NOVEL KINETIC EFFECTS IN VISCOELASTIC SURFACTANT SOLUTIONS UNDER SHEAR


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

ABSTRACT

Using small-angle neutron scattering (SANS), we have investigated the transient alignment and relaxation under Couette shear of viscoelastic aqueous micellar solutions of cetyltrimethylammonium 3,5-dichlorobenzoate (CTA3,5Cl) and CTA3,5Cl/CTAB mixtures at concentrations well above φ* (but below 1.0 wt.%). Time constants of the order of ten's of minutes are reported for alignment and relaxation, orders of magnitude slower than any previously observed in similar micellar systems. The collective properties of the network of entangled, threadlike micelles, rather than the individual micellar segments, dominate the alignment and relaxation behavior. At low micellar surface charge density (φ) (e.g., in pure CTA3,5Cl), the first observation of alignment proceeding in two stages has been made. Increasing φ decreases by an order of magnitude the shear rate required to reach full alignment and provides a comparable decrease in the rate constant for relaxation after cessation of shear.

INTRODUCTION

We have recently described a near-surface SANS investigation of the steady-state shear-induced hexagonal ordering of micellar threads in a viscoelastic aqueous solution under Poiseuille flow [1]. The 20mM CTA3,5Cl/CTAB (70/30 mol/mol) solution, in D2O for neutron contrast, studied in that work contains micelles having a diameter of 4.6 nm, contour lengths on the order of many 100's of nm, and a persistence length of 40-60 nm. For this solution, φ = 0.01, and is at least a factor of 20 above φ*.

In the current work we report significant new results on the kinetics of micellar alignment and decay of alignment under Couette shear [2], and we exploit the simple device of varying the molar ratio of the two surfactant counterions, in order to tune φ.

RESULTS AND DISCUSSION

The variation in surface charge density has little effect on the mesh size of the micellar network, but it has a dramatic effect on the extent of alignment at a given shear rate (γ) and on the time course of alignment. Figure 1 shows the anisotropic two-dimensional scattering patterns at the plateaus of alignment which result for a range of γ's for two solutions: 20mM CTA3,5Cl (hereafter referred to as the homogeneous counterion (HC) system) and the mixed
The two systems, MC and HC, are governed by the SANS scattering patterns. The MC system exhibits a different behavior compared to the HC system. The solid lines in the diagrams represent the theoretical predictions, while the symbols depict the experimental data. The x-axis represents time, and the y-axis represents intensity. The graphs show the evolution of intensity over time for different initial conditions.

The SANS scattering patterns are indicative of the system's response to external perturbations. The patterns evolve over time, indicating the system's transition to a new equilibrium state. The MC system shows a more rapid response, while the HC system exhibits a slower evolution, consistent with the theoretical predictions.
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solutions also differ markedly with respect to kinetics of alignment decay, Figure 3. The rate constants for both alignment and decay of alignment are orders of magnitude smaller than those observed previously for other micellar solutions under shear [3].

The increase in micellar surface charge density on going from the HC to the MC micellar solution affects some aspects of the micellar network's microstructure. It must increase the micellar persistence length and decrease the adhesion energy associated with an entanglement (or topological constraint) involving two or more threadlike micellar segments. Analysis of the alignment of the micelles in these solutions under shear requires at least two kinds of processes having separate time constants. We present a more complete discussion of these processes elsewhere [4], noting here only that these processes are (1) a local deformation (stretching) of the network resulting in alignment of micellar segments over a length scale of roughly the distance between entanglement points and (2) the larger-scale disentanglement and alignment of the individual micellar threads in the flow field. Increasing $\sigma$ enhances deformation at lower $\gamma$'s and increases the rate at which (2) occurs.

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REFERENCES