

SUPPORTING INFORMATION:

Rheology and neutron reflectometry of an anionic surfactant at the solid-liquid interface

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Rheology Data

Two sets of rheological data were collected: that from the reflectivity experiment where the sample was overloaded (overfilled), and offline measurements from a different instrument which were filled correctly. The offline measurements were taken using a Bohlin CVO controlled stress rheometer, with a cone diameter of 40mm and angle of 4°. A controlled rate shear ramp was measured followed by the time dependence of the AOT solution at a range of shear rates from 4 to 15 s⁻¹.

A shear ramp from 0.1 to 100 s⁻¹ was measured with the offline rheometer, which indicated Newtonian behavior, as expected for this relatively low concentration solution, up to approximately 20 s⁻¹, followed by slight shear thinning. On applying a steady shear rate, there was an initial rise in viscosity, which was similar for each applied rate, and was followed by a peak in viscosity with time (i.e. an overshoot in viscosity). Figure S1 shows the viscosity measurements for each shear rate as a function of strain amplitude (shear rate*time). When plotted in this way, the different shear rates show the same overall trend in behavior, with the peak occurring around 1600, in very good agreement with the NR peak observations (critical strain amplitude of 1800). If the viscosity (η) at this peak position is plotted as a function of shear rate ($\dot{\gamma}$) for 5, 7, 10 and 15 s⁻¹, it is found that $\eta \propto \dot{\gamma}^{-0.88}$. This is a similar exponent to that found on MLV formation.^{1,2} Most of the existing literature has considered higher concentrations of AOT, but Valdes et al.³ have found a viscosity of approximately 0.3 Pa s at rates up to 4 s⁻¹ for 5 wt.% AOT. This also agrees reasonably well with the increasing viscosity with time observed in this work.

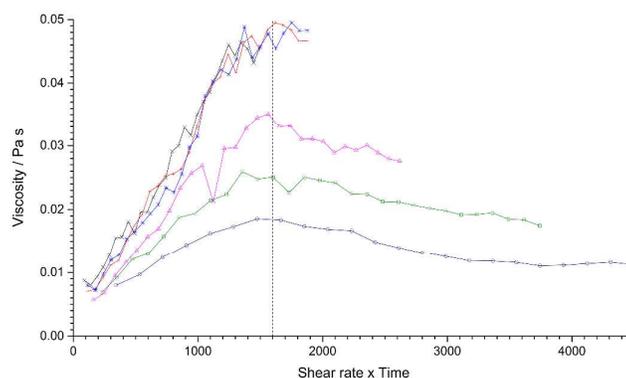


Figure S1: Viscosity versus strain amplitude from offline rheology measurements at: black cross= 4 s^{-1} , red plus and blue star= 5 s^{-1} , pink triangle= 7 s^{-1} , green square= 10 s^{-1} and dark blue circle= 15 s^{-1} . The vertical dashed line shows strain=1600.

The in-situ rheology data, taken from the sample on the neutron instrument, also showed a slight increase in viscosity with time at each shear rate, with the data becoming much noisier and plateauing after the Bragg peaks were lost within the NR measurement. This suggests that the change in near-surface ordering occurs with a simultaneous change in the bulk, as the rheometer is predominantly a “bulk” probe. On lifting the rheometer cone, “clumps” of surfactant were observed on the liquid surface suggesting a possible flocculation/phase separation of the surfactant on destruction of the lamellar phase and possible reformation of another phase.

The rheology results under oscillatory shear also show a change in behavior after the 'plateau' in Bragg peak intensity observed in the reflection data. Under oscillatory conditions, the rheology phase angle was predominantly 90° indicating a pure liquid-like response to the applied shear strain. The 500%, 1 Hz and 2 Hz samples showed slightly lower phase angle, with an average of 81° and 82° respectively. This indicates a small solid-like contribution and is consistent with a stable bulk lamellae phase.

- (1) Bergholtz, J.; Wagner, N. J. Formation of AOT / Brine Multilamellar Vesicles. *Langmuir* **1996**, *12*, 3122–3126.
- (2) Escalante, J. I.; Hoffmann, H. Non-Linear Rheology and Flow-Induced Transition of a Lamellar-to-Vesicle Phase in Ternary Systems of Alkyldimethyl Oxide / Alcohol / Water. *Rheol. Acta* **2000**, *39*, 209–214.
- (3) Valdes, M.; Manero, O.; Soltero, J. F. A.; Puig, J. E. Rheology of Lyotropic Liquid Crystals of Aerosol OT 1. Low Concentration Regime. *J. Colloid Interface Sci.* **1993**, *160*, 59–64.