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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** SHEAR-INDUCED TRANSITIONS IN CATANIONIC UNILAMELLAR VESICLES	**Experiment number**: SC-3131
Beamline:	**Date of experiment**: from: 22/07/2011 to: 25/07/2011	**Date of report**: 11/09/2012
Shifts: 9	**Local contact(s)**: Theyencheri Narayanan	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Introduction: The hexadecyltrymethylammonium octylsulfonate (TASo) – water system forms a dilute lamellar phase down to 2.6 wt%. At lower concentrations, the lamellar phase is dispersed in a dilute L_1 phase. Cryo-TEM and SANS measurements have shown that between 1.2 and 0.3 wt% the dispersed lamellae is essentially in the form of unilamellar vesicles. Recently, steady-state rheology experiments have detected a strange shear-thickening regime when these vesicle phases are subjected to increasing shear-rate conditions. This regime must imply strong structural changes in the sample, hard to predict with current models of self-assembly under shear. This type of phenomena is interesting both from a fundamental and practical point of view, since these soft materials are present in everyday life under stress/flow conditions. At the beamline ID02 at the ESRF we reproduced the shear-experiments while simultaneously measuring the in-situ scattered intensity. This allowed extracting valuable structural information of the system as it responds to the external shear fields. As this work is still in progress, in this report we show the main findings so far.

Results

Summary: In Figure 1 we show a summary of the rheo-SAXS experiments for a 1.6 wt% sample, showing the viscosity and shear-rate as a function of time, together with the simultaneous scattering profiles in the neutral and flow directions (c.f. caption for details).

The sample initially at rest (Figure 2) displays a lamellar phase pattern with a spacing of about 138 nm. This is somewhat larger than the equilibrium spacing (about 103 nm[1]). When shear is applied at 1000 s^{-1}, the Bragg peak of the lamellar phase starts shifting rapidly to higher q values, reaching the expected equilibrium spacing before more drastic changes take place. Around 30 minutes, the shape of the scattering curve is also already significantly different from the original lamellar profile, indicating a novel structure, as will be discussed ahead. When the shear rate decreases again to 200 s^{-1} the lamellar scattering profile appears again, with the equilibrium d spacing. This value is practically constant until the shear rate increases again to 800 s^{-1}, which means that shearing the sample accelerates equilibration of

its *d* spacing. In order to have a well defined initial state to obtain reproducible results, we start experiments at 1000 s^{-1} (shear-annealing the sample), go down to 5 s^{-1} in shear-jumps, and go up again to 1000 s^{-1}.
It should also be noted that 1.2 wt% samples show a high abundance of unilamellar vesicles, so it is very likely that besides the measured lamellar phase, the sample also contains a significant fraction of polydisperse unilamellar vesicles (not distinguishable from the lamellar phase in these scattering experiments).

Low shear-rate regime (5-200 s^{-1}): In Figures 2 and 3 we show the scattering profile of the sample filled in the shear cell before starting the shear-rate curve (i.e. the sample is subjected only to a minimal shear from the syringe and from mounting the rotor). Together, we show the scattering curves averaged over the final 5 minutes of each shear rate (when steady state conditions were already reached). Comparing the scattering intensity of the sample as filled with the intensity of the sample under shear, one can see that in the neutral direction, the sheared samples have a higher intensity than the unsheared sample. Conversely, in the flow direction, the opposite happens, with the sheared samples showing a lower intensity than the unsheared sample. This suggests that the lamellar phase is in the form of distorted onions, probably with a prolate shape (with the major axis aligned in the flow direction) that resists less to flow (a shear-thinning type of transition, which we observe between 5 and 200 s^{-1} before the shear-thickening regime is entered). In this new distorted onion shape, the amount of lamellae in the *a* orientation (producing a scattering signal in the neutral direction) should increase, while the amount of lamellae in the *b* orientation (scattering signal in the flow direction) should decrease with the same proportion as the *a* orientation increases. This is in agreement with the experimental results. If we were in the presence of planar lamellae instead of onions, the expected behavior would be a shear-induced preferential alignment of the lamellar layers in the *c* orientation, which would produce different results.
The lamellar peaks were fitted with a Lorentzian function (not shown), from which we can extract the half-width at half-maximum (HWHM) of the peak (inversely proportional to the domain size). Even though the peak position is essentially the same for both *a* and *b* domains of the deformed onions, the HWHM of the *b* orientation is larger than in the *a*. This could indicate that the domain size in the *b* side of the prolate is smaller, perhaps, due to a higher distortion/bending of this side of the particle.

High shear-rate (300-1000 s^{-1}): The steady state scattering profiles at 1000 and 800 s^{-1} are identical. At 500 s^{-1} a very slight decrease at low q is noticed, and at 300 s^{-1} the intensity decreases a little more at low q and a small increase is noticed at the position where the lamellar Bragg peak will appear at 200 s^{-1}. Focusing then on the structure at high shear (mostly 1000 and 800 s^{-1}), the scattering curve is dominated by an oscillation with a very shallow well at $q \approx 0.12$ and broad peak at $q \approx 0.07$ nm^{-1}. The broad peak could well be the precursor to the lamellar Bragg peak. In a similar experiment (different sample, same concentration) we changed the q range to probe smaller q values (Figure 4). The previously mentioned shallow well and broad peak remain, but in addition a new inflexion at $q \approx 0.03$ nm^{-1} followed by a high increase at lower q values with a slope of $q^{-3.3}$ become visible. The scattering pattern agrees with structures that on the length scale equivalent to q=0.03-0.5 nm^{-1} correspond to disc-like objects (thickness 2.7 nm – same as lamellae; $R \approx 70$ nm). The low-q scattering, however, clearly shows that these discs are not independent, but assemble into aggregates or possibly irregularly shaped vesicles.

