Experimental report

19/09/2016

Proposal: **9-10-1382** **Council:** 4/2014

Title: Flow instability in a nonionic lamellar phase: 1-2 flow prospective

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: tetraethylene glycol monohexadecyl ether

Instrument	Requested days	Allocated days	From	To
D33	0	0		
D22	3	2	28/10/2015	30/10/2015

Abstract:

Unstable temporal viscosity behavior, with periodic oscillations, has recently been observed in a nonionic surfactant lamellar phase system under steady shear. The flow conditions imply shear-induced multilamellar vesicle (MLV) formation, but the origin of this instability is not yet fully understood. Previous time-resolved SANS experiments indicate a correlation between viscosity oscillations and a variation in the MLV fraction [1]. These experiments were performed in Couette geometry using a “radial” beam configuration detecting the scattered intensity in the velocity-neutral (1-3) plane. Here, we propose to perform complementary experiments in velocity-gradient (1-2) plane in order to obtain information that is critical to resolve this very unusual and spectacular rheological behavior of an important soft matter system. The experiments will make use of a newly constructed novel (1-2) shear cell available at ILL. Previous results for a similar system were illuminating to understand the mechanism of formation of MLVs [1]. Recording the temporal structural evolution in this newly developed sample environment will be essential to understand flow instabilities.

Viscosity and Intensity oscillations: relation between structure and flow dynamics

Strong viscosity oscillations were observed in the binary water-$C_{16}E_4$ lamellar phase system, where $C_{16}E_4$ is a non-ionic surfactant composed of a C_{16} hydrocarbon chain and a block of tetra(ethylene oxide) as the polar "head" [1]. A separation into millimeter wide shear bands was also observed in the vorticity direction [1]. The observation of vorticity banding is consistent with shear thickening transition as described phenomenologically by the Johnson–Segalman model [2]. Previously time-resolved and spatially-resolved rheo-small angle neutron scattering experiments were carried out using Couette geometry in the radial beam configuration, probing the scattering in the velocity-vorticity (1-3) plane. Oscillation in the neutron-scattered intensity in the flow (x) and vorticity (z) directions were observed. The correlation between intensity and viscosity oscillations indicate a fluctuation in MLV and planar lamellae fractions [1].

Here the SANS experiments were performed by using the specially designed shear cell available at ILL, where SANS is performed in the velocity-gradient (1-2) plane. The experiments were performed to study the structural variations during viscosity oscillations. Spatial resolution experiments in the Couette gap were performed to localize structures (MLVs or Lα), Figure 1. The maximum neutron scattering intensity at the Bragg peak was monitored as a function of time during a constant shear rate of 2 s^{-1} at 40 °C. The time-resolved experiment was performed at all 4 gap positions resulting in a spatial-time resolved experiment. In the position closer to the outer wall (-7.8) the intensity of the specular peaks were oscillate alternately each other. One should also consider inertia ratio and mechanical resonance phenomena, i.e. when the motor is controlled, the resonant frequency is changed depending on the structure and the tuning of control loops this result in vibrations/ oscillations. On the other hand Bragg peak should oscillate in the same way, while here are oscillating in a specular way, further investigation are need on this point. In Figure 2 the SANS intensity at the Bragg peak centered at 110 and 290° is reported as a function of time. Figure 2 shows intensity oscillations at the position -7.8, i.e. close to the outer wall. Moreover, these intensity oscillations are specular respect to the two Bragg Peaks. On the other hand, no oscillation behaviours were observed in the other positions. A Fourier transform of the intensity in position -7.8 reveals a periodicity of 200 s. The periodicity of the viscosity oscillations was 1150 s, one can speculate that oscillation periodicity is also related to the couette geometry, in particularly to the size of the surface walls, since the gap was the same for rheological experiments and rheo-SANS. However, there are two open questions: (i) which is the phenomenon behind the complementary intensity oscillations of the two Bragg peaks at the outer wall? (ii) is the phenomenon related to the wall surface?. There are no intensity oscillations in the other x-positions. However, the average intensity of the two Bragg peaks are closer each other only at position -7.5 and slightly at -7.3, i.e. in the middle of the gap, as one can aspect. Increasing the temperature to 45 °C a lamellar and MLVs coexistence has been clearly individuated only at outer wall position (-7.8) at 2 and 5 s^{-1}. Figure 3 reports SANS profiles for a selected pattern at 2 and 5 s^{-1}. SANS profiles were obtained averaging the overall pattern and averaging a selected zone at 45° (size 10°). The lorentzian fitting of the SANS

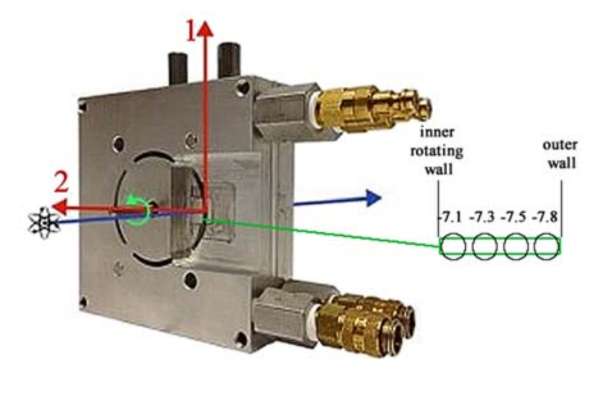

Figure 1: 1-2 shear cell allows scattering in the 1-2 plane. The 1-, 2-, and 3- directions are defined as the velocity, velocity gradient and vorticity directions, respectively. The position in the couette gap were defined by using the table with x,y,z,w positioning plus (q)-goniometer. Position -7.1 along x correspond to the point closer to the inner wall, while -7.8 to the outer wall.

