

LETTERS

Kinetics of Alignment and Decay in a Highly Entangled Transient Threadlike Micellar Network Studied by Small-Angle Neutron Scattering

P. D. Butler,^{*,†,‡} L. J. Magid,^{†,‡} W. A. Hamilton,[‡] J. B. Hayter,[‡] B. Hammouda,[§] and P. J. Kreke[†]

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996; Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831; and National Institute of Standards and Technology, Building 235, E151, Gaithersburg, Maryland 20899

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We report on a study of the kinetics of alignment and decay of alignment, using small-angle neutron scattering (SANS), of a complex fluid under Couette shear containing a highly entangled network of threadlike micelles. The time scales of alignment revealed are dominated by the collective properties of the network rather than the individual micellar segments. This results in rates orders of magnitude slower than any previously observed in similar systems as well as in the first observation of an alignment proceeding in two stages.

Introduction

In solution many surfactants aggregate into cylindrical macromolecular structures. In some cases these threadlike micelles are so highly extended that even dilute solutions, with volume fractions (ϕ_s) less than 1%, are above the overlap concentration (c^*) at which interaction between cylinders becomes significant. Elucidation of the microstructure and complex fluid dynamics exhibited by such systems at rest and under shear is an area of considerable theoretical, experimental and practical interest. To a first approximation cylindrical micelles in solution can be treated theoretically as high molecular weight polymers.^{1,2} However two critical differences must be taken into account: (1) these self-aggregating structures are transient rather than permanent, constantly breaking and recombining; (2) their diameter is relatively large (roughly twice the extended length of the hydrocarbon tail), making them considerably stiffer than typical flexible polymers.

Micellar solutions containing cylindrical micelles aligned by shear flow were first investigated by small-angle neutron scattering (SANS) by Hayter and Penfold³ and by Hoffmann and co-workers.⁴ Since 1984, SANS has been used to study various aqueous micellar solutions under shear below and slightly above c^* .^{5,6} More recently, time-dependent SANS has been used to study the kinetics of alignment and decay. Studies on two systems containing shear-induced structures (SIS, so-called type II micelles) have found characteristic times on the order of seconds.^{7,8}

Here we report the first observation in isotropic micellar or polymer solutions of characteristic time constants which are orders of magnitude larger. This work uses SANS to study the kinetics of alignment under (cylindrical) Couette shear in a strongly viscoelastic micellar solution of the cationic surfactant cetyltrimethylammonium 3,5-dichlorobenzoate (CTA3,5ClBz) well above c^* . At 20 mM, the solution is a Maxwell fluid,

with a zero-shear viscosity, η_0 , of 1200 Pa s and $G_0 = 2.4$ Pa.⁹ The diameter of the micelles formed is 4.6 nm, and the persistence length, l_p , is 40–60 nm.¹⁰ Dynamic rheological measurements allow evaluation¹¹ of (1) the mean micellar length, 8.7 μm in this highly polydisperse micellar population; (2) ξ , the distance between entanglements, of 120 nm; and (3) a contour length between entanglement points l_e of 210 nm. The micellar surface charge density can be tuned without appreciably changing ξ (as assessed by G_0) by replacing a portion (here 30%) of the 3,5-dichlorobenzoate counterions by bromide ions, which increases the extent of counterion dissociation. Thus, the two systems discussed here are the homogeneous counterion (HC) system with 20 mM of CTA3,5ClBz, and the mixed counterion (MC) system containing 14 mM CTA3,5ClBz and 6 mM CTABr, making it 70 mol % in CTA3,5ClBz. We have reported previously on the steady-state shear-induced hexagonal ordering of these micellar threads for the MC system in Poiseuille flow near a plane quartz surface.¹² The Couette shear cells were of standard design,³ and the data were acquired and corrected in the usual fashion.^{13,14} We define $Q_{||}$ and Q_{\perp} directions as parallel and perpendicular to the flow direction, respectively.

Results and Discussion

For each sequence of shearing or relaxation, data were acquired over time intervals of 2.5, 5, or 10 min. The ring of scattering in the top image of Figure 1 shows the isotropic ordering of the entangled micellar network of the HC system at rest. The middle and bottom images of Figure 1 contrast the scattering pattern taken at 200 s^{-1} during the first 5 min to that observed in the $t = 25$ –30 min time slice. The middle pattern exhibits broad off-axis scattering which suggests that the initial alignment may be due mainly to stretching of the network rather than to its topological rearrangement. Full alignment as displayed in the bottom image, which requires that the network be disentangled, develops more slowly.

