



<b>ESRF</b>	<b>Experiment title:</b> Bio-mineralization at lipid membranes: Crystallization of nanoparticles under different insoluble monolayers	<b>Experiment number:</b> SI-1965
	<b>Beamline:</b> 10B	<b>Date of experiment:</b> from: 18.11.2009                      to: 24.11.2009
<b>Shifts:</b> 18	<b>Local contact(s):</b> Alexei Vorobiev	<i>Received at ESRF:</i>
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Report:

The aim of the experiment SI-1965 was the investigation of the mineralization of iron oxide underneath insoluble monolayers of fatty acids. The biomineralization process was monitored by x-ray reflectivity (XRR) and grazing incidence diffraction (GID). Stearic acid was chosen for these experiments because of its negatively charged head-group which attracts the positively charged Fe ions. The mineralization of iron oxide underneath the monolayer was studied as a function of the surface pressure. Thereby we were able to study the nucleation of particles as a function of the interface charge.

Iron(II)chloride and iron(III)chloride were dissolved in ultra pure water (resistance 18.2 MΩ cm) to achieve a concentration of 8 mmol. Stearic acid was dissolved in chloroform with a concentration of 2 mmol. After preparation of the subphase the stearic acid monolayer was spread onto the surface. After the chloroform was evaporated the monolayers were compressed to surface pressures of  $\Pi = 10$  mN/m,  $\Pi = 20$  mN/m and  $\Pi = 30$  mN/m. The measurements were always proceeded in the same sequence: after the deposition and compression of the monolayer the initial state was characterized. Afterwards ammonia was added to the air volume above the sample in order to start the mineralization process.

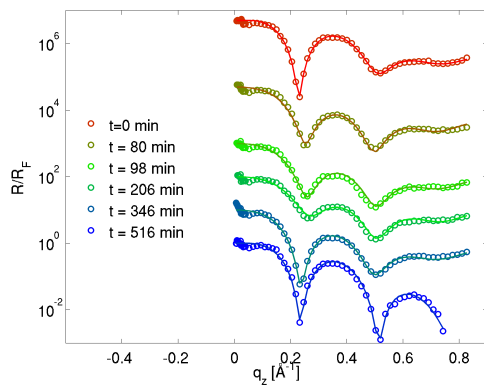


Figure 1: XRR spectra of steric acid on iron(III)chloride solution with a surface pressure of  $\Pi=10$  mN/M at different times, after  $t = 80$  min ammonia was added.

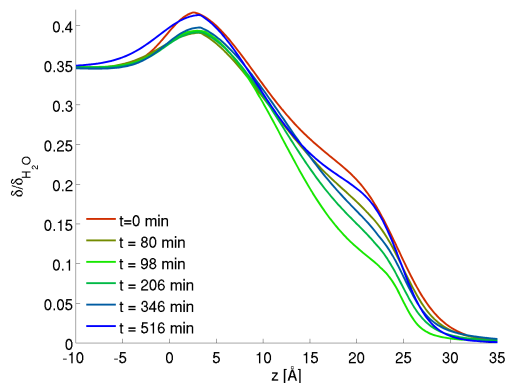


Figure 2: Electron density profiles obtained by the refinement of XRR data.

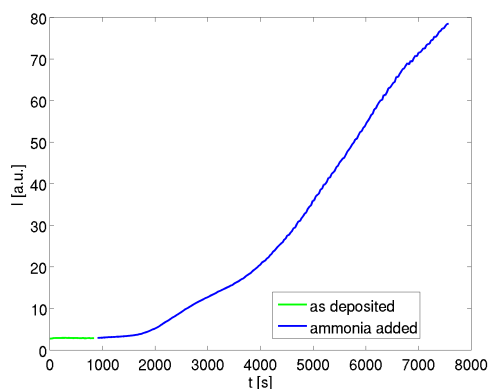


Figure 3: Intensity of Fe fluorescence at 6.4 keV as function of time.

To summarize by using iron(III)chloride the biomineralization can be controlled by the surface charge density. Depending on the compression of the monolayer an enrichment of iron ions below the monolayer takes place. In contradiction iron(II)chloride also mineralizes at low surface pressures which indicates that the iron(II)chloride has a stronger affinity to the charged interface.

Figure 1 shows XRR data and their refinements of a steric acid monolayer compressed to  $\Pi = 10$  mN/m spread on an iron(III)chloride solution. In Figure 2 the electron density profiles obtained by the refinements are shown. The evolution of the sample system was monitored for 8 h. The data clearly show no layer formation under the steric acid film. The GID data (not shown) show two weak reflections at  $q_z = 0$  indicating a non-tilted phase. In the following a steric acid monolayer spread on an iron(III)chloride solution at a surface pressure of  $\Pi = 20$  mN/m was investigated. Here the surface roughness increased dramatically which results in an extremely strong decrease of the reflected intensity. An inspection of the samples surface showed macroscopic formation of iron oxide, which goes in hand with a complete destruction of the Langmuir film. Thus, the electrostatic interaction could be identified as one of driving forces for the iron oxide formation.

In contrast iron(II)chloride measured under steric acid showed biomineralization independent on surface charge. Here the extreme roughening of the surface was observed too. The mineralization of iron(II)chloride under steric acid was then monitored by the intensity of the iron fluorescence at an energy of 6.4 keV (Figure 3). For these measurements an incident angle of  $\theta = 0.05^\circ$  was chosen in order to be surface sensitive. The data clearly show after addition of ammonia the accumulation of iron oxide which did not stop within the measuring time.