Standard Project

Experimental Report template

Proposal title: pH-resolved in-situ study of biosurfactant-biopolymer colloidal solutions		**Proposal number: SC-5125**
Beamline: BM26	**Date(s) of experiment:** from: 09/11/2021 to: 11/11/2021	**Date of report:** 17/07/2023
Shifts: 6	**Local contact(s):** Daniel Hermida-Merino	*Date of submission:* **17/07/2023**

Objective & expected results:
The goal of this proposal was initially to study the effect of pH in mixtures of biosurfactants and biopolymers, and in particular how pH-induced phase transitions in biosurfactants affect the nanostructure in the combined system. The results from this study were to be correlated with rheology data recorded elsewhere.

Reorientation of the project:
Due to an unexpected excess of beamtime allocated to us by other beamlines at ESRF and Soleil during the year 2021, and mainly due to the lack of foreign users caused by COVID restrictions, the experiments described in the objective were able to be performed elsewhere, prior to the present beamtime. For this reason, the SC-5125 proposal was dedicated to study a wide variety of biosurfactant systems, for which complementary SAXS data were needed in view of future publications. This strategy revealed itself successful, as the data collected during SC-5125 have been used in three different peer-reviewed articles, mentioned in the last section of this document.

Results and the conclusions of the study (main part):

Basic beamline setup: the beam center was set at X= 0.00455; Y= 0.08431. The temperature was set at 25°C, unless otherwise stated. The energy of the beam was set at 12.00 KeV and the sample-to-detector distance at 2.6 m. The signal was integrated azimuthally at the beamline using the given software and in order to obtain the I(q) vs. q spectrum after masking systematically wrong pixels and the beam stop shadow.

Sample environments: 1) Linkam for temperature-dependent experiments (available at the beamline) combined to a 2 mm capillary; 2) Flow-through capillary (brought by us), for single samples (gels, solutions).

Samples. We have analyzed three sets of unrelated systems.
The first one was constituted by a glucolipid undergoing a lamellar to vesicle transition upon heating and a vesicle to nanotube transition upon cooling. This system was studied between 25°C and 110°C using a heating and cooling rate of 10°C/min and 1°C/min and an acquisition time of 1 s and frequency of acquisition of 15 s. For this specific experiments, we have also employed the WAXS detector. The selected SAXS-WAXS data are shown in Figure 1 and are published in (Baccile et al. 2022).

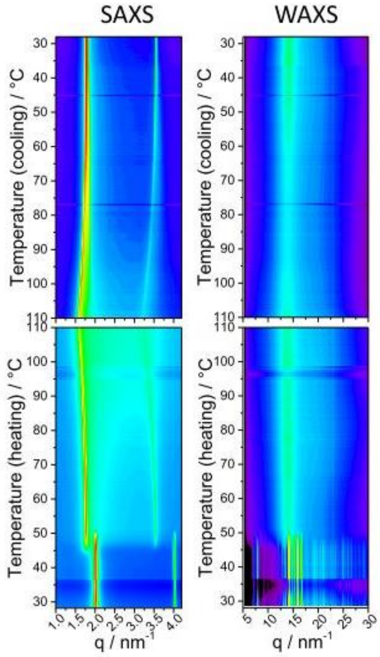

Figure 1 - Temperature-resolved in situ SAXS-WAXS experiments recorded on a G-C18:1-OH sample at 50 wt% in water.(Baccile et al. 2022)

The second set of samples was constituted by glucolipid metallogels recorded in a 2 mm flow-through capillary at room temperature, using an acquisition time of 1 min. Capillary was loaded with a 1 mL syringe. These experiments were necessary to complete a previous dataset and in particular to study the effect of specific cations on the fibrillation of a biobased glucolipid. In this study, we have tested Ca^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+} and Au^{3+} metal ions in gels prepared at concentration of 1 wt% and pH 8. Typical SAXS data were exploited in (Poirier et al. 2022), from which Figure 2 is extracted.

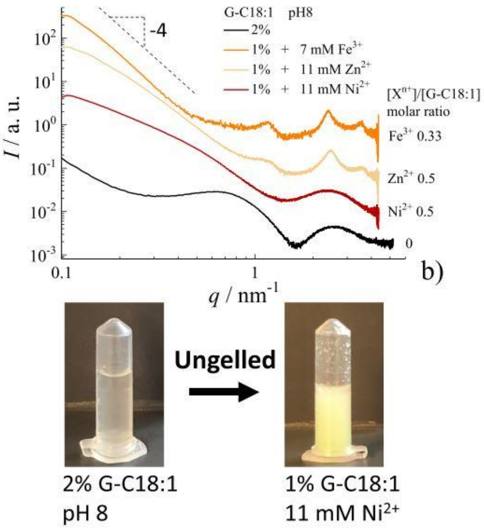

Figure 2 - SAXS profiles of G-C18:1 aggregates containing Fe^{3+}, Ni^{2+}, and Zn^{2+}. The image of the reverse tube illustrates the transition from a single phase, micellar solution, to a two-phase, metal-containing glucolipid aggregate in water.(Poirier et al. 2022)

The third set of experiments consisted in studying the self-assembly of RhaRhaC10C10 rhamnolipids using a flow-through 2 mm capillary, loaded with a 1 mL syringe. In this case, the lipid concentation was 2.5 wt%, studied at room temperature and pH 7.5, 6.05 and 5, with an acquisition time of 1 min. The data from this experiments are published in (Baccile et al. 2023).

Data treatment

The 2D SAXS signal was treated (integration, correction for absolute intensity and background subtraction) at the beamline soon after acquisition using the local software. Further analysis of the background-subtracted signal depend on the project. For instance, temperature-resolved experiments were arranged in a contour plot fashion (Figure 1), while data recorded on rhamnolipids were analyzed using model-dependent and model-independent approaches. (Baccile et al. 2023)

Justification and comments about the use of beam time:

The use of the beamline was justified by the appropriate q-range, which matched our needs, but also the possibility to combine SAXS-WAXS and to adapt the sample environment (Linkam or flow-through capillary) to the topic under study.

Problems during beamtime:

We did not experience major problems during the beamtime. The beamline was well prepared prior to our arrival and assistance was guaranteed by the local contact all along.

Publications associated to the data collected during beamtime:

Baccile, Niki, Cédric Lorthioir, Abdoul Aziz Ba, Patrick Le Griel, Javier Perez, Daniel Hermida-Merino, Wim Soetaert, and Sophie L. K. W. Roelants. 2022. “Topological Connection between Vesicles and Nanotubes in Single Component Lipid Membranes Driven by Head-Tail Interactions.” *Langmuir* 38 (48): 14574–14587. https://doi.org/10.1021/acs.langmuir.2c01824.

Baccile, Niki, Alexandre Poirier, Javier Perez, Petra Pernot, Daniel Hermida-merino, Patrick Le Griel, Christian C Blesken, Conrad Mu, Lars M Blank, and Till Tiso. 2023. “Self-Assembly of Rhamnolipid Bioamphiphiles: Understanding the Structure−Property Relationship Using Small-Angle X- ray Scattering.” *Langmuir*, 10.1021/acs.langmuir.3c00336. https://doi.org/10.1021/acs.langmuir.3c00336.

Poirier, Alexandre, Patrick Le Griel, Javier Perez, Daniel Hermida-Merino, Petra Pernot, and Niki Baccile. 2022. “Metallogels from Glycolipid Biosurfactant.” *ACS Sustainable Chemistry & Engineering* 10 (50): 16503–16515. https://doi.org/10.1021/acssuschemeng.2c01860.