

Version Date: July 15, 1997

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

P. D. Butler^a, W.A. Hamilton^a, L. J. Magid^b, T. M. Slaweck^c, Z. Han^b, and J. B. Hayter^a^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

MASTER

corresponding author:

Paul Butler
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6393

FAX: (423) 574-6268

Phone: (423) 576-7747

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-96OR22464. Accordingly, the U.S. Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of the contribution, or allow others to do so, for U.S. Government purposes."

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 $30 \mu\text{m}$ 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

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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 **01** and **10** 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 **01** 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.

Acknowledgments This work was supported by the U.S. Department of Energy under contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. Some of the measurements were performed on the NIST NG3 spectrometer which is supported by NSF under agreement DMR9122444. Identification of certain equipment or materials does not imply recommendation by NIST.

REFERENCES

1. See for example the review article: M. E. Cates and S. J. Candau, *J. Phys.: Condens. Matter* 2 (1990) 6869.
2. P. D. Butler, W. A. Hamilton, L. J. Magid, J. B. Hayter, T. M. Slawewski and B. Hammouda, *Faraday Discussion* 104 (1997) 65.
3. 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 (1994) 2219.
4. W. A. Hamilton, P. D. Butler, John B Hayter, L. J. Magid and P. J. Kreke, *Physica B* 221 (1996) 309.
5. P. D. Butler, L. J. Magid, W. A. Hamilton, J. B. Hayter, B. Hammouda and P. J. Kreke, *J. Phys. Chem.* 100 (1996) 442.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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 ($t=0$).





