Neutron transmission measurements of concentration profiles in non-homogeneous shear flows

M. E. Helgeson[1], N. J. Wagner[2], L. Porcar[3]

Many complex fluids exhibit non-homogeneous flows under certain conditions, in which the flow field separates into regions of different local deformation rate. For example, wormlike micelles (WLMs), comprised of long thread-like surfactant aggregates, are a well-studied class of materials that exhibit this "shear banding" [1, 2]. These flows can be accurately modeled using non-monotonic rheological constitutive relations between the local shear stress and shear rate [1-3], which are unstable between two critical shear rates $\dot{\gamma}_{1c}$ and $\dot{\gamma}_{2c}$ (Fig. 1, dotted line). Because these models qualitatively resemble thermodynamic phase separation, this has spurred debate as to whether or not inhomogeneous flow is accompanied by macroscopic concentration gradients within the fluid. However, validation of this "flow-concentration coupling" has proven difficult because no methods currently exist to make local composition measurements within the shear banded flow field. Thus the direction, and even existence of, shear-induced concentration gradients remains a hotly contested theoretical problem.

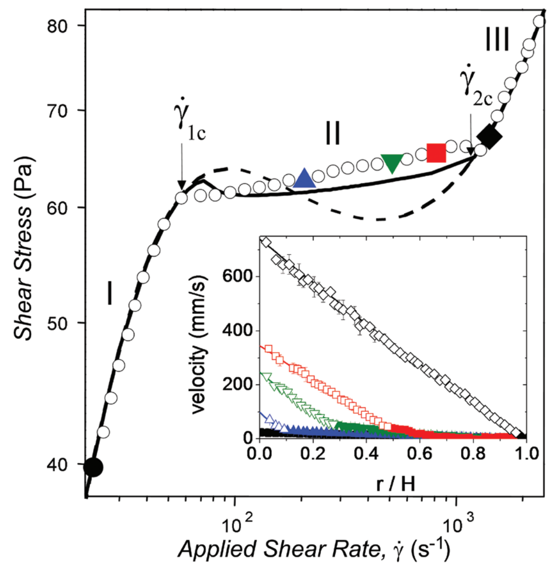

FIGURE 1: Steady state rheology of shear banding CTAB wormlike micelles [3, 5]. Open circles: data, curves: model. Inset: velocity profiles vs. relative position (r/H) for region (II), $\dot{\gamma}_{1c} < \dot{\gamma}_0 < \dot{\gamma}_{2c}$, are characteristic of shear banding. The data point colors and shapes correspond to points in the outer graph. Closed and open symbols represent points in the low-shear band (I) and high-shear band (III), respectively.

We have recently devised a method to directly measure the local concentration of fluids under shear using neutron transmission profiling [4]. Because the neutron attenuation is an absolute quantity, it can be generally applied to any fluid with sufficient neutron contrast. To review, the neutron transmission, T, of a two-component fluid is given by $T = \exp\{-t[\Delta\sigma_{s12}\phi + \Sigma'_a]\}$ where t is the sample thickness, $\Delta\sigma_{s12}$ is the difference in coherent cross-section between components 1 and 2, ϕ is the volume fraction of component 2, and Σ'_a is the total incoherent cross-section. Thus, spatially-resolved transmission measurements enable direct determination of the concentration profile of material within the flow field.

In order to carry out these measurements, we use a recently developed Taylor Couette shear cell for small angle scattering measurements in the flow-gradient shear plane (Fig. 2a). The cell is equipped with a translating slit aperture to allow for translation of the incident neutron beam across the Couette gap, yielding position-dependent scattering and transmission measurements [6]. Because the measured transmission can often be convoluted by forward scattering in ordinary SANS measurements, we have modified the experiments to be compatible with ultra-small angle neutron scattering (USANS). The resulting technique, scanning narrow aperture flow-USANS (SNAFUSANS), yields accurate transmission measurements with precise spatial resolution.

To test the existence of flow-concentration coupling, we have made SNAFUSANS measurements on a model shear banding WLM fluid comprised of CTAB, a cationic surfactant, in D_2O near an equilibrium isotropic-nematic phase boundary [3, 5]. Our previous flow-SANS measurements have shown that shear banding in this system is due to a shear-induced, first-order phase

[1]Massachusetts Institute of Technology, Cambridge, MA 02139
[2]University of Delaware, Newark, DE 19716
[3]Institute Laue-Langevin, Grenoble, France

