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Shear-induced structures formed during thixotropic loops in dilute worm-micelle solutions

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Abstract

The shear stress response of the system CTAB/NaSal/water is studied using strain thixotropic loops in the low concentration regime and [NaSal]/[CTAB] = 1. Stress response during up-shear curves depends on the ramping rate. However, stress response during down-shear curves collapses in one curve, no matter the rate used during the ramping down process; it does not depend on the history of the system. In the process of ramping up during the thixotropic loops, the system forms shear-induced structures. We were able to observe them through the scattered light produced by those structures, when the fluid is under shear in the gap of a transparent Couette cell. During the ramping down, the shear-induced structures survive until the shear rate vanishes. Models that describe the form of the up-shear and down-shear curves were presented, as well as, how thixotropic loops can give information about this kind of systems. In particular, for down-shear curves, we can define a decay shear rate constant that follows an Arrhenius temperature dependence.

Keywords: Thixotropic loops; Wormlike micelle; Shear-induced structures; CTAB/salicylate

1. Introduction

Certain surfactant molecules in liquid solution are known to spontaneously self-assemble into cylindrical micelles. Cylindrical micelles in water are usually made of cationic surfactants and of anionic benzyl hydrophobic moieties. In equilibrium and at low surfactant concentration, micelles in the system hexadecyltrimethylammonium bromide (CTAB)/sodium salicylate (NaSal)/water have a radius of ∼2 nm [1], a persistence length of ∼38 nm [1], and micelle contour lengths of ∼10–40 times the persistence length, depending on $R =$ [NaSal]/[CTAB] [1]. These cylindrical micelles [2–5] interact electrostatically among them. Addition of salts in these solutions results in screening the electrostatic micelle interaction and in aggregate growth [1]. These micelles (wormlike) make the fluid where they are embedded to present a strong nonlinear response under imposed flow fields. In the low-concentration micellar regime (<10 mM), wormlike micellar solutions show intriguing properties like shear thickening and rheopexy. Although, quantitative features change from one system to another, wormlike micellar solutions have many characteristics in common. Curves of apparent viscosity vs shear rate, when shear rate is imposed, present shear thickening above a critical shear rate $\dot{\gamma}_c$. After reaching a maximum, where apparent viscosity jumps up by a factor of 20–30, the system shear thins at higher shear rates; before this $\dot{\gamma}_c$ the system is Newtonian or slightly thinning [6,7]. $\dot{\gamma}_c$ increases with concentration as a power law and presents an Arrhenius temperature dependence [2,4–6], i.e., $\dot{\gamma}_c(\phi, T) \sim \phi^{\alpha} \exp[-E/k_B T]$, where E is an activation energy and ϕ is the surfactant concentration. After a sudden application of a constant shear rate larger than $\dot{\gamma}_c$, there is an induction period, τ_{ind}, where shear stress begins to increase sharply up to a steady-flow plateau; $\tau_{ind} \sim 1/\dot{\gamma}_c$ [8]. The higher the temperature the longer the induction period [8]; shear thickening also decreases with temperature [2]. After the induction period, the stationary stress reached at the steady-flow plateau fluctuates appreciably as time elapses (10–50%) [6,8]. Cylindrical micellar solutions that present electrostatic interactions are strongly flow history dependent [8], so specific protocols have been developed to study them [10,11]. It has been

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noticed by stress relaxation that a major portion of the stress relaxes rapidly upon turning off the flow, but a small stress persists for a long time [12]. Also, these solutions present flow birefringence. The development of a highly aligned phase approximately coincides with the shear thickening transition [3]. For a given shear rate, both the steady-state shear stress and the steady-state flow birefringence, decrease with added salt. As salt concentration increases τ_{ind} and $\dot{\gamma}_c$ increase, and the relaxation time decreases [12]. These results have been interpreted as a consequence of an increase in micelle contour length and micelle lifetime [3]. It has been suggested that micelle aggregation occurs already at shear rates smaller than $\dot{\gamma}_c$, and that the shear thickening occurs once the mean size of the aggregates has reached some critical value [13]. Small-angle neutron scattering (SANS) also shows that structures induced by shear remain long time after the cessation of the shear [14]. However, if the shear rate is removed during the induction period, the stress vanishes to zero instantaneously [8]. SANS studies strongly suggest that the increase in viscosity observed above $\dot{\gamma}_c$ is associated with a shear-induced growth of the micellar aggregates [14]. From SANS scattering data under shear [2], it was established a correlation between flow and structure. In the thickening region, observations are attributable to the superposition of two coexisting states, one made of a viscoelastic entangled sheared network and another made of short aggregates purely viscous. At higher $\dot{\gamma}$, the former state dominates and an increasing orientational order results in shear thinning. Light scattering experiments [6,15,16] suggest that the shear thickening effect is a shear-induced gelation followed by a fracture of the gel [13]. The sheared–induced gel-like and oriented phase is made of shear-induced structures (SIS) forming large fluctuating domains that are coexisting with a homogeneous fluid phase containing small rod-like micelles. In particular, using small angle light scattering, it was clear the emergence of long rod-like structures along the flow direction, which start their formation at the shear-thickening transition, where stress also starts to grow up [6]. No appreciable spacing correlation between them was observed along the flow direction, and light scattering experiments indicate that the rod-like structures may be long micellar bundles forming entangling fibers [6].

