In-Situ Shear of Adsorbed Surfactant Layers at the Solid/Liquid Interface: A Neutron Reflection Study

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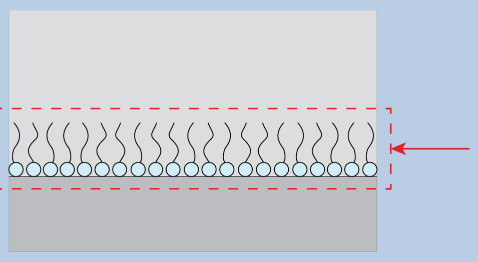
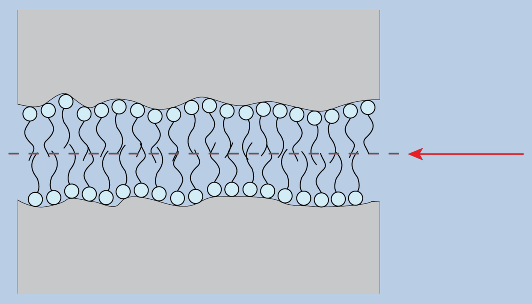
Motivations

Organic additives are widely used to manipulate the surface properties of a material. Many of these scenarios work under dynamic conditions with a flowing liquid.



Anti-corrosion additives

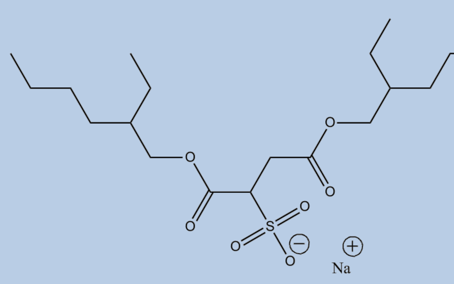


Lubrication additives

But how do these adsorbed layers change under "working" conditions?

⇒ Are they worn away? Do they continue to protect the surface?

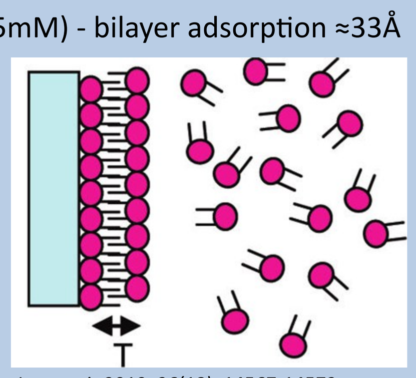
Here we show changes in the adsorption of the surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT) on alumina under applied shear with neutron reflectometry (NR).



AOT

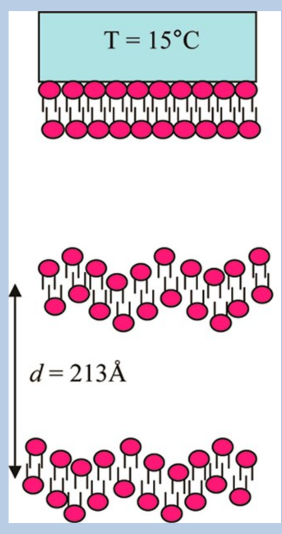
AOT adsorbs on Al_2O_3 as a bilayer, with multi-lamellae at higher concentrations. The lamellae allow the molecular order to be tested under shear at different length -scales :

CMC (2.5mM) - bilayer adsorption ≈33Å



Langmuir 2010, 26(18), 14567-14573.

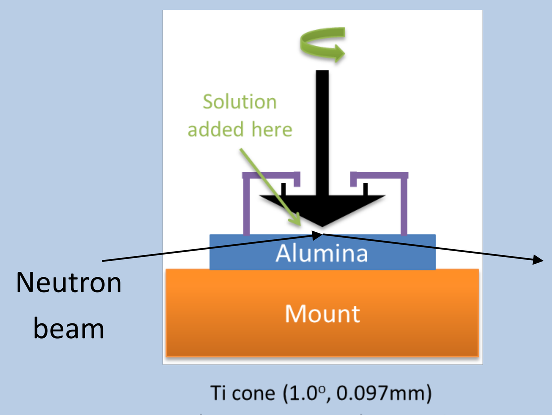
2wt% (45mM) - bilayer plus lamellae spaced ≈213Å



Langmuir 2011, 27, 4669-4678.

