Experimental report

29/11/2023

Proposal: CRG-2962 **Council:** 10/2022

Title: Adsorption to hair-mimetic thiol surfaces

Research area: Soft condensed matter

This proposal is a new proposal

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Local contacts: Alexei VOROBIEV

Samples:
D2O
NaCl
Chitosan
Deuterated Sodium Dodecyl Sulfate
Deuterated tetradecyltrimethylammonium bromide
Tetradecyltrimethylammonium bromide
18-MEA thiol
N-(2-sulfanylethyl)eicosanamide
sodium 3-mercaptopropanesulfonate

Instrument	Requested days	Allocated days	From	To
SUPERADAM	4	4	22/06/2023	26/06/2023

Abstract:

This proposal is to support 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. Neutron reflectometry 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, June 22nd to 26th – instrument: SuperADAM

The aim of this experiment was 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 the hydrophilic, negatively charged surface of partly or fully damaged hair. Healthy hair is characterized by the presence of a lipid layer, which is removed in part or fully depending on the extent of the damage caused by processes such as bleaching. Models can be produced by self-assembly of chosen thiols on gold surfaces. So, the two test surfaces produced for this experiment were:

- Mixed 18-MEA/sulfonate thiols (partly damaged hair model). 18-MEA is the most abundant component of the hair lipid layer.
- 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:

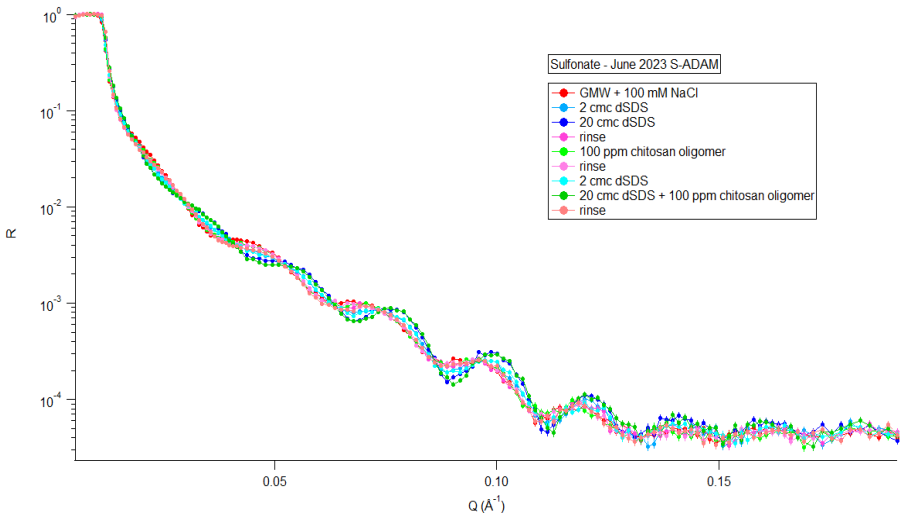
- Deuterated anionic surfactant d-SDS, at concentrations of 2 and 20 cmc (critical micellar concentration), followed by a rinsing step. Anionic surfactants are the main component of shampoos.
- 100 ppm chitosan oligomer, followed by rinsing and again 2 cmc d-SDS, to check adsorption after exposure of the surface to a polyelectrolyte.
- Mixture of d-SDS and chitosan at a cosmetically relevant ratio, followed by rinsing.

Additional steps were then performed on the partly damaged hair model, to compare with the sequence applied to the fully damaged hair model during experiment 9-13-1052 on FIGARO. These steps where:

