

KINETICS OF SHEAR INDUCED MICELLAR ASSOCIATION

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ABSTRACT

Rheological measurements have been used to study the kinetics of shear induced association for rod-shape micelles formed by mixtures of ADHAB and salicylic-sodium salt. Pronounced hysteresis and large fluctuations were found in the stress-shear rate diagram. We investigate the association and dissociation mechanism through stress quench experiments where viscosity measurements study the system relaxation. The association process was found to be a single exponential with a relaxation time of about 1 minute, whereas the dissociation process was much slower and was non-exponential. In the semidilute regime, the critical shear rates increase with concentration, contradictory with existing theories.

INTRODUCTION

The structure of self-assembling surfactant systems in the aqueous phase has been studied extensively from both theoretical and experimental viewpoints [1-6]. This is due to their importance in a wide variety of applications and also to the fundamental interests such as possible phase transitions and anomalous behaviors in the nonequilibrium state. One of the striking features that is common to the surfactant micelles is shear thickening, possibly due to shear induced structuring. The relationships between the thickening and structuring mechanisms have been extensively studied both experimentally [3,7,8] and theoretically [9,10]. Based on the proposed mechanism of micelle collisions prompting association, the theories predict that the critical shear rate decreases with surfactant concentration [9,10]. We have set out to investigate these problems experimentally.

Rheological and dynamic light scattering measurements are used to study the structure and kinetics of the rod-shaped micelles. We focus our attention on the kinetics of the system under shear. Investigation of the association and dissociation mechanisms are done through stress quench experiments where viscosity measurements study the system relaxation.

EXPERIMENTAL

Materials

The sample is a semi-dilute, aqueous solution of allyl dimethylhexdecylammonium bromide (ADHAB) and salicylic-sodium salt in equimolar ratios. The sample concentrations ranged from 0.01 to 0.25 %wt. Dynamic light scattering and scanning electron micrographs show that the system forms rod-like micelles with mean lengths of 500 Å (60% polydispersity) and monodisperse diameters of 50-60 Å (about twice as large as an individual

surfactant monomer). This mean micelle length in the semidilute regime scales as $c^{0.57}$ similar to that reported by Candau et al. [2]. This exponent decreases as the concentration approaches c^* .

Experimental apparatus

We use a Zimm viscometer to measure the viscosity of the micelle solution. This viscometer has a couette geometry with a fixed outer cylinder which also holds the sample. A slightly under buoyant inner cylinder suspended in the sample automatically centers itself in the outer cylinder through surface tension. A cylindrical aluminum block placed in the inner cylinder controls the buoyancy and couples to an external rotating magnetic field. The magnetic field is produced by a U-shaped magnet positioned around the outer cylinder. The rotating magnet drives the inner rotor through induction in the aluminum block. In our experiment we control the shear stress which is proportional to the rotation speed of the magnet and measure the shear rates through the responding rotation rate of the inner cylinder. The shear rates are calculated through the geometry of the cylinders while the applied stress is calibrated against the viscosity of pure water. In this report all our measurements were done at shear rates well below the onset of the Taylor instability.

Rheological measurements

Figure 1 shows typical shear stress vs. shear rate relationships for several different concentrations. Here the stress is slowly ramped up to a high stress and then ramped back down while a computer reads stress and shear rate data. Note that our independent variable is plotted on the vertical axis, this was done for the ease of reading the viscosity which is

