ESRF	**Experiment title:** Surface tension anomaly in ferric stearate membranes	**Experiment number**: SC1081
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Report:

From our experiments at Beamline BM32, ESRF in November, 2001 we have evidence from surface pressure − area isotherms and preliminary x−ray measurements that our membranes have a symmetrical structure around the trivalent Fe ion, exposing organic tails to *both* air *and* water, contrary to standard Langmuir monolayers. We also have evidence of formation of nearly incompressible domains even at zero pressure. Therefore, the real molecular area is different from the average area measured on the Langmuir trough, and can only be measured from x−ray scattering. In those experiments, large diffuse component in the x−ray scattering indicated giant fluctuations normally not observed with Langmuir monolayers [2]. These fluctuations can be attributed to an extremely low surface tension. This low surface tension is most probably due to the large hydrophobicity resulting from the unique molecular conformation and to the strong cohesion and incompressibility brought by the trivalent ions. This effect is strongly dependent on the trough area, in particular normal fluctuations are observed for large trough areas. Isolated domains of constant specific area try to cover as large a water surface as possible in order to minimize free energy. The effective surface tension is then that of water. Upon compression these domains come into contact at a given trough area, and the resultant membrane becomes free to fluctuate. An alternative explanation tracing the surface tension anomaly to an *asymmetric to symmetric* change in molecular orientation can however not be ruled out. The aim of our experimental studies at 10IDB Beamline was to test these scenarios in order to understand the surface tension anomaly. We also compared the results with conventional monolayers of this system obtained by spreading stearic acid on ferric chloride subphase.

Ferric stearate prepared by stepwise formation of sodium stearate from stearic acid and sodium hydroxide, and exchange of this sodium stearate with ferric chloride, as described in ref.[1], was checked in the powder form with FTIR. The spectrum showed absence of any OH and COOH bands, and medium strong COOM (M = metal) bands, indicating absence of hydroxy−stearates and free stearic acid while an almost total conversion to metal−stearate salt. This powder was dissolved in chloroform to give about 1.1g/L spreading solution. About 100µL of this solution was spread over ~ 800cm^2 on de−ionized water in the trough, and the resulting monolayer was compressed at an extremely slow rate (~ 1mm^2 min^{-1}) to give the condensed phases. This constitutes the experimental condition of the ferric stearate Langmuir monolayer used for studies of transverse scattering of x−rays in the vertical plane as well as the horizontal plane,

including grazing incidence diffraction. Comparative studies were carried out with transverse scattering in the vertical plane on monolayers of stearic acid obtained from 100μL of 1.2g/L solution of the acid in chloroform, while the aqueous subphase contained ~ 10^{-4}M ferric chloride. All data were taken at room temperature and the monolayers were kept under oxygen−free condition (residual oxygen level monitored), by passing helium, to reduce both radiation−damage and background. The Langmuir trough was mounted on an anti−vibration stage.

A monochromatic beam (8 keV) collimated to the dimensions 100μm x 400μm was incident at 1.87 mradians (107.2 mdegrees), i.e., just below the critical angle for total external reflection from water, on the air−water interface of the Langmuir trough. This grazing incidence serves to limit penetration into bulk water. Diffuse−scattered x−rays were detected in the vertical−plane (plane of specular reflection) by a point detector. The vertical angle ($\theta_{vertical}$) was varied from 0.05° to 15.0°. The background radiation was collected for each data point by lowering the trough out of the beam and turning the detector below by twice the angle of incidence. About 1 to 1.5 hr was required to collect background−subtracted data for each value of surface pressure of a monolayer. Data were collected for clean water surface, for ferric stearate monolayers on pure water at surface pressures (π) of 5mN/m, 10mN/m and 20mN/m, and for stearic acid monolayers on 10^{-4}M $FeCl_3$ at π = 5mN/m and 20mN/m.

Diffuse scattering in the horizontal plane was measured by a linear detector (position sensitive detector, PSD). The incident beam was widened to 300×400μm to enhance scattering. The in−plane angle ($\theta_{horizontal}$) was varied from 0.1° to 40.0° to include the in−plane grazing incidence diffraction peaks due to the monolayer. At each point of the horizontal scan the x−rays scattered in the vertical plane are collected in the PSD as a function of vertical angle. The collection time for a complete horizontal scan took about 6 hours. Background data, complete with all rods, was collected for each horizontal scan by lowering the trough out of the beam. Thus each background subtracted horizontal scan took about 12 hours to complete.

Background−subtracted transverse diffuse scattering data, including grazing incidence diffraction, were collected for pure water and for a Ferric Stearate Langmuir monolayer on pure water at π−values of 1mN/m, 5mN/m and 10mN/m, all during compression. Besides, grazing incidence diffraction data were collected for the monolayer at the Surface Pressures of 0.1mN/m, 15mN/m while compressing and at 1mN/m and 0.1mN/m while decompressing.

We have demonstrated by x−ray diffuse scattering that an artificial membrane of preformed ferric stearate drastically enhances capillary wave uctuations on the water surface. The membrane is composed of a symmetrical bilayer on top of a monolayer in contact with water. The enhanced fluctuations can be explained by a large reduction in surface tension down to 1mN/m due to the combination of symmetric−asymmetric molecular assembly and strong electrostatic interactions. These results have been communicated as a paper entitled *Dramatic enhancement of capillary wave uctuations in membrane covered water surface* by A. Datta, S. Kundu, M.K. Sanyal, J. Daillant, D. Luzet, C. Blot and B. Struth.