profiles in the region of the main peak reveal a *d*-spacing of 7.4 and 7.5 nm for 2 and 5 s^{-1} considering the SANS profile obtained by averaging the all 2D patterns. On the other hand considering the SANS profile obtained in the selected zone at 45° clearly one can estimates the *d*-spacing for the MLV as 7.3 nm for both shear rates, while the *d*-spacing of the lamellar phase is 6.6 and 5.9 nm at 2 and 5 s^{-1}, respectively. In the previous experiments performed with the shear cell in the radial beam configuration there was no difference between the *d*-spacing of the MLV and the planar lamellae. However, in the radial beam configuration it is possible to detect the planar lamellae in the *a*-orientation (bilayers with their normal parallel to the vorticity direction). Here with 1-2 shear cell we are looking at the main orientation of the planar lamellae, i.e. *c*-orientation (bilayers with their normal parallel to the gradient direction). In conclusion we detect a specular intensity oscillation in the Bragg peaks at 40 °C and shear rate of 2 s^{-1}, while we clearly detected a coexisting state between MLV and planar lamellae at 45 °C, where d-spacing of the planar lamellae is lower than the one for MLV. Moreover, increasing the shear rate the *d*-spacing decreases. Since this happening at the outer wall, it is possible to speculate about an adhesion effect to the wall where the MLVs with a “critical size” are destroyed, while new a MLVs are formed since we are continuously shearing.

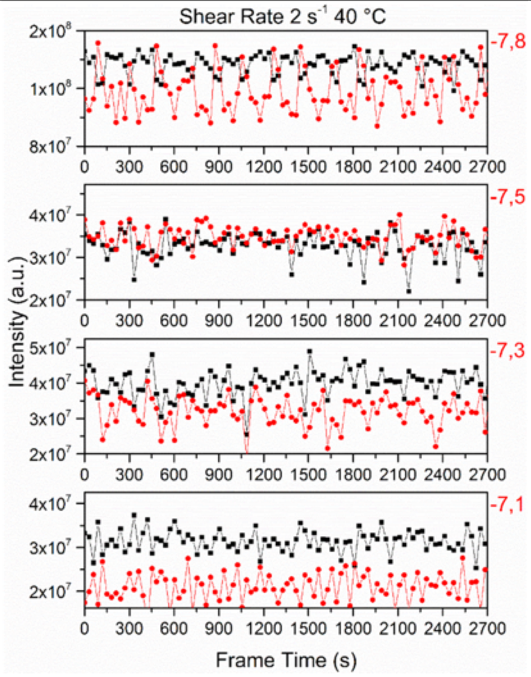

Figure 2: SANS intensity at the two Bragg peaks at 110° and 290° (averaging 20°) as a function of time (red and black respectively). The Figure reports the intensity behaviours at all 4 gap positions.

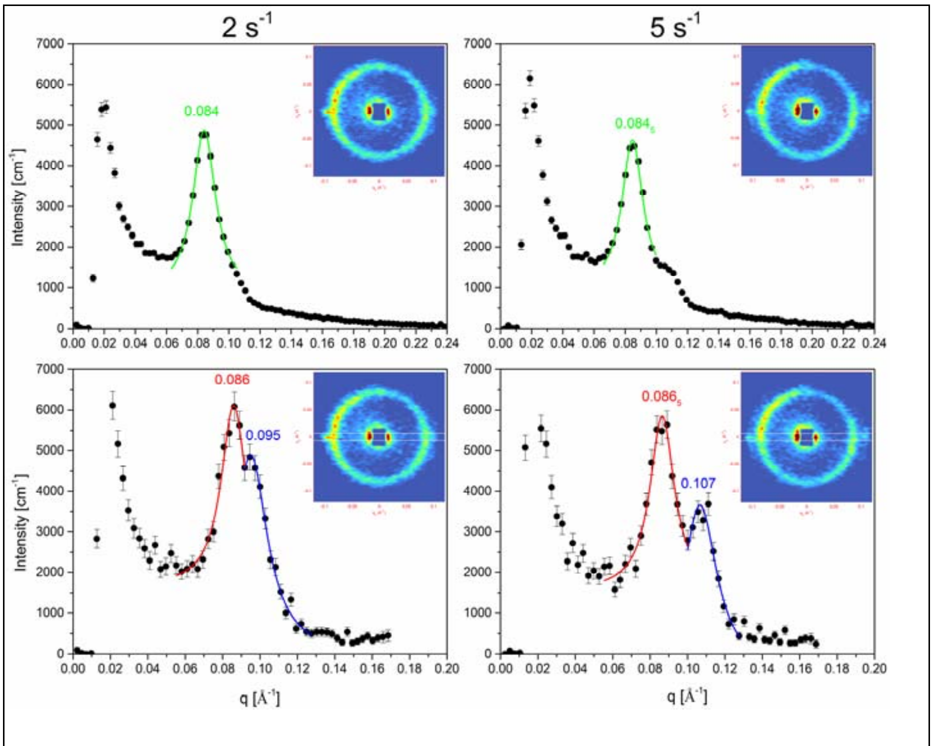

Figure 3: Scattering profiles of selected 2D SANS patterns at 2 s^{-1} (left) and 5 s^{-1} (right) at 45 °C. The figures on top are radial average of the overall 2D pattern, while the profiles in the bottom are average of the selected zone (white rectangular). Patterns collected at the outer wall position (-7.8).

References:

[1] L. Gentile, B. F. B. Silva, S. Lages, K. Mortensen, J. Kohlbrecher and U. Olsson, Soft Matter, 9 (2013) 1133–1140

[2] Johnson and Segalman J. Non-Newt. Fl. Mech 2 (1977) 255–270