Experimental Report

25/01/2014

Proposal: **9-10-1308** **Council:** 10/2012

Title: Shear-induced transitions in a surfactant lamellar phase studied in the newly available velocity-gradient plane of a shear cell environment

This proposal is a new proposal

Researh Area: Soft condensed matter

Main proposer: **GENTILE Luigi**

Experimental Team: BEHRENS Manja
GENTILE Luigi
OLSSON Ulf
NDONG Rose

Local Contact: PORCAR Lionel

Samples: triethylene glycol monododecyl ether (C12E3)
Pentaethylene glycol monododecyl ether (C12E5)

Instrument	Req. Days	All. Days	From	To
D22	4	3	05/04/2013	08/04/2013

Abstract:

Despite major experimental efforts over the past 20 years there is yet not significant understanding of the shear induced structural transition observed in many surfactant lamellar phases. Here we propose a study of the shear-induced multilamellar vesicles (MLVs) mechanism from lamellar phase systems. The proposed experiments include time resolved SANS recorded in all three planes: velocity-vorticity (1-3), gradient-vorticity (2-3) and velocity-gradient (1-2), respectively. The aim of the experiments is to characterize the structure(s) on the colloidal length scale and to understand the mechanism of transition under shear flow from the “new” gap prospective. Moreover we would like to study the stability and the spatial distribution of the intermediate structures, i.e. multilamellar cylinders, MLCs, or oily streaks lamellar defects. The experiments will make use of the newly developed rheometer sample environment which allows to record the scattering in the three different planes of the shear flow geometry. Recording the structural evolution in all three planes will be necessary for a full characterization and to understand the origin of this spectacular flow instability.

Shear-induced transitions in a surfactant lamellar phase studied in the newly available velocity-gradient plane of a shear cell environment

Luigi Gentile[1,2], Manja Behrens[2], Lionel Porcar[3], Norman J. Wagner[4] and Ulf Olsson[2]*

[1] *Department of Chemistry and Chemical Technologies, University of Calabria, Pietro Bucci 12C, 87036 Rende, Italy*
[2] *Division of Physical Chemistry, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden*
[3] *Large Scale Structure Group, Institut Laue Langevin, Grenoble, France*
[4] *Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy St, Newark, DE 19716, USA*

For the first time the lamellar phase of the $C_{12}E_5/D_2O$ system was extensively investigated under shear flow by using time resolved SANS experiments in the specially designed flow-gradient (1-2) shear cell. The lamellar-to-multilamellar vesicles (MLVs) transition was observed from this "new" available gap-space. During the lamellar-to-multilamellar vesicle transition the primary Bragg peak from the lamellar ordering was observed to tilt and this gradually increased with time leading to an anisotropic pattern with a primary axis oriented at ~25° relative to the flow direction. These novel measurements provide fundamentally new information about flow orientation of lamellae in the plane of flow that cannot be anticipated from the large body of previous literature showing nearly isotropic orientation in the 2,3 and 1,3 planes of flow. These observations are consistent with models for buckling-induced MLV formation and therefore, identify the mechanism of MLV formation in simple shear flow.

In the lamellar phase (L_α), surfactants are organized in essentially flat and infinite bilayers, which are stacked with one-dimensional order. In many systems, these layered structures are found to be unstable under a shear flow and the structure is converted into multi-lamellar vesicles (MLVs) or onions [1-4]. Nonionic surfactants of the ethylene oxide (E) type are susceptible to the shear flow especially the lamellar phase due to the low bending rigidity. The pathway of the MLV formation under shear flow is characterized by an intermediate structure between the planar lamellar and the MLVs identified as multilamellar cylinders (MLCs). $C_{12}E_5$ is a non-ionic surfactant with an alkyl chain of 12 carbon atoms and 5 E-units. For $C_{12}E_5/D_2O$ system at 40 wt% the MLV formation was reported at 55 °C [3]. Further rheo-small angle light scattering (SALS) experiments revealed a changing in the pathway of the MLV formation mechanism depending on the shear rates. At low shear rates no MLCs intermediate state appears, on the contrary at high shear rates MLC structure factor appears.

The lamellar-to-multilamellar vesicles transition was observed by flow-SANS from the newly available gap prospective, i.e. 1-2 plane [5]. Figure 3 shows the 2D SANS patterns obtained during MLV formation at a shear rate of 10 s^{-1}.

