Experimental report

17/12/2020

Proposal: 9-13-915 **Council:** 4/2020

Title: Measuring the bending modulus of lamellar gels composed of new microbial glycolipids

Research area: Soft condensed matter

This proposal is a resubmission of 9-10-1543

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Local contacts: Ingo HOFFMANN

Samples: glycolipid

Instrument	Requested days	Allocated days	From	To
IN15	3	3	18/09/2020	21/09/2020

Abstract:

Microbial glycolipids are natural molecules obtained from the microbial digestion of fatty acids and sugars. They have low toxicity, high biodegradability and their synthesis process (industrial microbiology) is environmentally friendly. The most important molecules studied so far are called sophorolipids, rhamnolipids and glucolipids. All of them have in common a sugar headgroup (sophorose, rhamnose or glucose) covalently bonded to a lipid with a free COOH group available at the other end of the molecule. They have been initially developed as green detergents to replace petrochemical ones, but this seemingly promising usage starts to be disregarded due to the high cost/benefit ratio. In a recent set of works we have shown that a single-glucose lipid forms lamellar hydrogels, which can then open new perspectives of applications. We found that the hydrogel elastic properties depend on pH and ionic strength. We believe that the bending modulus of the lipid membrane is important for the gel properties and that the modulus vary with pH and ionic strength. However, the modulus is unknown for this new class of lipids and we aim at measuring it using neutron spin echo experiments.

Standard Project

Experimental Report template

Proposal title: Measuring the bending modulus of lamellar gels composed of new microbial glycolipids		**Proposal number: 9-13-915**
Beamline: IN15	**Date(s) of experiment:** from: 18/09/2020 to: 21/09/2020	**Date of report:** 17/12/2020
Days: 3	**Local contact(s):** I. Hoffmann	*Date of submission: 17/12/2020*

Background:
Microbial glycolipids are natural molecules obtained from the microbial digestion of fatty acids and sugars. They have low toxicity, high biodegradability and their synthesis process (industrial microbiology) is environmentally friendly. The most important molecules studied so far are called sophorolipids, rhamnolipids and glucolipids. All of them have in common a sugar headgroup (sophorose, rhamnose or glucose) covalently bonded to a lipid with a free COOH group available at the other end of the molecule. They have been initially developed as green detergents to replace petrochemical ones, but this seemingly promising usage starts to be disregarded due to the high cost/benefit ratio. Fortunately, other properties have been reported, i.e. soil remediation, nanoparticle stabilization, antibacterial and, in some cases, anticancer. However, even in niche applications, the immediate employment of the most promising microbial glycolipids has historically been hindered by the lack of physico-chemical characterization. One of the properties which widely characterizes lipids and lipid membranes is the bending modulus, BM, κ, unknown for microbial glycolipid membranes.

Results and the conclusions of the study (main part):
Neutron Spin-Echo (NSE) measurements have been performed at the instrument IN15. Four different wavelengths (λ) have been used, namely 13.5, 12, 10 and 8 Å allowing to reach maximum Fourier times, t, of 477, 335, 194 and 99 ns, respectively and covering a q range from 0.03 to 0.14 $Å^{-1}$, where $q = 4\pi/\lambda \sin(\theta/2)$ is the modulus of the scattering vector with scattering angle θ. For fitting the data, the Zilman-Granek model was applied. In this model the intermediate scattering function is given by Eq. 1

$$S(q,t) = e^{-(\Gamma_{ZG} t)^{\frac{2}{3}}} \quad \text{Eq. 1}$$

With

$$\Gamma_{ZG} = \alpha\gamma\left(\frac{k_bT}{\kappa}\right)^{\frac{1}{2}}\left(\frac{k_bT}{\eta}\right)q^3 \qquad \text{Eq. 2}$$

where $\gamma \approx 1$ for $\frac{k_bT}{\kappa} << 1$, η is the solvent viscosity k_b is the Boltzmann constant, T is the temperature and κ is the bending rigidity. The relaxation mode observed in the q and t range of NSE is not a pure bending mode but a combined bending-stretching mode, which also depends on the compressibility modulus κ, which itself is proportional to the bending rigidity and results in a renormalised bending rigidity, which can simply be used in the framework of the Zilman-Granek model and results in a modification of the prefactor α in eq. (2). The exact value of that prefactor is still a matter of debate but the current consensus seems to point towards a value of α= 0.0069.

