Experimental report

16/09/2019

Proposal: 9-10-1479 **Council:** 4/2016

Title: Precise determination of concentration gradient in shear banding wormlike micelle solutions

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: Lionel PORCAR

Experimental team: Michelle CALABRESE

Local contacts: Lionel PORCAR

Samples: CTAB
CPCl

Instrument	Requested days	Allocated days	From	To
D22	2	2	03/02/2017	05/02/2017

Abstract:

The search for the physical origin of shear banding has motivated many theoretical and experimental studies and yet no consensus has emerged. Thanks to the 1-2 shear cell and its spatially-resolved measurements taken along the velocity-gradient direction, it is now possible to elucidate the shear banding behavior of WLM solutions quite precisely. A combination of measurements of sample transmission, coherent scattering and incoherent scattering will be used to determine whether concentration gradients are present in a couple of shear banding WLM solution while simultaneously decreasing the associated uncertainties of the measurements and shedding light to the basis of this phenomenon.

Title: Precise determination of concentration gradient in shear banding wormlike micelle solutions

Michelle A. Calabrese[1], Joao T. Cabral[2], Lionel Porcar[3]

Affiliation:
[1]Center for Neutron Science
Department of Chemical and Biomolecular Engineering
University of Delaware, Newark, DE 19716
[2]Department of Chemical Engineering
Imperial College London, UK
[3]Large Scale Structures, Institut Laue-Langevin
Grenoble, France

Structured surfactant and polymer solutions such as worm-like micelles (WLMs) are commonly used in applications ranging from consumer products to oil and energy recovery fluids. WLMs can exhibit shear banding flow instabilities under deformation, phenomena where the flow organizes into macroscopic bands of high shear rate (low viscosity) and low shear rate (high viscosity). These instabilities may be detrimental to such applications. Complex fluids known to exhibit shear banding have been studied extensively both experimentally using NMR velocimetery [1], flow velocimetry [2], and flowSANS and SAXS [3] as well as using constitutive modeling methods [4-6]. Although search for the physical origin of shear banding in concentrated solutions has motivated many theoretical and experimental studies, no consensus has emerged and opposing predictions in the literature surrounding flow-concentration coupling have resulted [4-7].

A 1-2 plane flow cell developed in the ILL Large Scale Structures group in collaboration with the NIST Center for Neutron Research has enabled the measurement of WLM microstructure under time- and spatially-dependent flows [3]. Further advances in SANS data collection at the ILL have increased the temporal resolution of these responses. By using the 1-2 shear cell to take measurements at multiple positions across the Couette gap during time-dependent deformations, shear banding can be precisely identified experimentally. A combination of measurements of sample transmission, coherent scattering and incoherent scattering will be used to determine whether concentration gradients are present in a couple of shear banding WLM solution while simultaneously decreasing the associated uncertainties of the measurements and shedding light to the basis of this phenomenon.

Here, we investigated WLMs formed from several surfactants and polymers, all at concentrations high enough that flow-concentration coupling has been predicted (≥15% wt). These samples include CTAB, at several concentrations (15-23%) including that previously concluded to have demonstrated flow-concentration coupling [7], Pluronic P84 at 15%, and CPyCl/Hex at 31%, and CPClO3 at 32%. The absolute transmission of the sample is directly related to the volume fraction; therefore, by directly measuring the transmission using SANS along the velocity gradient direction the surfactant volume fraction is defined. The main difficulty faced in measuring transmission under shear flow is the variation of the transmission due to any concentration gradient (and the incoherent and absorption contributions) or a coherent cross-section variation (as shear also induces structural changes such as large scale fluctuation). We aim to minimize and optimize the configurations to combat these issues, and have chosen solutions of short, stiff WLMs such that the length effects are limited.

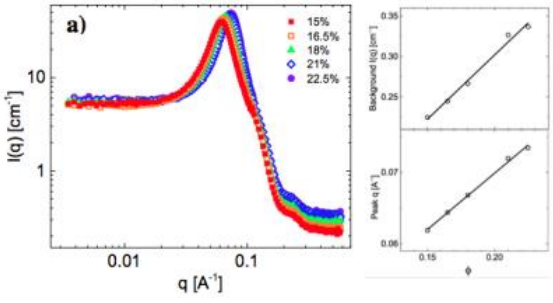

Figure 1: Static SANS of CTAB concentration series corresponding to the expected concentration changes with shear banding from ref [7]. The location of the interaction peak and the incoherent background are clearly dependent on CTAB concentration.