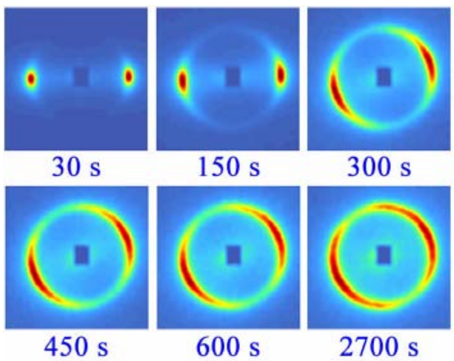

Figure 1: *2D-Scattering patterns in the flow-gradient plane as a function of time at constant shear rate of 10 s^{-1} and a temperature of 55°C for 40 wt% $C_{12}E_5$ in D_2O.*

In the following discussion Lα will be used to indicate planar lamellae. The prominent Bragg peak at 30 s, corresponds to a major population of bilayers with their normal parallel to the gradient direction which is denoted as *c*-orientation [6]. This is the first important result, i.e., the existence of the Lα in the c-orientation is proven here by SANS experiments in the 1-2 plane, while previous measurements could only detect a minority population of bilayers with their normal parallel to vorticity direction, i.e., a-orientation, because they were performed using the radial beam configuration [4, 7]. The sequence of structure evolution evident in Figure 3 for 1-2 flow SANS corresponds to that observed in Figure 2 using flow-SALS, where a transition occurs and saturates by about 300 s. Importantly, the sequence of structural evolutions in Figure 3 was observed to be the same for clockwise and counter-clockwise directions (see supporting informations, Figure 1S), where the 2D patterns are rotated 90° upon reversal of direction of the flow. This confirms that the tilting of the lamellar phase is due to the shear flow.

Figure 2 shows the time evolution of azimuthal or angular variation of the diffracted SANS intensity within a sector mask of 360° in the q-range between 0.07 and 0.09 Å-1. The GRASP output references the angle of 0° to be the positive vertical direction in the SANS patterns, which corresponds to the flow direction. The azimuthal trace changes from the c-orientation (90° and 270°) toward a broader, tilted pattern with peaks centered at XX and YY degrees, over a transition of about 800 seconds, then no further changes are observed. There is an increase of the SANS intensity at 9±1° and 189±1° upon reduction in the c-orientation peaks.

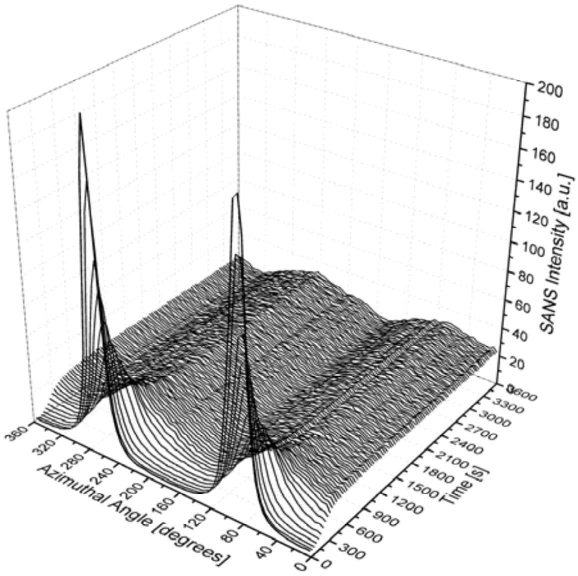

Figure 2: *Time evolution of the azimuthal traces for 40 wt% $C_{12}E_5$ in D_2O at shear rate of 10 s^{-1} and 55°C. The azimuthal traces were extracted from a sector masks of 360° in the q-range between 0.07 and 0.09 $Å^{-1}$.*

For the first time the mechanism of MLV formation can be described. The MLV formation occurs when the applied flow is able to tilt the lamellae of the lamellar phase. The presence of defects enables the collapsing of the tilted lamellae on themselves, which leads to the formation of the vesicles.

After 800 s no substantial changes in the azimuthal traces are observed indicating the final state of the transition. The Lα-to-MLVs transition follows a similar pathway at different shear rates. In Figure 3 the SANS intensities of boxes centred at 10° and 190° were averaged (tilted-flow direction, blue). The same procedure was done for the boxes at 90° and 270° (gradient direction, red) and 80° and 260° at 10 s-1 and 60° and 240° at 20 and 60 s-1 (tilted-gradient direction, green). Along the averaged intensity in the tilted gradient direction a maximum appears between 1200 and 2200 strain units that can be attributed to the presence of the MLC structure. Moreover after 3000 strain units the intensity time-profiles become similar in the all three directions, that is related with the beginning of the formation of MLV. After 8000 strain units for all shear rates the transition reaches is final state, the MLVs are formed.

2D-SANS patterns with 1-2 plane configuration observed for $C_{12}E_5/D_2O$ binary system are shown in Figure 4. By means of the powerful ILL D22 instrument and the new experimental environment the lamellar phase of the $C_{12}E_5/D_2O$ system (40 wt%) was investigated. The relative stability of MLVs and planar lamellae was mapped as a function of temperature (spontaneous curvature) and shear rate. The MLVs are distorted in the flow direction, in fact the 2D SANS patterns in the 1-2 plane are anisotropic. It can be observed that MLVs are formed at low shear rate, whereas at higher temperatures and high shear rates the MLV phase competes with the L_α. In fact at 200 s^{-1} between 64 and 70°C the SANS patterns can be attributed to the reverse transition MLV-to-Lα.