More intensive analysis and perhaps more experiments will be needed to confirm that the structure at high shear is indeed bilayer disks, but so far, this idea sounds physically feasible. The onions that are visible at low shear may become unstable at very high shear rates, and break down into bilayer fragments that take the form of disks. The observed increment in viscosity could result from the inability of the disks to align in the shear flow due to the very high shear rates that may cause tumbling. The fact that the rims of the disks may be sticky may also cause some special effects. As the shear rate decreases, the shallow peak at $q \approx 0.07$ nm^{-1} starts to develop into a lamellar Bragg peak and gradually shifting to $q \approx 0.06$ nm^{-1} (which corresponds to d=104 nm – the equilibrium lamellar spacing). This could indicate a gradual transition from the disks, which may start to grow to larger radii and/or starting to stack into small lamellar domains, before folding into the onions.

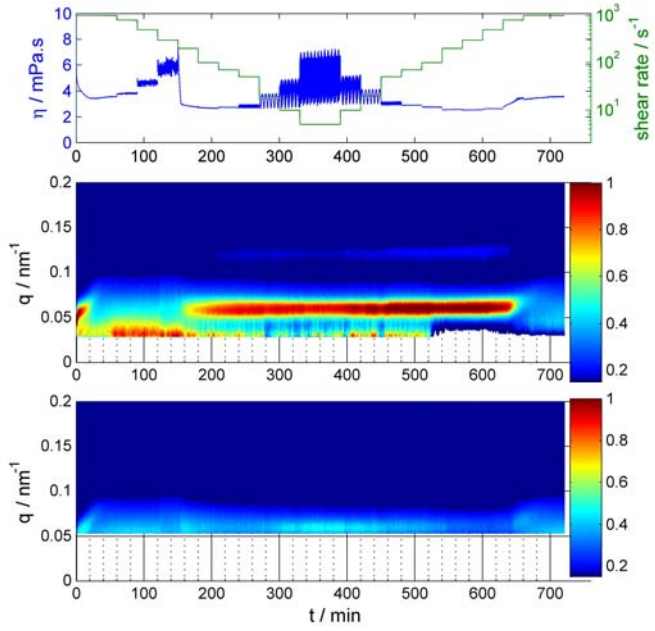

Figure 1. (**Top**) Viscosity as a function of shear rate and time. Steady state for a new shear rate is always reached in less than 30 minutes. The oscillations in the viscosity near 300-450 s^{-1} result from instrumental noise. (**Middle**) Scattering curves in the neutral direction (155-205º interval) averaged to 1 minute, plotted as a function of time. The scale is the same as for the viscosity curves, so both measurements (SAXS and rheology) can be directly compared. (**Bottom**) Scattering curves in the flow direction (65-115º).

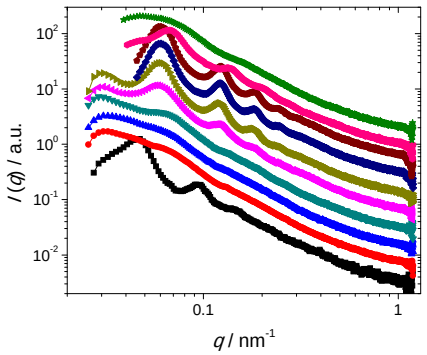

Figure 2. Scattering intensity profiles in the neutral direction (155-205º interval) for "as filled", 1000, 800, 300, 200, 5, 200, 300, 800 and 1000 s^{-1} (bottom to top).

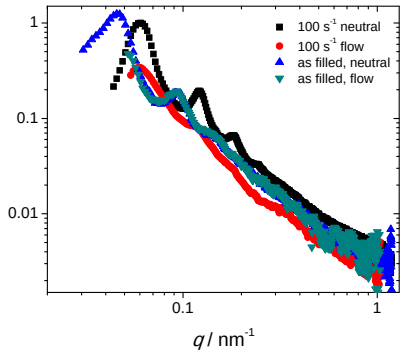

Figure 3: Comparison between the scattered intensity in the neutral and flow directions at rest and 100 s^{-1}.

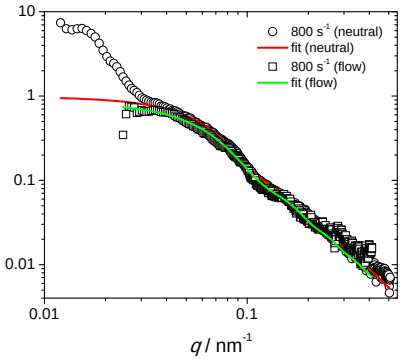

Figure 4: Scattering profiles at high shear rate. If the upturn at low q is neglected, the data can be fitted with a disk form factor (thickness 2.71 nm, R=70 nm).

(1) Silva, B. F. B.; Marques, E. F.; Olsson, U. *Langmuir* **2008,** *24*, 10746.