For the CTAB system (16.7%) studied in [7] the authors determine that during shear banding the WLM solution has a concentration gradient along the velocity gradient direction where there exists a surfactant rich phase in the high shear band coexisting with a surfactant lean phase of WLMs in the low shear band. However, Figure 1 shows our contradictory results to [7] from flow-SANS experiments on the same solution. In Figure 1, SANS measurements show the shift in peak q-position and incoherent scattering background for various

concentrations of CTAB that correspond to the concentrations measured in [7] during shear banding. Clearly the peak q-position and incoherent background level are strong functions of CTAB concentration.

Figure 2 summarizes the 1-2 plane flow-SANS results during shear banding. In Figure 2a, the 1-2 plane scattering under shear is shown at the inner wall (r/H=0.1) and outer wall (r/H=0.9) along the velocity gradient direction at a shear rate corresponding to the shear banding condition. A total of nine gap positions were taken during these measurements, at multiple configurations to look for differences in transmission and incoherent background. In Figure 2b, a largely aligned state nearer the rotor in the high shear band coexists with a comparatively isotropic scattering pattern indicative of an entangled state of the WLM solution in the low shear band closer to the stator. In both Figure 2a and b, neither the peak q-position nor incoherent background change at various gap positions (and multiple configurations) despite the supposed concentration gradient. These measurements were performed at nine gap positions, three configurations, and five shear rates, and in no case was a change in the peak position or incoherent background with shear observed. The peak a-position also does not change under shear versus the peak position at rest, which is also required to signal concentration gradients (as shown by the results in Figure 1). To verify the incoherent background results, solvents matched with the same hydrogen content as the concentrations reported in [7] were measured in this same cell, the incoherent background change was easily detected and found to be significant.

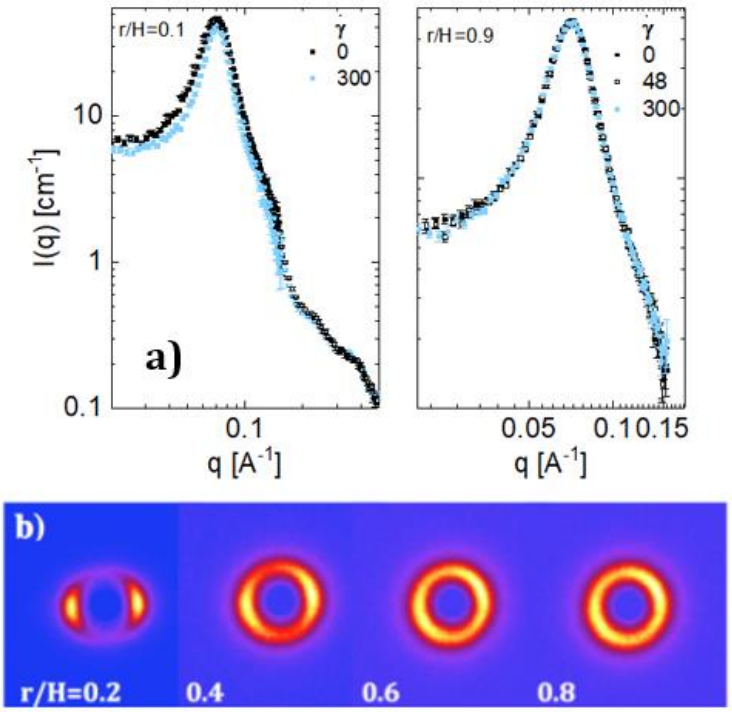

Figure 2: Flow-SANS results in the 1-2 plane for 16.7% wt CTAB. a) The peak position and incoherent background do not change as a function of shear rate at the inner or outer walls of the Couette, where the most dramatic effects from flow-concentration coupling are expected. b) 1-2 plane patterns confirm shear banding in this solution.