Methods

Combined neutron reflectometry (NR) and rheometry are used to study the changes in adsorption on a molecular scale. Steady and dynamic shears were applied; shear rates up to $500s^{-1}$ and frequencies up to $100s^{-1}$ at 500% strain.



Rheometer schematic

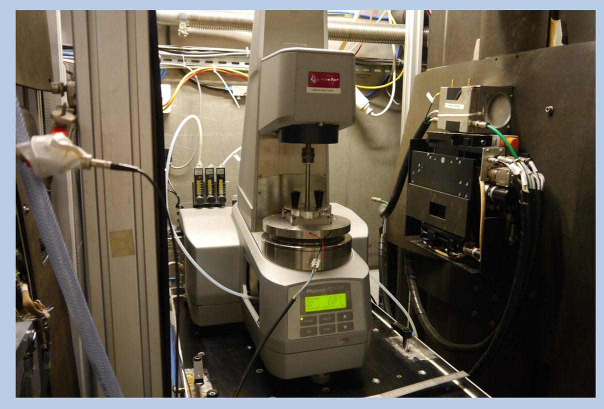
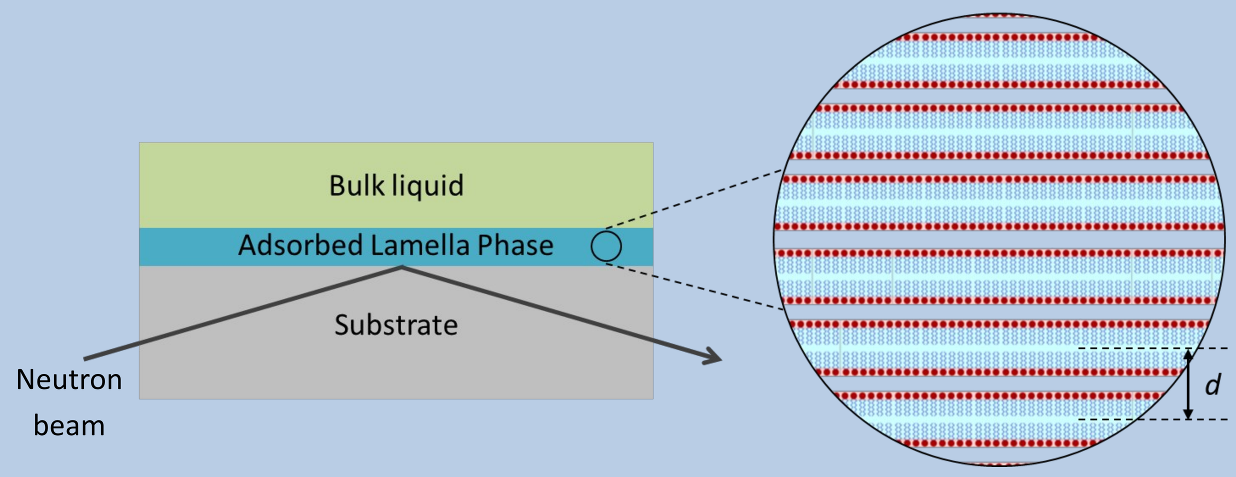


