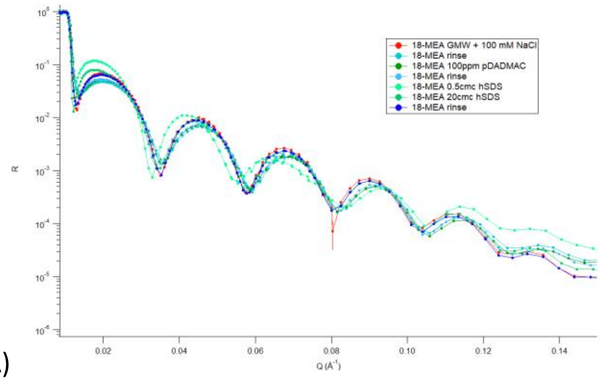


A)

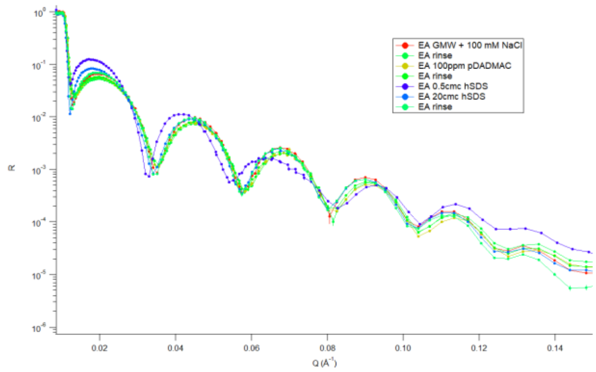


B)

Figure 2. NR curves for A) 18-MEA thiol and B) EA thiol in the presence of chitosan oligomer and polymer, and d-SDS. Variations for the mixed 18-MEA/sulfonate thiols are the same as A (not shown). Variations are littler than in Fig.1. Rinsing removes more of the adsorbed layer on B than on A.

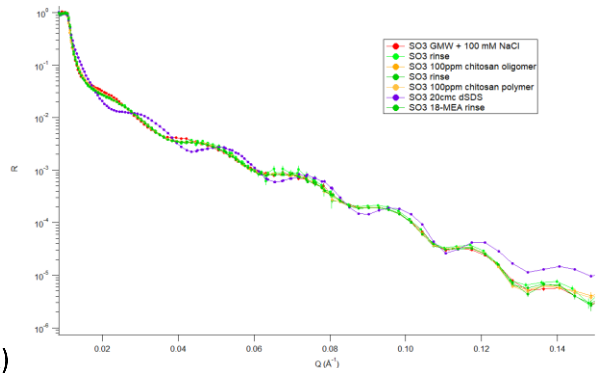


A)

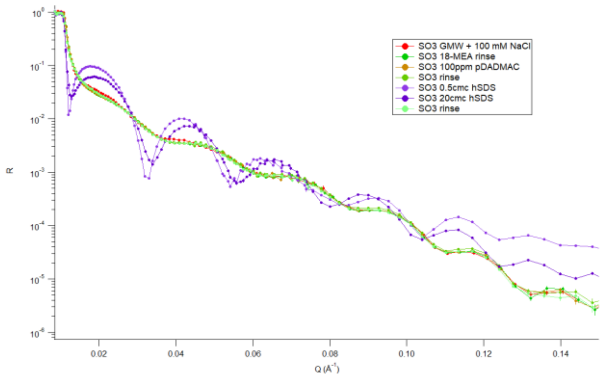


B)

Figure 3. NR curves for A) 18-MEA thiol, and B) EA thiol in the presence of pDADMAC and h-SDS. The shifts after addition of h-SDS are evident due to the different contrast. The final rinse brings the curves almost fully back to the initial ones.



A)



B)

Figure 4. NR curves of the sulfonate thiol surface in the presence of A) chitosan, oligomer and polymer, and d-SDS, and B) pDADMAC and h-SDS. Due to the different contrast of this surface with the adsorbed layers, shifts of both d-SDS and h-SDS are clearly visible. Rinsing brings the curve back to its initial state.