From the theoretical point of view, the dynamics of self-assembly of rigid rod-like micelles under both shear and elongational flow has been studied neglecting long-range forces among micelles [17,18]. In elongational flow, at some critical flow rate, a gelation transition was predicted to a phase of extremely long rods, which are aligned with the flow axis. For the case of shear flow it is expected that inter-micelle interactions, even if small, could induce a similar transition. Kinetic theory suggests a flow-induced first-order gelation due to the increase in rodlike micelle size as a consequence of the shear [19].

The aim of this paper is to present for the first time a convenient flow history to study formation and dismantling of SIS in the system CTAB/NaSal/water, in the low concentration regime (0.2–3 mM) at $R = 1$. Stress response measurements and direct SIS observation using light scattering during strain thixotropic loops were carried out. This experimental method allowed us to split the shear stress response during up shear thixotropic curves in two contributions, one from SIS formation and another from the supporting unstructured fluid. A population growth model, supported by the light scattering experiments, captures SIS formation. In addition, we show that thixotropic down-shear curves are independent of the flow history. Again, direct observation of SIS allow us to propose a viscoelastic model that captures SIS dismantling. This model provides us a way to define a decay shear rate constant that follows an Arrhenius behavior with temperature.

2. Experimental methods

2.1. Materials

CTAB, ⩾99%, from Fluka (Switzerland) and NaSal, ⩾99.5%, from Sigma-Aldrich (USA) were used as received. Micellar solutions were prepared by weight. Measurements were made at least three days after the solution preparation to allow them to reach equilibrium [20]. To assure that the solution was above the critical micelle concentration (CMC), we determined it. CMC = 0.093 mM in CTAB for $R = 1$, at 20 °C (details in the Supporting material).

2.2. Methods

Rheometric measurements were made with a modified cone–plate rheometer (RV-III + Brookfield, USA), a Bohlin Gemini HRnano (Malvern Instruments, UK), and a homemade transparent Couette rheometer. The cone–plate rheometer controls shear rate and was modified to include in the plate a glass window for allowing fluid visualization (diagram in Supporting material). Most of the rheometric measurements were done using the same cone–plate geometry (1.565°, 48 mm diameter). When other geometries are used, the shape of flow curves is the same; although, the actual stress response values are different. A study involving different geometries has been made by Hu et al. [13,21]. The transparent Couette rheometer (Fig. 1) is made

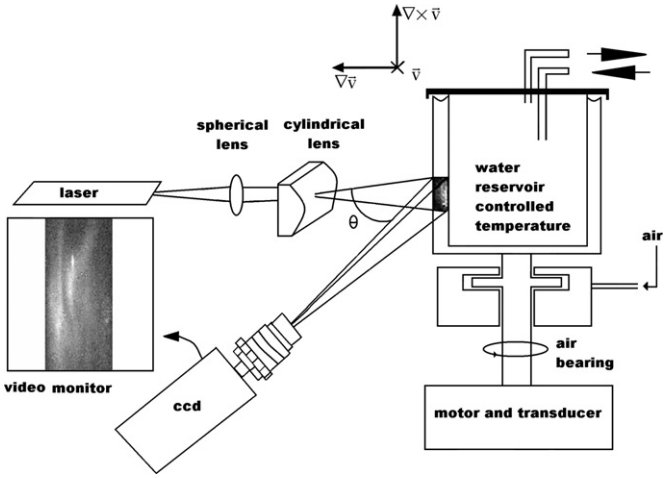

Fig. 1. Transparent Couette rheometer formed by two concentric quartz cylinders. The external cylinder rotates over air bearings. The fluid in the gap (2.5 mm) is visualized with the aid of a CCD camera and a zoom lens focused at a sheet of light made with a Ne–He laser beam and a couple of lenses.