Effect of a solid/liquid interface on bulk solution structures under flow

P. D. Butler*, W.A. Hamilton*, L. J. Magid*, T. M. Slawec**i, Z. Hanb, and J. B. Hayter*

*aSolid State Division, Oak Ridge National Laboratory, Oak Ridge TN 37831-6393 USA,
bChemistry Dept., University of Tennessee, Knoxville TN 37996-1600 USA, National Institute of Standards and Technology, Gaithersburg MD 20899 USA.

It has been known for some time that a shear field can impart enough energy to a liquid system for it to exhibit a phase change. Not as well appreciated is the fact that non Newtonian solutions can be driven into a quasi phase separation due to the vastly different shear rates between the bulk and near surface regions. Using a variety of scattering techniques we have probed the interfacial and near surface region of a system of wormlike colloidal particles under flow separately from the bulk. We find that the hexagonal phase which forms under flow near the surface, does not persist into the bulk. We also present data showing substantial differences in the kinetics of alignment and relaxation of the two phases.

Keywords: micelles, shear, flow

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Many of the technological applications of viscoelastic surfactant solutions depend on their drag reducing and shear thinning properties. While such systems have been studied for over a decade[1], the focus has almost always been on the bulk, whereas these important phenomena clearly must be governed by the fluid microstructural behavior under flow near a surface. In this paper we report on an investigation of a viscoelastic system of cetyltrimethylammonium cationic surfactant, with a 7:3 mixture of 3,5dichlorobenzoate:bromide counterions, in the proximity of a quartz surface while undergoing shear.

Neutron reflectivity measurements, probing structures in a direction normal to the surface that are highly correlated with that surface, indicate the existence of a 2.5+/-0.5 nm layer of surfactant adsorbed onto the quartz surface[2]. Furthermore, this layer appears to be independent of flow. Using near-surface small angle neutron scattering (NS-SANS) however, we have observed that under Poiseuille shear conditions remarkable near-surface hexagonal ordering occurs[3]. This ordering occurs within a 30μm layer next to the surface, the depth to which NS-SANS can penetrate in this system[4], and is oriented with respect to that surface (a “single crystal” structure). The rods in this system align themselves under flow with a nearest neighbor separation of 45nm. In order to examine the extent to which this ordering is purely a surface phenomena, we have made SANS measurements of the bulk solutions under shear using a Couette shearing device (Fig. 1). Since observation of the first order peak requires a different crystal orientation than is required for observation of the second order peak, the existence of both peaks in our data shows that the shear oriented hexagonal structure cannot persist into the bulk. Further, attempts to fit the data with a 2D hexagonal powder
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model failed, indicating that the most likely bulk ordering is that of a 2D liquid with the rods oriented in the flow direction. Thus the hexagonal structure seems to be completely driven by the proximity of the surface rather than the flow field.

Structural relaxation in the two regions was also studied. Relaxations were quantified by following the normalized intensities of both the $0\overline{1}$ and $1\overline{0}$ peaks of the hexagonal structure (Fig. 2) and the intensity in the direction perpendicular to the flow (the peak region) in the case of the Couette data (Fig. 3). The bulk 2D liquid alignment[5] decays very slowly with a decay constant of 25 minutes (1500 seconds), while the decay constant for the hexagonal structure is only 3.5 seconds. Further, although the relative strength of the $0\overline{1}$ peak and its persistence in more turbulent steady state flow regimes has seemed to indicate that the hexagonal structure is better ordered and in some sense “stiffer” in the shear gradient (surface normal) direction, both peaks decay at the same rate. The three orders of magnitude difference in the decay constants between the two regions coupled with their very different steady state structures leads to the conclusion that these systems can truly be thought of as biphasic. This is undoubtedly due to “micro-rheological” hydrodynamic effects acting within a few tens of microns of the surface.

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FIGURE CAPTIONS

1. Plot of a vertical slice through the detector image (at \( Q_x = 0 \)). The solid line represents the best 2D powder model fit to the data.

2. Decay of integrated \( 01 \) and \( 10 \) diffraction peak intensities [shown in inset] after cessation of flow (\( t=0 \)).

3. Decay of the integrated intensity in a narrow vertical stripe on the detector perpendicular to the flow (“swath”) after cessation of shear (\( t=0 \)).