

Kinetics and Molecular Origin of Shear Banding in Wormlike Micellar Solutions

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Abstract

The shear banding phenomenon refers to the formation of distinct regions within a material, each exhibiting different shear rates while subjected to the same shear stress. This flow phenomenon has been observed in various complex fluids, including suspensions, soft glassy materials, and wormlike micelles (WLMs). Shear banding plays a crucial role in these materials' flow behavior and stability, influencing their performance in numerous industrial and scientific applications, such as enhanced oil recovery, drug delivery, and food processing. Despite substantial research into shear banding, many aspects of its underlying mechanisms, including the formation, propagation, and stability of shear bands, remain less understood. Wormlike micelles serve as an ideal model system for investigating shear banding. The objective of this research is twofold. First, to investigate the kinetics of shear banding flow formation, with a particular focus on how surfactant chemistry, fluid rheology, and flow geometry influence the evolution of flow profiles leading to shear band formation. This is achieved by measuring the spatio-temporal evolution of the flows using a custom-built rheo-optical method. Secondly, the microstructural origin of shear banding in a range of wormlike micellar solutions is examined, with a particular focus on the role of shear-induced micellar chain scission in the formation of shear bands. The second objective is achieved through the use of various rheo-NMR-based techniques, including diffusive (rheo-DOSY-NMR) and quantitative (rheo-qNMR).

Our first study examines the nonlinear flow response of two shear-banding WLM solutions with different surfactant chemistries (CTAB/NaSal and CPyCl/NaSal) under step shear across various Weissenberg numbers, fluid elasticity, and flow curvature. The CTAB/NaSal solution exhibits transient flow reversal beyond a critical threshold, while CPyCl/NaSal does not. We attribute this difference to stronger electrostatic repulsions in CPyCl micelles, which reduce their susceptibility to flow-induced structural changes, highlighting the need for models that incorporate surfactant chemistry in shear-banding dynamics. The second study explores the sensitivity of quiescent ^1H NMR diffusometry that was used to investigate the micellar microstructure and topological transitions for three micellar systems based on CTAB/5mS, OTAB/NaOA, and CPyCl/NaClO₃ at various counter-ion concentrations. In the absence of counter-ions, surfactants diffuse freely within the micelles with a mean squared displacement $Z^2 \sim T\text{diff}$. As counter-ion concentration increases, self-diffusion becomes restricted, with $Z^2 \sim T\text{diff}^\alpha$, where α approaches 0.5. For the OTAB/NaOA system, which exhibits a linear-shorter linear micelle transition, $Z^2 \sim T\text{diff}^{0.5}$. In contrast, the CTAB/5mS system, which undergoes a wormlike-vesicle transition, recovers free self-diffusion beyond the viscosity peak. These findings underscore the sensitivity of ^1H NMR diffusometry to micellar topological changes. The third study utilizes Rheo-DOSY-NMR to investigate shear-induced micellar breakage in a shear-banding CPyCl/NaSal system. By simultaneously measuring the local velocity field and spatio-temporal evolution of surfactant self-diffusivity within the Taylor-Couette cell, our results reveal shear band formation. However, the local diffusivity of surfactant molecules does not vary significantly between high and low shear bands, suggesting no substantial change in micellar length across the bands. This finding challenges the theoretical hypothesis that shear-induced micellar breakage drives shear banding. Additionally, a preliminary Rheo-qNMR study provides further insights into flow-induced concentration coupling in micellar solutions under shear.