NOVEL KINETIC EFFECTS IN VISCOELASTIC SURFACTANT SOLUTIONS UNDER SHEAR

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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 (σ) (e.g., in pure CTA3,5Cl), the first observation of alignment proceeding in two stages has been made. Increasing σ 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 D_2O 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, $\phi_s = 0.01$, 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 σ.

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 ($\dot{\gamma}$) 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 $\dot{\gamma}$'s for two solutions: 20mM CTA3,5Cl (hereafter referred to as the homogeneous counterion (HC) system) and the mixed

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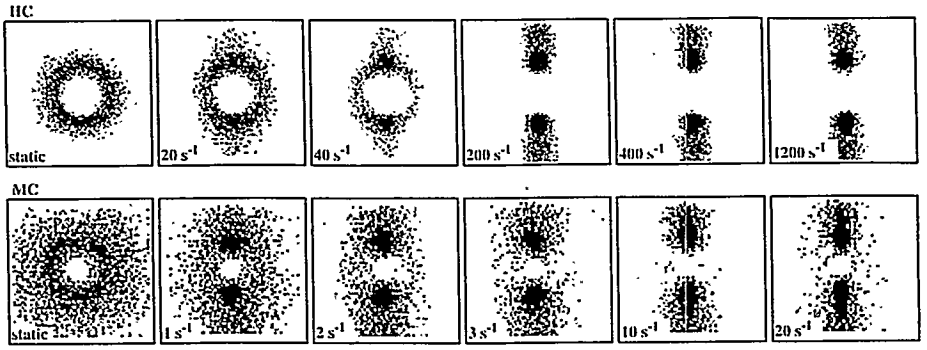

Fig. 1. Steady-state 2D SANS scattering patterns at a range of $\dot{\gamma}$'s for the 20 mM HC and MC aqueous micellar solutions. Individual runs beyond the plateau of alignment were summed to improve S/N. The scattering geometry is: the incident neutron beam and the shear gradient $\dot{\gamma}$ are along the y axis; the flow direction is along the x axis, and the 2D detector is in the x-z plane. The $Q_\perp$ direction referred to in the text is the z axis. The patterns are 0.8 nm^{-1} on a side.

counterion (MC) system studied previously under Poiseuille flow. Since scattering from micellar segments along the flow direction is predominantly along $Q_\perp$, we track the time course of alignment by integrating the scattered intensity over a $Q_\perp$ swath. Figure 2 compares the resulting swath intensities for the two solutions. Note that the HC solution exhibits an apparent stepwise approach to full alignment at 200 and 400 s^{-1}, while the MC system does not at the (correspondingly) lower $\dot{\gamma}$'s required for its full alignment. The two

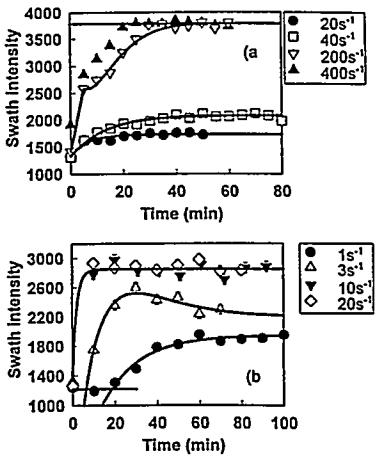

Fig. 2. Time course of alignment at a range of $\dot{\gamma}$'s for a) the HC system and b) the MC system. The solid lines are only a guide to the eye.

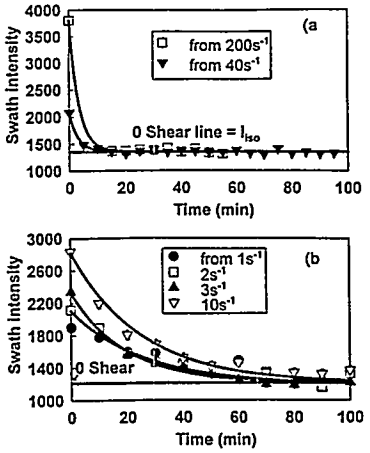

Fig. 3. Time course of the relaxation from the plateau of alignment at various shear rates for a) the HC system and b) the MC system.

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 σ enhances deformation at lower $\dot{\gamma}$'s and increases the rate at which (2) occurs.

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REFERENCES

[1] W. A. Hamilton, P. D. Butler, S. M. Baker, G. S. Smith, J. B. Hayter, L. J. Magid, and R. Pynn, Phys. Rev. Lett. **72**, 2219 (1994).

[2] J. B. Hayter and J. Penfold, J. Phys. Chem. **88**, 4589 (1984).

[3] V. K. Jindal, J. Kalus, H. Pilsl, H. Hoffmann, and P. Lindner, J. Phys. Chem. **94**, 3129 (1990); Ch. Münch, H. Hoffmann, K. Ibel, J. Kalus, G. Neubauer, U. Schmelzer, and J. Selbach, J. Phys. Chem. **97**, 4514 (1993).

[4] P. D. Butler, L. J. Magid, W. A. Hamilton, J. B. Hayter, B. Hammouda, and P. J. Kreke, submitted to Phys. Rev. Lett.