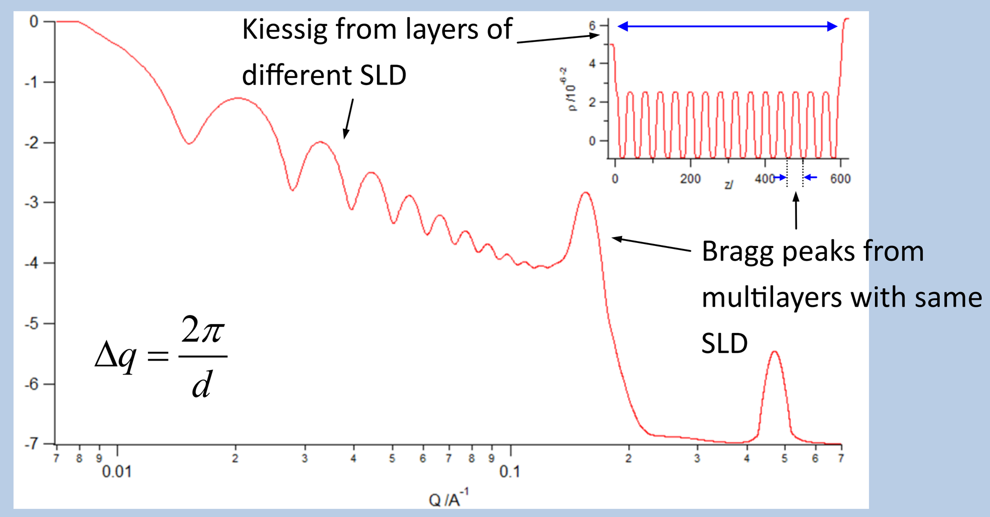
Photo of set-up of rheometer on FIGARO, ILL.

NR provides structural information perpendicular to the surface. These layers give Kiessig interference fringes, as well as Bragg peaks from multi-lamellae.

Layers of different SLD (neutron refractive index) → Kiessig fringes

Repeating layers of same SLD (neutron refractive index) → Bragg peaks



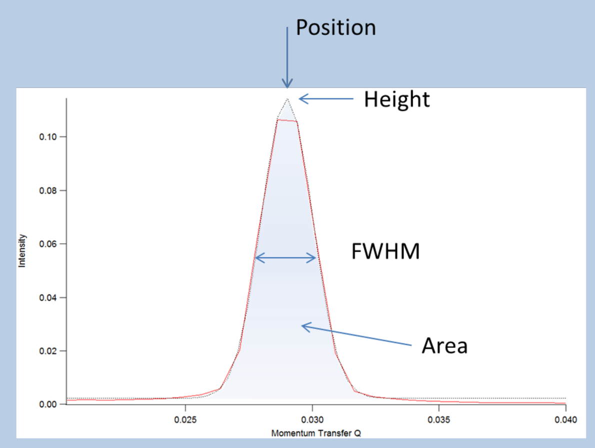


Simulation of reflectivity showing Kiessig and Bragg interference peaks.

Fitting a Gaussian to the Bragg peaks provides information on changes in longer-range order:

Position → multi-layer separation

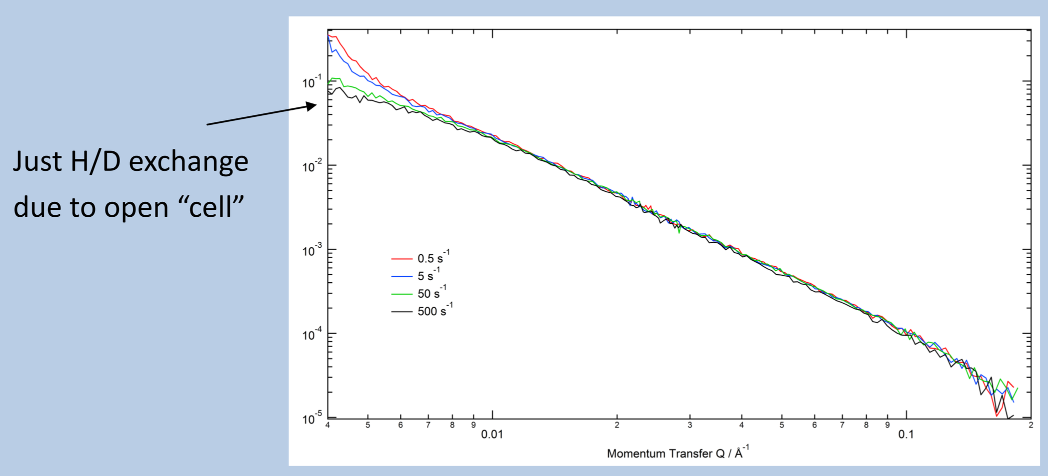
FWHM (β) → no. of ordered layers (n), where $n = \frac{K\lambda}{\beta\cos\theta}$



