Experimental report

02/10/2025

Proposal: EASY-1216 **Council:** 4/2023

Title: Structural characterization of self-assembled highly organized hydrogels composed of a glycolipid-silver nanoparticles complex

Research area: Soft condensed matter

This proposal is a new proposal

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Local contacts: Lionel PORCAR

Samples: glycolipid

Instrument	Requested days	Allocated days	From	To
D22	12	12	26/10/2023	27/10/2023

Abstract:

We recently published (10.1039/ D2SM01218A; 10.1021/acssuschemeng.2c01860) the synthesis of metallogels from biobased glycolipids (GLs). SAXS, cryo-TEM and solid-state NMR had shown that GLs/Ag+ complex fibrillates to form a hydrogel at RT. A broad set of SAXS data shows a series peaks in a 1:2:3...ratio, suggesting a lamellar, raft-like, arrangement of the fibers.
Unpublished high-resolution cryo-TEM experiments actually reveal that the core of the fibers is composed by monodisperse silver nanoparticles (NPs, d= 2.5 nm) co-aligned with the fiber's longest (infinite) axis. The presence of the NPs in the absence of reducing agents is puzzling as well as their structural role. Since, both SAXS and TEM could reduce silver during observation, SANS is required for two critical reasons: 1) neutrons won't reduce Ag+ during analysis; 2) difference in contrast between SANS with SAXS will help determining the relative contribution between GLs and silver (Ag+ or NPs). We'll learn if the 1:2:3... peaks in SAXS belong to the GLs or Ag NPs. We plan to study not more than 10 samples at [0.001 < q/Å^-1 < 0.7]: 2 controls + 8 time stamps, from mixing of GLs with Ag+ solution, t_0h, to t_24h.

Standard Project

Experimental Report template

Proposal title**:** Structural characterization of self-assembled highly organized hydrogels composed of a glycolipid-silver nanoparticles complex		**Proposal number:** **EASY-1216**
Beamline: D22	**Date(s) of experiment:** from: 26/10/2023 to: 27/10/2023	**Date of report:** 02/10/2025
Days: 1	**Local contact(s):** L. Porcar	*Date of submission:* **02/10/2025**

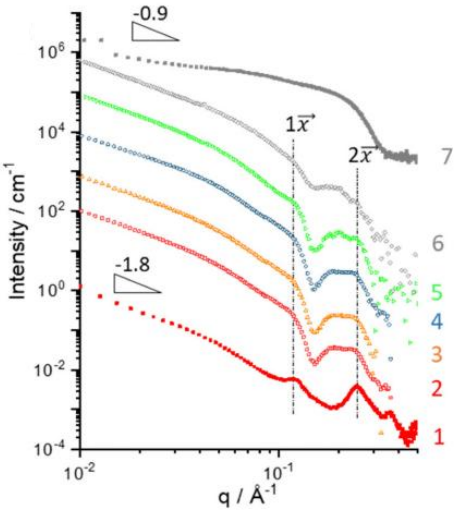
Background:
In recent publications (10.1039/ D2SM01218A; 10.1021/acssuschemeng.2c01860), we have shown that silver (Ag) metallogels can be prepared from a biobased single-glucose lipid (GL). The combination of SAXS, cryo-TEM and solid-state NMR had shown that GL/Ag complex fibrillates to form a hydrogel at RT. A broad set of SAXS data shows a series of peaks in a 1:2:3...ratio, suggesting a lamellar, raft-like, arrangement of the fibers. Interestingly, high-resolution cryo-TEM experiments actually reveal that the core of the fibers is composed by monodisperse silver nanoparticles (NPs, d= 2.8 nm) co-aligned with the fiber's longest (infinite) axis. The presence of the NPs in the absence of reducing agents is puzzling but explained by the fact that X-rays and electrons reduced silver during analysis. SANS is then required for various reasons: 1) neutrons are not expected to reduce silver during analysis; 2) The difference in contrast between SANS and SAXS should help determining the relative contributions between GLs and silver to the scattering signal. The goal will then be double: a) collect the signal of the GL/Ag fibrous systems before reduction and avoiding beam damage; b) determine whether or not the 1:2:3... peaks in SAXS belong to the periodic arrangement of GL fibers or to the Ag NPs. Considering the short time, we plan to study not more than 10-20 samples in the q-range at [0.001 < q/$Å^{-1}$ < 0.7].