Figure 2 shows a series of scattering patterns for the HC system and the MC system at steady-state alignment for a range of shear rates, all well into the nonlinear viscoelastic regime

* Corresponding author.

[†] University of Tennessee.

[‡] ORNL.

[§] NIST.

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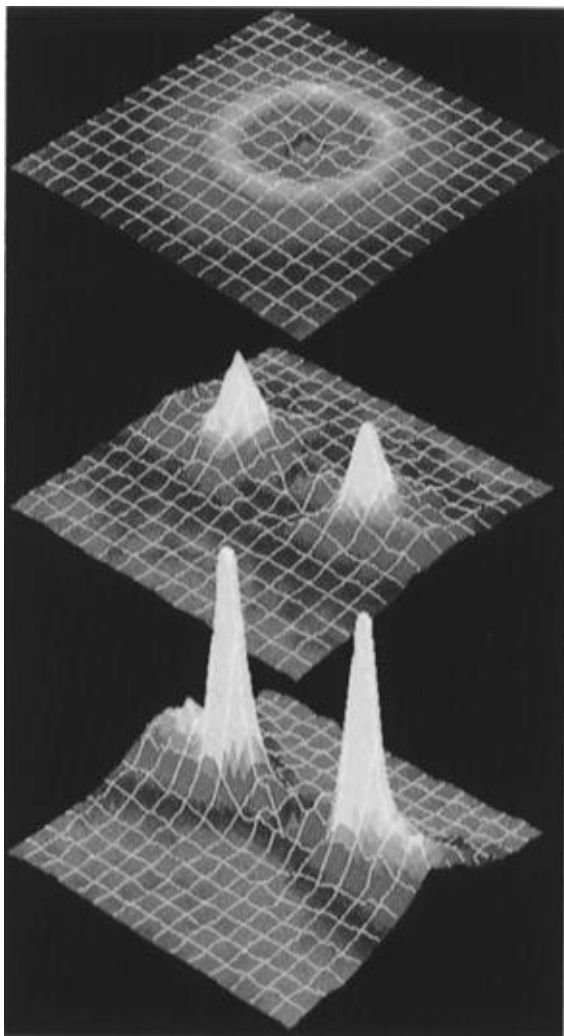


Figure 1. At rest, initial (0–5 min) and alignment plateau (25–30 min) scattering patterns for the HC system at a shear of 200 s^{-1} . The patterns are 0.8 nm^{-1} on a side and to the same vertical scale.

($\dot{\gamma}\tau \gg 1$).^{15,16} The scattering patterns become increasingly anisotropic with shear, with the intensity in the isotropic ring gathering into two peaks centered about $Q_{||} = 0$. As has been observed previously, the Q position of the maximum in intensity in both systems does not change with shear.^{3,7} However, below full alignment, the two solutions have markedly different behaviors at a given $\dot{\gamma}$. At 20 s^{-1} , the HC system shows only weak alignment, as evidenced by significant scattering remaining

along $Q_{||}$, while the MC system is fully aligned. Indeed, the MC system exhibits scattering at 1 s^{-1} having an anisotropy greater than that of the HC system at 40 s^{-1} . The HC system displays full alignment at shears $\geq 200 \text{ s}^{-1}$. Since scattering from micellar segments aligned along the flow direction is predominantly along Q_{\perp} , we may conveniently track the time course of alignment by integrating the scattered intensity along the Q_{\perp} axis (at $Q_{||} = 0$) over a swath the width of the instrument resolution in $Q_{||}$. Figure 3 compares the resulting swath intensities for the two solutions.

The two samples also differ markedly with respect to kinetics of alignment decay (Figure 4). Within 10 min of cessation of shear on solutions at their respective plateaus of alignment, the scattered intensity in the Q_{\perp} swaths for the HC system at 40 and 200 s^{-1} (i.e., weakly and strongly aligned, respectively) has decayed to the zero-shear isotropic value. In contrast, 80–120 min is required for the corresponding decay of intensity in the MC system. The decay curves can be fit to first order using a single-exponential leading to relaxation times, τ_d , in the range of 20–25 min for the MC system and $\tau_d < 3.5$ min for the HC system.