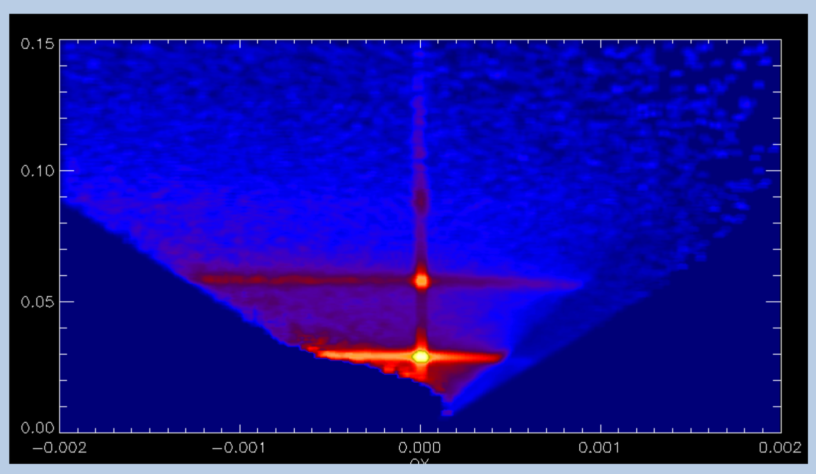
Example Bragg peak fitting.

Results - Low Concentration

At low concentrations (2.5 mM) AOT adsorbs as a bilayer on the Al_2O_3 surface, with no change under the applied steady or dynamic shear.



Reflectivity profile of 2.5mM AOT on Al_2O_3 under increasing steady shear (from 0.5 to $500s^{-1}$).

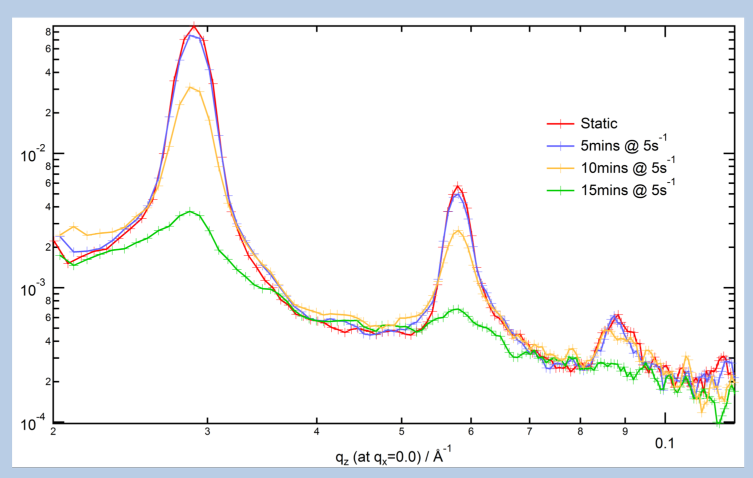


Example Q_x-Q_z plot from 2D detector of FIGARO, ILL.

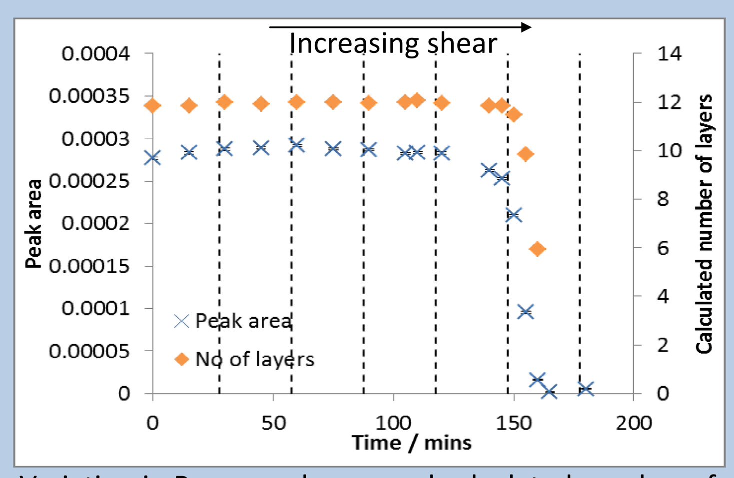
Results - High Concentration

At high concentrations (2 wt% / 45 mM) AOT adsorbs as multi-lamellae, giving rise to Bragg peaks in the reflectivity curve. This longer range order is lost under applied shear. The surface bilayer always remains.