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

The samples studied in this short proposal are composed of 2 wt% of glucolipid G-C18:1 in water at pH 8 to which a known content of Ag^+ ions is added, so that the final molar ratio between the lipid and silver ions is one. This sample spontaneously forms a gel at room temperature and it is considered hereafter as the control, before reduction. Eventually, reduction can be performed in various ways, using radiolysis with γ-rays, ascorbic acid or X-rays when SAXS is employed.
In this respect, neutrons are complementary to X-rays to study the structure of matter due to the differences in its scattering length densities (sld) towards these sources of radiation. Indeed, the contrast between silver and water (Δ(sld)= 68.4 $\cdot 10^{-6}$ $Å^{-2}$) using X-rays is so high that the spatial organization of the silver nanoparticles dominates the SAXS scattered intensity both on the control and reduced (gel) sample. On the other hand, when a neutron source is used, the contrast between silver and (heavy) water is much smaller (Δ(sld)= 2.9 $\cdot 10^{-6}$ $Å^{-2}$), and actually smaller compared to the contrast between organic matter and D_2O (Δ(sld) ~6 $\cdot 10^{-6}$ $Å^{-2}$). Another advantage of neutrons is that they do not reduce silver, even though one could question the reduction by gamma rays. Although possible, this event is most likely excluded, as the acquisition time for a single SANS spectrum is 5 min, while γ-rays reduction experiments have shown that at least 2 hours of continuous irradiation are required to start to observe a change in color (from white to yellow-brown). For these reasons, SANS is essentially sensitive to the fiber-solvent

contrast both in the control and in the reduced samples. Finally, in order to differentiate the scattering signals of fibers and nanoparticles, the liquid sample irradiated by γ-rays for 28 hours is used as an additional control. Indeed, in this sample, nanoparticles and fibers coexist, but without co-alignement. Therefore, SAXS characterizes a suspension of nanoparticles, while SANS a dispersion of fibers.

The unique simultaneous SAXS-SANS (D22 beamline, ILL) coupled experiment (Figure 1) was then performed on the control $\{Ag^{+}\}$G-C18:1 and reduced $\{Ag^{0}\}$G-C18:1 (gel and liquid) samples in order to better understand both the impact of the silver nanoparticles on the fibers' organization and the fibers' structure prior to reduction. First of all, the scattering profiles of the overly reduced liquid $\{Ag^{0}\}$G-C18:1-radiolysis (28h) sample are completely different if probed by SAXS (7 in Figure 1) or SANS (6 in Figure 1), performed on the same sample, where both techniques are combined. The former signal is representative of spherical objects while the latter is characteristic of anisotropic flat structures (slope of -1.8 at low-q). This control experiment demonstrates that in the absence of co-alignment, the SAXS and SANS profiles are different for the same sample. Similarly, combined SAXS and SANS profiles of the same $\{Ag^{+}\}$G-C18:1 control sample (1 and 2 in Figure 1) are also quite different. The SAXS pattern, dominated by the Ag^{0} NPs (*in situ* reduction), reveals the long-range side-by-side arrangement of the fibers. In the SANS spectrum, on the contrary, one recognizes the profile of individual fibers, same as for 6 in Figure 1, but with a contribution at 0.12 $Å^{-1}$ and 0.24 $Å^{-1}$, identified as a lamellar periodicity due to the raft-like association of the fibers. Indeed, very similar profiles are observed for all reduced samples (3, 4, 5 in Figure 1), except for 6 in Figure 1, the only sample in which fibers do not align. Interestingly, neither the diffraction peaks of SAXS, nor the form factor of SANS are shifted upon reduction, thus indicating that the NPs are well embedded in the network of G-C18:1 ribbons and their presence neither disrupt the organization of the fibers nor cause significant displacement of the glycolipids within the fibers themselves. These experiments were published in 10.1039/D5MH00105F.



Profile	Technique	Sample
7	SAXS	*γ-rays 28h (Liquid)*
6	SANS	*γ-rays 28h (Liquid)*
5	SANS	*γ-rays 4h30 (Gel)*
4	SANS	*Ascorbic Acid (Gel)*
3	SANS	*In situ X-rays (Gel)*
2	SANS	*Control (Gel)*
1	SAXS	*Control (Gel)*

Figure 1 – SAXS and SANS profiles of Ag/GL samples prepare from the glucolipid G-C18:1 at 2 wt% in water at pH 8. Control stands for the gel before reduction. The reduction method is given in the table next to each sample. Profiles 1-2 and 6-7 correspond to the same sample where acquisition was made with combined SAXS/SANS

Data treatment

All data have been treated on site with the help of the Local Contact.

Justification and comments about the use of beam time:

The coupled SAXS-SANS experiment is unique and the only possibility to decouple the contribution of the organic fibers from the inorganic NPs, but also to analyse the sample before in situ reduction by the X-rays. In the present experiment, the sample-to-detector distances were 8 m and 1.4 m for SANS and 0.56 m for SAXS, and the experiments were performed at a

wavelength of 6 Å for SANS and 1.54 Å for SAXS

Problems during beamtime:

We did not experience any trouble during the beamtime.