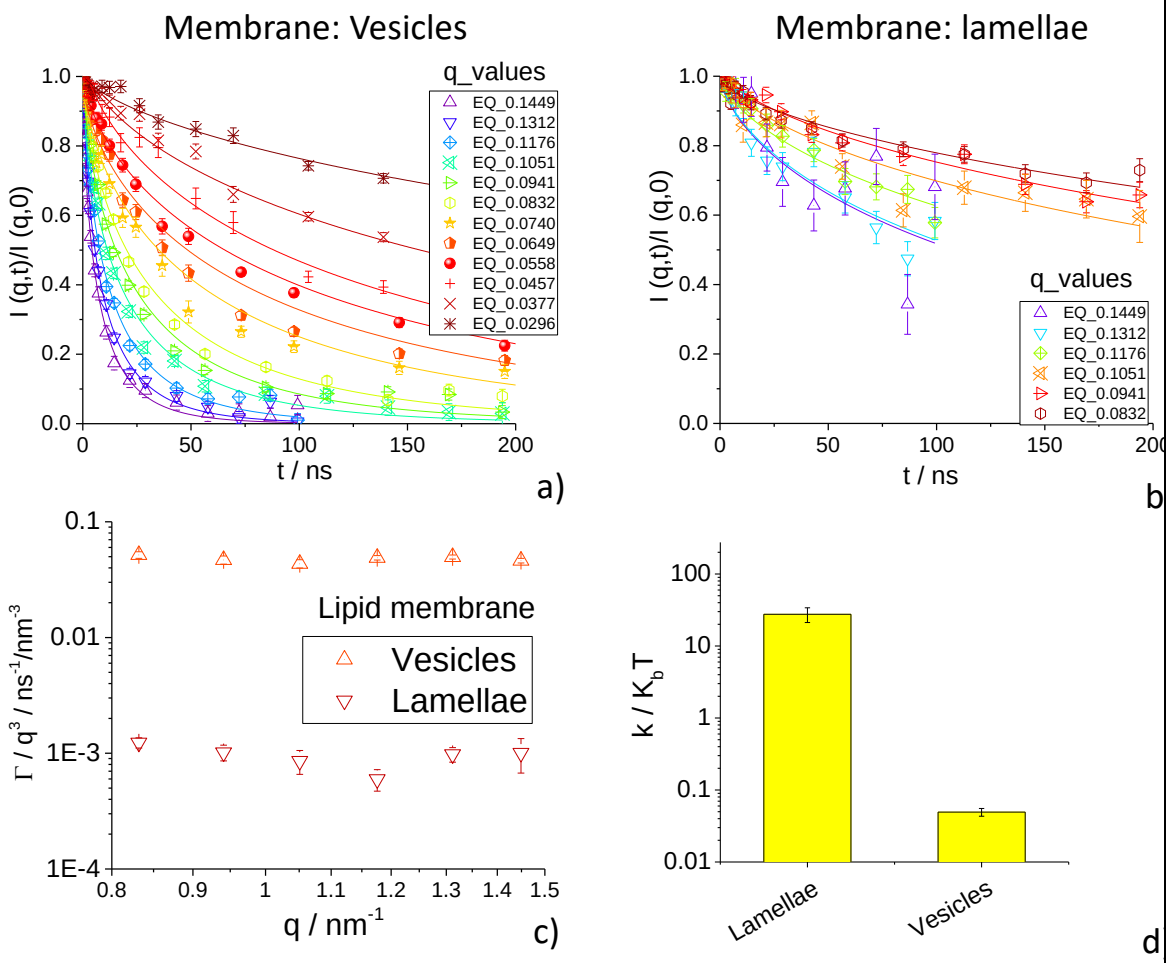

Figure 1 – NSE decay profiles of the normalized intensity recorded against spin echo time for various q-values. Experiments are recorded for glycolipid bilayers in the morphology of a) vesicle and b)

lamellae. c) q-independent evolution of γ_{zg}/q^3 between 0.8 Å^{-1} and 1.5 Å^{-1}. d) Bending rigidity of microbial glycolipid vesicles and lamellae.

Figure 1a and Figure 1b show the typical decay profile of microbial glycolipid bilayer membranes in the shape of, respectively, vescicles and flat lamellae. The faster decays observed in Figure 1b over a broad range of q-values is indicative of the flexibility of the membrane, when compared to slower decays of Figure 1b, indicative of stiffer objects. Plot of $\frac{\Gamma_{ZG}}{q^3}$ against q in Figure 1c for both samples show its expected indipendence against the wavevector in the q-range explored and, finally, Figure 1 d reports the scaled bending rigidity of both glycolipid membranes vesicles (κ = ~0.5 k_bT) and lamellae (κ = ~30 k_bT). These values quantify κ for these new systems and will be able to compare them to the bending rigidity of phospholipid membranes found in the literature.

Data treatment

Raw decay data were collected at the beamline and manually treated in house by the user. For each sample, the values of I(q,t)/I(q,0) are plotted as in Figure 1a,b with their respective error. Each curve is fitted individually using Origin software using Eq. 1. The quality of the fit is controlled for each profile. The value of $\frac{\Gamma_{ZG}}{q^3}$ is then calculated for each sample and each q-value so to verify the linearity of the results. From the rearranged Eq. 2, the value of the bending modulus is the calculated.

Justification and comments about the use of beam time:

The beamtime allowed to us was just about what we needed. These systems were nevered explored before and the user experienced NSE for the first time. We did then perform 3 to 4 preliminary experiments before running all samples under optimal conditions. Support by the local contact was full at all time. We run about 8 to 10 samples, of which the corresponding data were treated qualitatively during the beamtime and quantitatively immediately afterwards. A publication will be written as soon as possible in tight collaboration with the local contact, who verified at all time the quality of the data.

Problems during beamtime:

We did not experience any trouble during the beamtime.