Examination of Figure 3 highlights a very interesting feature: the alignment of the HC system at 200 and 400 s^{-1} , for which full alignment is eventually reached, proceeds in two stages. To our knowledge, this is the first time such a phenomenon has been observed, and it clearly indicates that at least two distinct processes, with very different time constants, are contributing to the full alignment of these solutions of entangled wormlike chains. The MC system, on the other hand, exhibits an alignment overshoot¹⁷ much like that seen in similar systems (albeit on a much shorter time scale).¹⁸

The results on the two systems may be summarized as follows: (1) full alignment under steady shear requires much higher $\dot{\gamma}$'s (by at least an order of magnitude) for the HC than for the MC system; (2) upon cessation of shear, the decay of alignment is an order of magnitude more rapid for the HC than for the MC system; (3) the two systems are further distinguished by the details of the temporal evolution of the alignment; (4) the times required for alignment, as well as the decay time for the MC system, are several orders of magnitude greater than any previously reported for isotropic solutions of either micelles or polymers. A significant input of energy is clearly required to initiate and complete disentanglement; for the HC and MC systems respectively, the plateaus of alignment are reached after $(1-5) \times 10^5$ and $(4-6) \times 10^3$ strain units ($\dot{\gamma}t$).

Our measurements demonstrate that increasing the micellar surface charge density σ (i.e., upon going from the HC to the

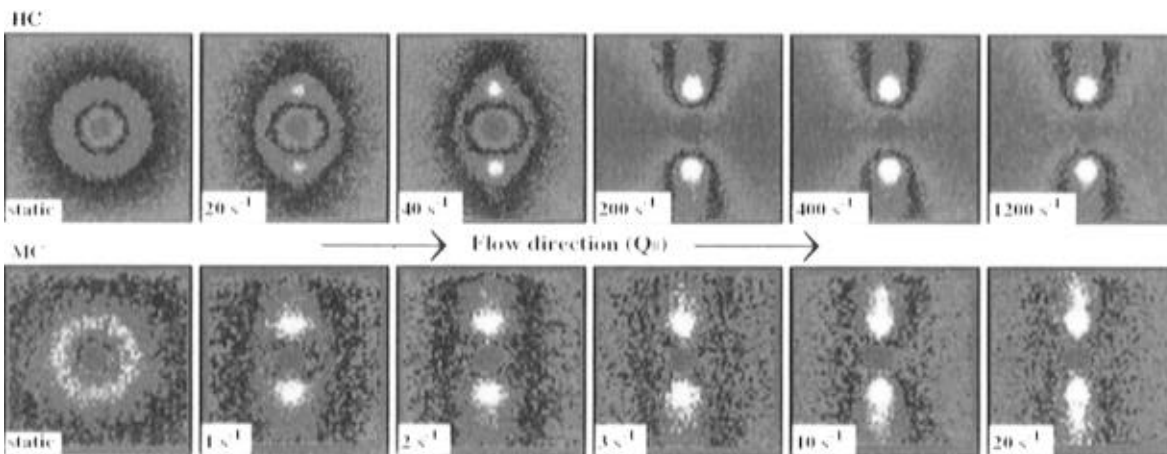


Figure 2. Steady-state scattering patterns at a range of shear rates for the HC and MC systems. Individual runs beyond the plateau of alignment were summed to improve S/N. The patterns are 0.8 nm^{-1} on a side.

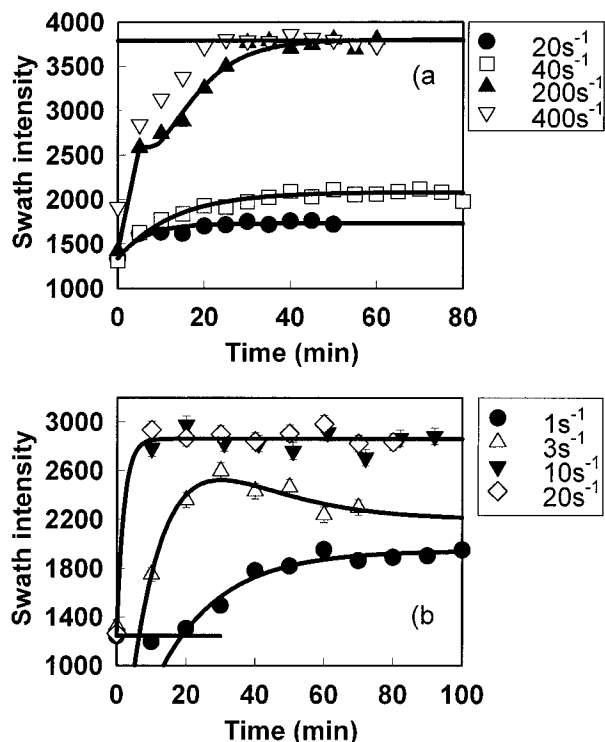


Figure 3. Time course of alignment at a range of shear rates for (a) the HC system and (b) the MC system. The solid lines are a guide to the eye.