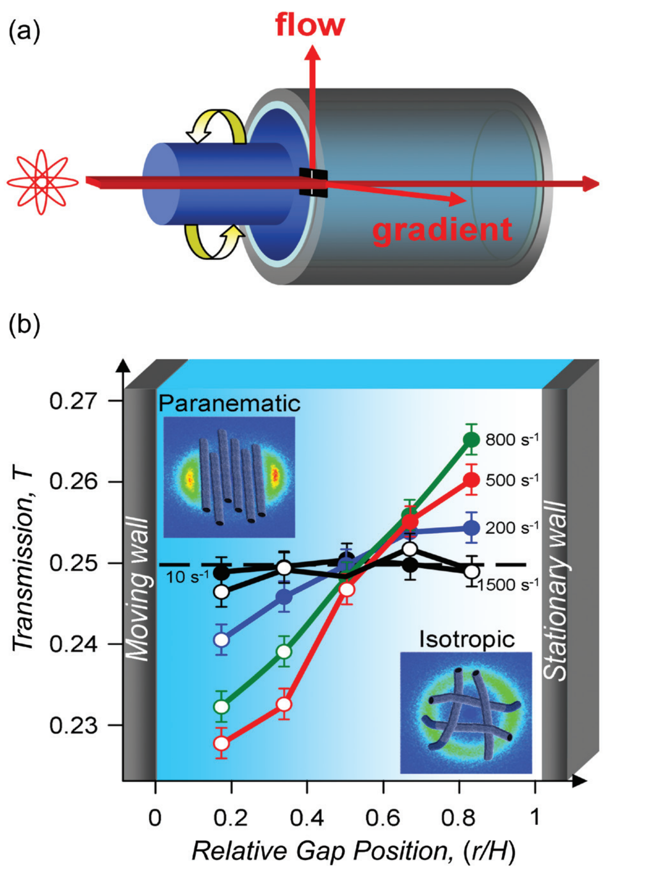

FIGURE 2: (a) Schematic of the SNAFUSANS shear cell, indicating the incident beam direction relative to the beam slit (black). (b) Absolute neutron transmission (T) profiles for shear banding CTAB wormlike micelles confirm the existence of flow-concentration coupling. Insets show 2D SANS profiles for positions in the high-shear (paranematic) and low-shear (isotropic) bands.

transition to a highly-aligned paranematic state in the high-shear band which coexists with a poorly-aligned isotropic state in the low-shear band [3, 5].

The measured transmission profiles for applied shear rates, $\dot{\gamma}_0$, spanning $\dot{\gamma}_{1c}$ and $\dot{\gamma}_{2c}$ and beyond confirm the existence of flow-concentration coupling during shear banding (Fig. 2b). For $\dot{\gamma}_0 < \dot{\gamma}_{1c}$ the transmission profile, and thus the surfactant concentration, is uniform with gap position, r/H, as expected for a homogeneously flowing fluid. However, for $\dot{\gamma}_{1c} < \dot{\gamma}_0 < \dot{\gamma}_{2c}$ where shear banding occurs, the transmission exhibits a significant gradient, with T decreasing for points in the high-shear band and increasing for points in the low-shear band. Finally, a uniform transmission profile returns for $\dot{\gamma}_0 > \dot{\gamma}_{2c}$, where the fluid is entirely paranematic in structure.

These results provide the first conclusive evidence for flow-concentration coupling in a shear banding fluid. Specifically, we find that the surfactant volume fraction increases in the high-shear band at the expense of the low-shear band (Fig. 3), and at significantly high γ_0 reaches that required for the formation of a single nematic phase at rest, further confirming the mechanism previously proposed for shear banding in the CTAB/D_2O system [5]. Combination of this local composition information with local microstructure and flow kinematic data has allowed for the construction of non-equilibrium phase diagrams, which serve as a quantitative “fingerprint” for the process of shear banding as it relates to the thermodynamics of the fluid [4].

In conclusion, the SNAFUSANS technique demonstrates unparalleled ability to interrogate both the structure and composition of complex fluids under shear. This initial study has, for the first time, confirmed flow-concentration coupling in a shear banding fluid, and provides a complete data set with which to test emerging theories. More generally, the method should be readily applicable to the growing number of materials that exhibit non-homogeneous flow, enabling significant advances in understanding the intricate relationships between composition, microstructure, and flow in complex fluids.

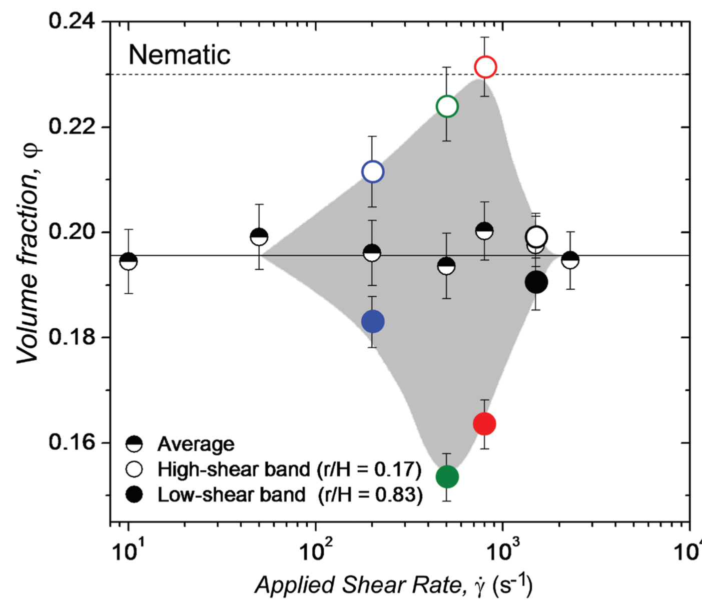

FIGURE 3: Measured CTAB volume fractions for the gap positions, r/H, indicated, indicating flow-concentration coupling during shear banding (shaded region). Solid and dashed lines give the concentration of the fluid at rest and that of an equilibrium nematic phase, respectively. Symbol colors correspond to the applied shear rates in previous figures.

References

[1] P. D. Olmsted, Rheologica Acta **47**, 283 (2008).

[2] J. K. G. Dhont and W. J. Briels, Rheologica Acta **47**, 257 (2008).

[3] M. E. Helgeson *et al.*, Journal of Rheology **53**, 727 (2009).

[4] M.E. Helgeson, L. Porcar, C. Lopez-Barron, and N.J. Wagner, Phys. Rev. Lett. **105**, 084501 (2010).

[5] M. E. Helgeson *et al.*, Soft Matter **5**, 3858 (2009).

[6] M. W. Liberatore *et al.*, Physical Review E **73** (2006).