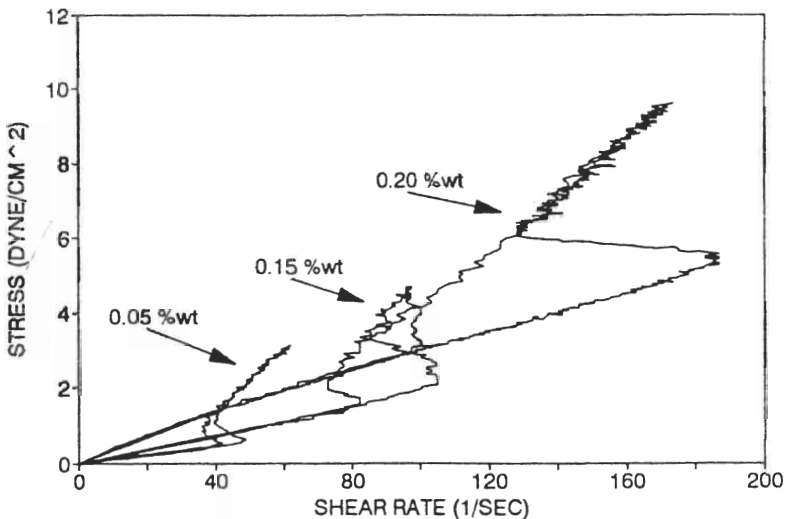


Figure 1. Stress-rate curves for several different surfactant concentrations

the stress/rate. In the two lower concentration samples we see initially Newtonian behavior with a viscosity of about 1 cp at the lowest concentration. At the higher concentration there is an initial shear thinning behavior. We define a critical shear rate at the point where the system begins to show the dramatic shear thickening behavior. At even higher stresses (not shown) this system returns to Newtonian behavior with a viscosity of about 5 times the original viscosity. Several other interesting features in the stress-rate curves are the critical shear rate at which the transition occurs, the hysteresis effect, and the large fluctuations in the shear thickening region. The large fluctuations have a time scale of one minute. These slow fluctuations and the hysteresis in the shear thickening region indicate that slow kinetic processes are occurring. The shear thickening behavior was studied with changes of concentration as well as temperature.

Kinetic measurements

Shear stress quench experiments were performed to study the kinetic processes of aggregation and dissociation. In the quench experiments we begin at either a low or high stress and then quickly change (jump or drop) to a higher or lower stress, as shown in figure 2. Due to the slow kinetic behavior, the system cannot readjust to the new stress quickly enough and must follow a Newtonian path to the new stress. Once the system reaches the new stress we are able to watch the shear rate change, the horizontal process, as the system relaxes back to a "steady state." From this we can determine relaxation rates for the association and dissociation processes.

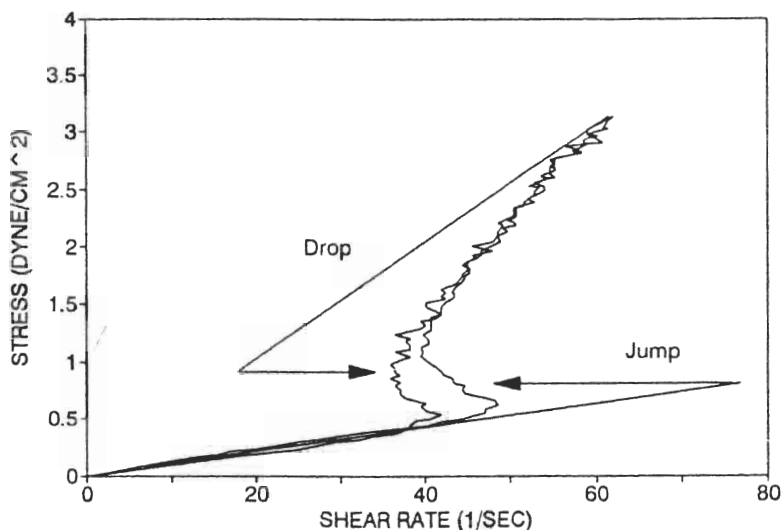


Figure 2. Quench experiments to study the kinetics of association and dissociation

RESULTS AND DISCUSSION

In the viscosity experiment, concentration and temperature dependence of the critical shear rate was observed. The critical shear rate increases linearly with concentration, figure 3, and exponentially with temperature, figure 4. The positive slope of the critical shear rate (γ_c) with concentration is rather surprising. Simple scaling arguments give a negative slope to this relation since $\ell \sim c^{0.37}$, the critical shear rate goes like

$$\gamma_c = \frac{1}{\tau_r} \approx \frac{1}{\ell^3} \sim c^{-1.71} \quad (1)$$

where τ_r is the rotational relaxation rate and ℓ is the average micelle length. Theoretical predictions by S. Q. Wang also give a negative slope with magnitude 1.37 [9]. It may be that these arguments are only good at higher concentration and we are planning to study these higher concentrations.