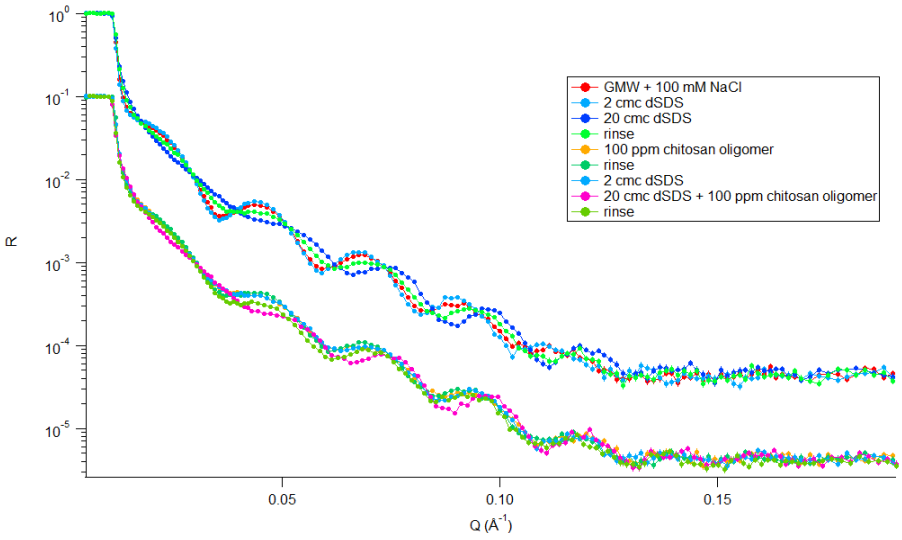
- Deuterated cationic surfactant d-CTAC, at concentrations of 0.1, 0.5, 2 and 20 cmc (critical micellar concentration). Cationic surfactants are used in shampoos to improve the properties of the formulations.
- Mixtures of d-CTAC with chitosan oligomer, at two different ratios to mimic in one case the same ratio in terms of cmc used with d-SDS, and in the second case (as the cmc of d-CTAC is very different from that of d-SDS) 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 polymer, to check effect of the molecular weight.
- 20 cmc h-SDS, to check adsorption of the anionic surfactant after surface exposure to the cationic species, followed by rinsing. Anionic surfactants are the main component of shampoos, so defining its action on pre-treated surfaces is of interest. The use of the hydrogenous instead of the deuterated species used in the beginning of the sequence allows us to have more information on the system thanks to the contrast variation.
- 100 ppm pDADMAC, to compare adsorption of the natural polymer chitosan to a synthetic one, followed by rinsing.

In addition, we planned to run a blank measurement repeating the same steps on a bare gold surface. We did not succeed, though, as we had problems with the supposedly clean gold-coated block, that showed some fringes, characteristic of an adsorbed layer on gold (data not shown).

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



A)



B)

Figure 1. NR curves of A) sulfonate thiol, and B) mixed 18-MEA/sulfonate thiols, in the presence of d-SDS, chitosan oligomer and d-SDS/chitosan solutions. Rinsing removes part of the adsorbed layers. The solutions containing 20 cmc d-SDS cause the biggest change, while the presence of chitosan is not easily detectable. To better understand the composition of the adsorbed layers, data fitting is needed.

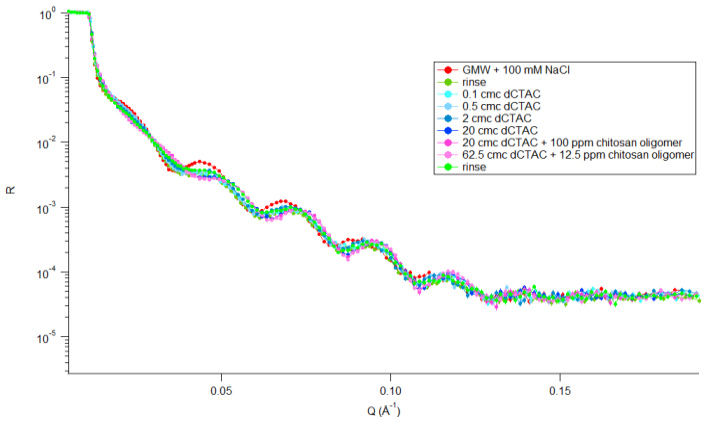
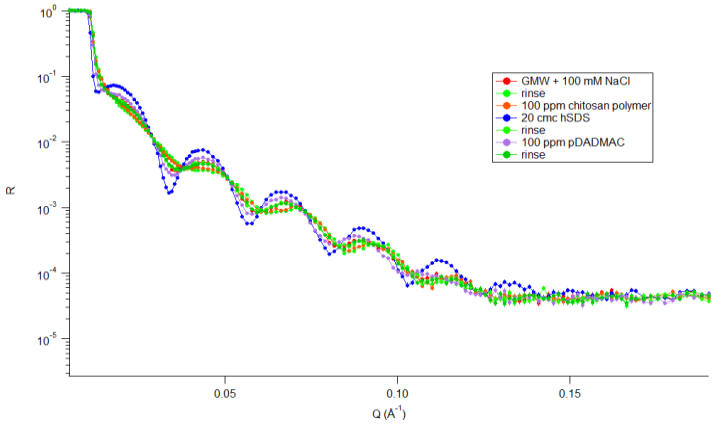


Figure 2. NR curves of the mixed 18-MEA/sulfonate thiols in the presence of d-CTAC and d-CTAC/chitosan solutions. Rinsing mostly does not remove adsorbed layers. To understand whether the adsorbed layer, in the case of the mixture, is composed of only one or both species and describe it fully, data fitting is needed.



D)

Figure 3. NR curves for the mixed 18-MEA/sulfonate thiols in the presence of chitosan polymer, h-SDS, and pDADMAC. 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.