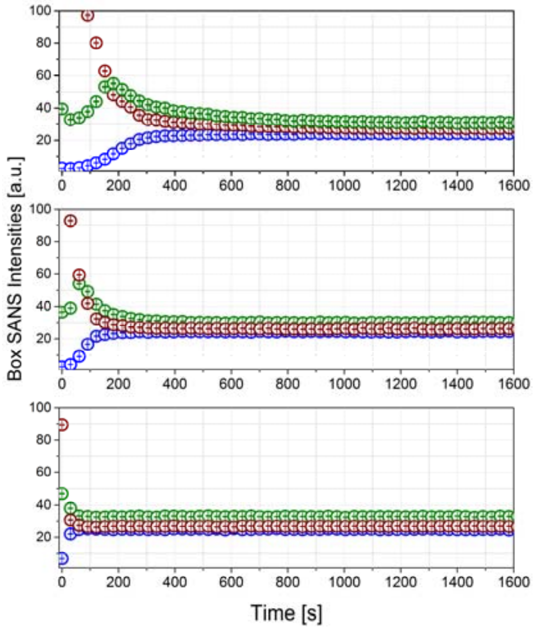

Figure 3: *SANS intensities of boxes centred at 10° and 190° were averaged (tilted-flow direction, blue). The same procedure was done for the boxes at 90° and 270° (gradient direction, red) and 80° and 260° at 10 s^{-1} and 60° and 240° at 20 and 60 s^{-1} (tilted-gradient direction, green). The intensities are plotted against time for 10, 20 and 60 s^{-1} from up to down, respectively.*

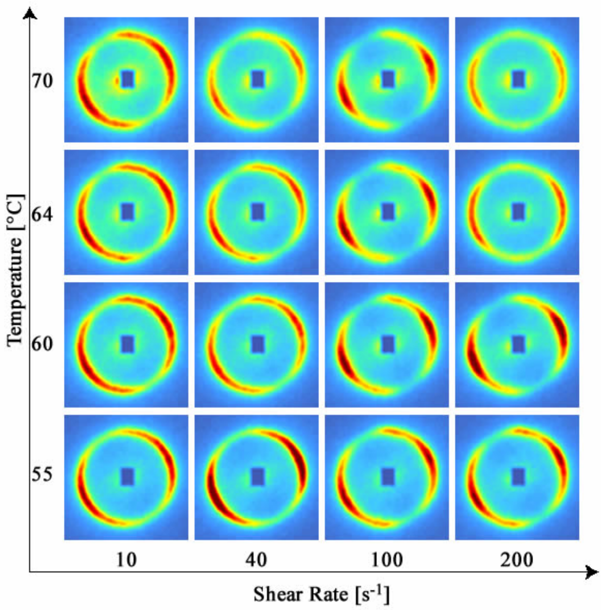

Figure 4: Steady-state scattering patterns as a function of temperature and shear rate for 40 wt% $C_{12}E_5$ in D_2O.

In conclusion, the patterns recorded in the flow shear gradient plane are due to the major population of bilayers, i.e. c-orientation. By following the transition from the Couette gap, a tilt in the angular position of the Bragg peak was observed due to the applied shear rate. The tilt is also present after the formation of the MLVs, however the Bragg peaks are broader than in the Lα and, the anisotropy in the patterns indicates a deformation of the vesicles shape.

References:

[1] L. Gentile, K. Mortensen, C. Oliviero Rossi, U. Olsson, G.A. Ranieri, J. Colloid Int. Sci. 2011, 362, 1;
[2] L. Gentile, B.F. Silva, S. Balog, K. Mortensen, U. Olsson, J. Colloid Interface Sci. 2012, 372, 32–39;
[3] L. Gentile, C. Oliviero Rossi, U. Olsson, G.A. Ranieri, Langmuir, 2011, 27, 2088–2092;
[4] F. Nettesheim, J. Zipfel, U. Olsson, F. Renth, P. Lindner, W. Richtering, Langmuir, 2003, 19, 3603;
[5] M. W. Liberatore, F. Nettesheim, N. J. Wagner PHYSICAL REVIEW E 73, 020504(R) 2006;
[6] C.R. Safinya, E.B. Sirota, R.F. Bruinsma, C. Jeppesen, R.J. Plano, Science 1993, 261, 588;
[7] T.D. Le, U. Olsson, K. Mortensen, J. Zipfel, W. Richtering, Langmuir 2001, 17, 999;