MC system) has a remarkable effect on the extent and kinetics of alignment in these highly entangled micellar solutions. Microscopically, this increase in σ must have at least two effects: first, it must increase the micellar persistence length, l_p , which results in fewer l_p 's per l_e in the MC case. Second, it must decrease the adhesion energy^{19,20} associated with an entanglement (or topological constraint) involving two or more threadlike micellar segments. Most interesting, however, is this two-step approach to alignment in which about 50% of the anisotropy develops within the first 5 min while another 25–30 min is required to achieve full alignment. This behavior is evidence of the operation of at least two kinds of processes with very different time constants.

We propose that the first step in the alignment process is a local deformation (stretching) of the network resulting in alignment of micellar segments over a scale $\approx l_e$, whose effect on the anisotropy of scattering at a given shear rate will be strongly l_p dependent. The higher the elastic restoring force resisting extension of micellar entanglement lengths in the flow field, the greater the shear required for alignment. In this respect, the HC system, with its lower σ and more flexible micelles, behaves relative to the MC system in a manner analogous to flexible synthetic polymers in flow fields, for example polystyrene as compared to poly(styrenesulfonate).²¹ Much smaller shear gradients are required to stretch poly(styrenesulfonate) than are needed for the corresponding polystyrene.

The second process is the larger scale disentanglement and alignment of the individual micellar threads in the flow field. We propose that the kinetics of this process is considerably retarded in the HC system due, primarily, to the substantial transient adhesive contacts between entangled micelles caused by the relatively small σ . As a result, the reptation time for a given length of micellar thread is large enough to lead to an observable difference in the characteristic times for the two

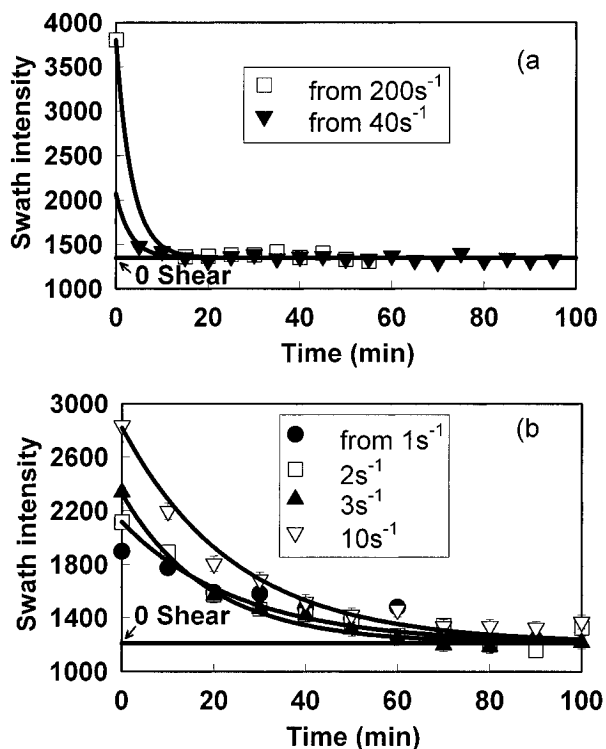


Figure 4. Time course of the relaxation from the plateau of alignment at various shear rates for (a) the HC system and (b) the MC system. processes in the HC system at 200 s^{-1} . To date, no such clearly distinguishable two steps have been observed for the MC system.

The different l_p 's caused by the difference in σ 's contribute to the marked difference in the kinetics of decay of alignment. Upon cessation of shear, the aligned micelles in the HC system show a more rapid decrease in root-mean-square end-to-end distance because of the less hindered motion allowed by their lower σ and greater flexibility. Note that recovery of the zero-shear swath intensity does not require the microstructure to be identical on all length scales to that present prior to shearing. The decay time τ_d is thus a lower bound on the characteristic time, τ_e , for reentanglement upon cessation of steady shear flow.

We have thus discovered the first example of alignment in a micellar living polymer system (HC) under shear which proceeds with two very different time constants. Furthermore the time constants observed for both systems are orders of magnitude larger than anything previously observed in similar systems. We have also demonstrated that tuning the surface charge density in a highly entangled transient micellar network provides a powerful means of controlling not only the extent but also the kinetics of micellar alignment.

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