MICROSTRUCTURE & RHEOLOGY OF SHEAR BANDING AND SHEAR INDUCED PHASE SEPARATING WORMLIKE MICELLAR SOLUTIONS

N.J. Wagner, A.B. Stiles, J.O. Stiles

University of Delaware, Department of Chemical Engineering, Center for Molecular and Engineering Thermodynamics, Center for Neutron Science, Newark, USA

wagnernj@udel.edu

Cationic surfactants that self-assembly into viscoelastic, worm-like micelles (WLM) can exhibit interesting flow anomalies such as shear-banding, which is characterized by extreme shear thinning and the formation of stratified flow, as well as shear induced phase separation (SIPS), which may have many rheological similarities. The shear banding transition in WLMs is usually associated with a flow-aligned state, which is often associated with a nearby (in composition space) equilibrium nematic phase. Shear induced phase separation is associated with stress-concentration coupling and the presence of intermicellar attractions due to micellar branching. Here, we exploit some unique opportunities afforded by the development of new flow-SANS and rheo-SALS instruments, coupled with rheology and particle tracking velocimetry, to elucidate the molecular mechanisms underlying these rheological anomalies.
Measurements of the micellar segmental alignment, flow kinematics, and mesoscale microstructure are presented for two model WLM solutions, providing the first local measurements of the microstructure and rheology through the shear banded state. Distinct differences in behavior are observed for two different classes of surfactants that correlate with the underlying equilibrium phase behavior and surfactant topology (linear versus branched). In one, shear banding is associated with increased segmental alignment of the WLM accompanied by a flow-induced concentration gradient, while in the other, shear banding results from strong density fluctuations associated with surfactant network formation. The results demonstrate that different flow-induced microstructures can result in shear banding and that the behavior correlates with the underlying phase behavior of each surfactant. Nonequilibrium state diagrams are demonstrated that connects this behavior to the underlying equilibrium phase behavior. We also demonstrate how the combination of rheology, flow kinematics, and SANS measurements of flow-induced microstructure locally in the flow field can be used to critically evaluate constitutive equations for WLMs.