Based on the work in [7] and the results shown in Figure 1, a shift in the incoherent background and peak q-position of between 10% and 20% is expected throughout the shear banding region. No substantial change in any of these values is seen across the multiple experiments, some of which are shown in Figure 2. The decrease in the absolute intensity in Figure 2a with shear can be fully explained by the orientation of the WLMs in solution, and fits to the 2D DREAM model confirm this hypothesis. We also confirmed this result taking measurements on the 16.7% CTAB sample at multiple temperatures (T=30, 31C) and by moving the CTAB concentration closer to the nematic transition concentration (19%). At 19%, measurements were taken at T=34, 34.5, 35, 35.5, 38 and 39 C. At none of these conditions despite identifying strong shear banding was any change in the peak position or incoherent background observed. These results were also replicated in the CPyCl/Hex solutions, and the P84 solutions.

Finally, using concentrated CTAB solutions, we were able to show via SANS that the increase in the apparent transmission during shear banding could be explained quantitatively by the alignment of the micelles (Figure 3). In Figure 3, for the same q-position for the primary peak (i.e. same concentration), an increase in apparent transmission is linearly related to the alignment factor. This increase in transmission is due to an increase in the low-q or forward scattering that results from micellar alignment. At the outer wall where the micelles are barely aligned (low shear rate band), the transmission is not convoluted by this forward scattering. As such, the transmission measurements in the low shear rate band will be an accurate measurement of the concentration, whereas those in the high shear rate band will not be. As such, the arguments put forth in [7] for why the SANS transmission cannot be used to determine concentration are not entirely valid. From here, we have strong evidence to suggest that flow-concentration coupling is not found in these systems, or the system in [7]. The system in [7] showed no change in transmission in SANS at the outer wall, despite that the transmission should have gone up by approximately 20% to account for the expected "lower" concentration. As a flat transmission is seen in the low shear rate band for all applied shear rates for this sample (and for all samples tested), we can conclude that flow-concentration coupling is not occurring in any of the measured samples.

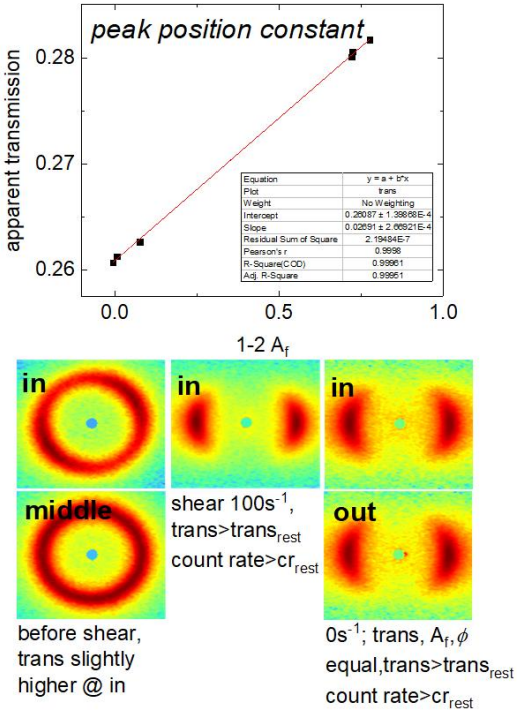

Figure 3: Results from 19% CTAB solution during shear banding and nematic transition. The apparent transmission linearly increses with alignment factor due to forward scattering from aligned chains. As the peak position is constant, the material is at the same concentration across the gap; this also holds true when the material is sheared to the nematic state across the gap. In both cases, no concentration gradients are observed, and the non-aligned transmission is representative of the true transition.

[1] E Fischer, & PT Callaghan, Phys Rev E 64 (2001). [2] P. Thareja et al., J Rheol 55 (2011).
[3] APR Eberle, & L Porcar, COCIS 17(2012). [4] PD Olmsted, and CYD Lu, Phys Rev E 60(1999).
[5]ME Cates & SM Fielding, Adv Phys 55(2006). [6]SM Fielding & PD Olmsted, Eur Phys J E 11(2003).
[7] M. E. Helgeson et al., Phys Rev Lett 105 (2010). [8] JF Berret, et al., Eur Phys J B 5(1998).
[9] V. Schmitt, et al., Langmuir 10(1994).