- Steady shear: peaks lost between 1 and $5s^{-1}$, and lost quickly (<30mins).



Example reflectivity profile of 45 mM AOT on Al_2O_3 under increasing shear rate.

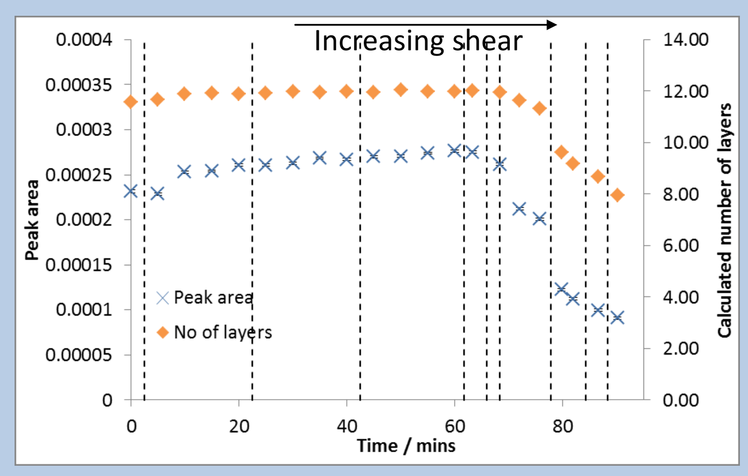


Variation in Bragg peak area and calculated number of multi-lamellae with increasing applied steady shear.

Dashed line=change in shear conditions

Each data point is a separate NR run

- Dynamic shear: onset of change is seen at 500% strain, between 1 and $5s^{-1}$. Peaks lost gradually - delamination.



As above, but under increasing oscillatory shear.

Moving Forward...

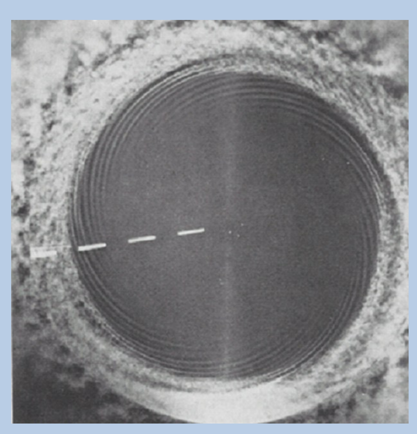
Is this loss of order due to the system or the experimental set-up?

- In fluid mechanics there is a critical point for onset of instabilities in "spinning discs": R_e=510 (*Lingwood 1996*).

$$R_e = \frac{Inertial\ Forces}{Viscous\ Forces}$$

- For the steady shear rates between which change was observed in this set-up: $1s^{-1}$ R_e≈150 and $5s^{-1}$ R_e≈750

∴ need to determine whether observed changes are due to the system or geometry



Onset of instability for a spinning disk.

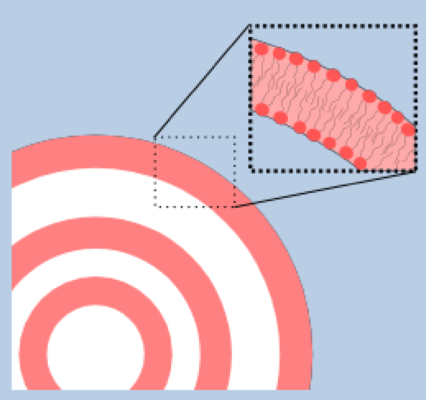
(Lingwood , J. Fluid Mech., 1996, 314, 373-405).

We have been awarded additional NR beam-time to:

a) address geometry dependence

b) complete conc. AOT dependence

c) explore additional surfactant systems e.g. multi-lamellae vesicle formation under shear



Schematic of a multi-lamellae vesicle.

Acknowledgements

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