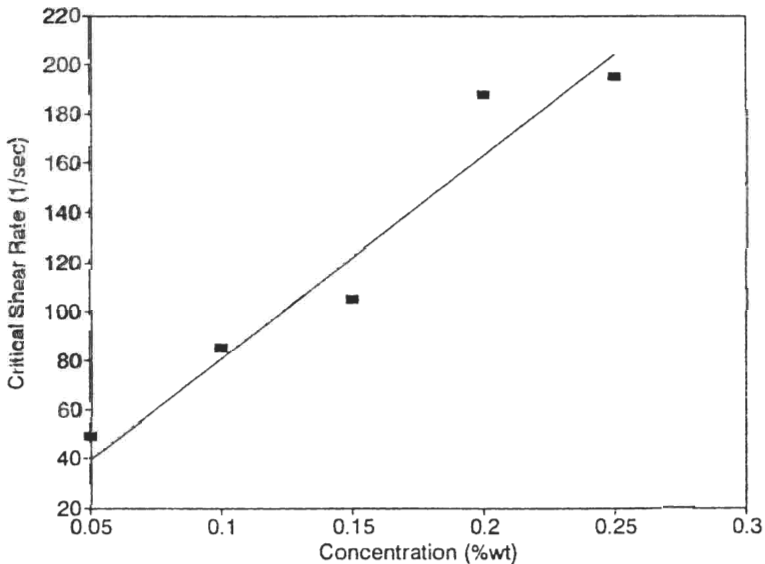


Figure 3. Critical shear rate vs. concentration

In the quench jump experiment we observed single exponential relaxations. These relaxation times were on the order of 10 seconds and decreased with an increase in temperature. However, the quench drop experiment showed a non-exponential decay. Drop relaxation rates depended on the shear stress to which the system was quenched and ranged from 10^2 to 10^4 seconds. The shorter relaxation rate was obtained for the higher final stresses.

The final stress dependence of the dissociation indicates that by adding energy to the system (through mixing in the shear field) the system was able to reach steady state more quickly. This trend was also observed in the static light scattering experiments. In our preliminary study, we found that in the shear thickened state, the forward scattering intensity was much stronger than in the quiescent state. This implies that more

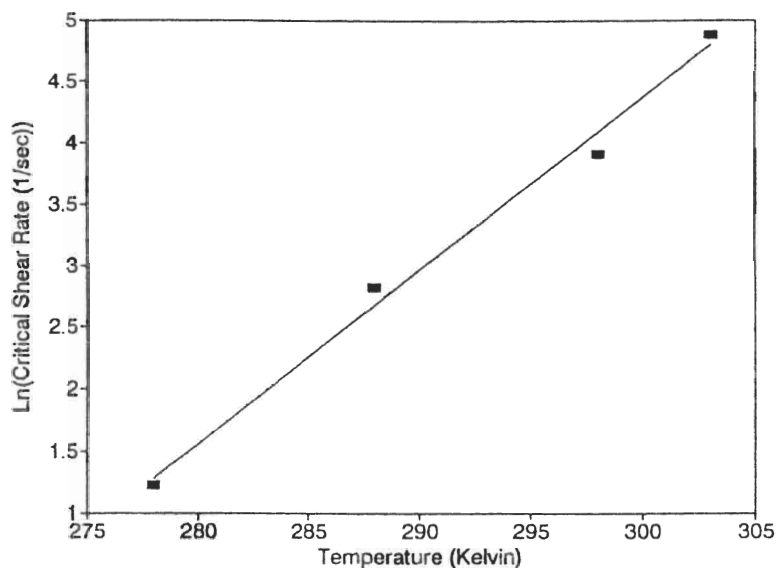


Figure 4. Ln(Critical shear rate) vs. Temperature

massive objects exist under high shear. We then followed the decay of scattering intensity after the shear was quenched down to a quasi-quiescent state (enough shear to homogenize the sample). We found an exponential relaxation with a decay time of about 10^4 second, much longer than the nonexponential relaxation when final stress was higher. In addition to this shear assisted process, other possible explanations for the non-exponential behavior may involve several possible dissociation channels to the final steady state. However, at this point we do not have experimental evidence or theoretical support for this.

SUMMARY

The kinetics of aggregation and dissociation of self-assembling surfactant micelles has been studied using rheological and light scattering measurements. We observed complicated kinetics associated with the shear induced structure. The kinetics were shown to be exponential for the aggregation and either exponential or nonexponential for dissociation, depending on the amount of shear mixing in the final state. It was also shown that for semi-dilute micelle samples the critical shear rate increases with concentration contradicting existing theories. Further work is planned to explore these kinetics more fully.

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