

The Investigation of phospholipid monolayers goes beyond the classic membrane biophysical aspect. The combination of lipid monolayers and aqueous clay sols raises series of novel issues as fundamental aspects of surface science are combined with properties of a complex fluid. Recently the formation and structural evolution of amphiphilic monolayers on a mineral sol undergoing a sol-gel transition have been studied by surface X-ray scattering techniques [1]. Due to the electrostatic interaction between the zwitterionic headgroup of the lipid (DPPC) and the charged faces of the mineral platelets a mineral monolayer is absorbed at the lipid sol interface forming a lipid mineral double layer.

A fundamental problem using lipid monolayers for applications via the Langmuir Blodgett technique is the high density of defects in the films: due to thermal fluctuations, known as capillary waves, the ordering of 2D organic monolayers on conventional liquids does not extend to long-range scales. By choosing a complex fluid like a sol as a substrate for the preparation of lipid monolayers the viscosity of the subphase is adjustable by the mineral concentration. In addition, the adsorbed monolayer of clay nanoparticles helps to stabilise the lipid film and damp surface fluctuations via an increased bending rigidity. Measurements of pressure area isotherms on a Langmuir trough show that remarkable higher surface pressures can be reached on sols compared to water without collapse of the film. In addition an effect similar to cooling can be observed. Both effects give rise to the assumption of increased van der Waals interaction between the lipid chains due to reduced surface fluctuations.

We studied lipid covered sol surfaces for several mineral concentrations by grazing incidence X-ray diffraction (GID) to prove the in plane structure of the lipid film and the mineral monolayer. The experiments were carried out in liquid surface geometry at the ID10B beamline. The experimental data obtained for GID measurements of the DPPC covered water on sol surface is shown in figure 1a). Due to the similarities in the d spacing for the lipids chain lattice and the lattice of the mineral nanoparticles (Laponite RD, Rockwood) an assignment of the peaks as mineral or as lipid peaks based on the intensities integrated over Q_z is impossible. Bragg rod analysis with a new developed model for superposition of a lipid and a mineral rod show that the measured Bragg rods for the (01) , $(0\bar{1})$, (10) , $(\bar{1}0)$, $(1\bar{1})$, $(\bar{1}\bar{1})$ and $(2\bar{1})$ lipid reflections exhibit contributions both from the mineral and the lipid. Especially the analysis of the $(2\bar{1})$ reflection proves that for the first time a higher order reflection for a lipid monolayer could be observed (see figure 1b) due to a reduced isotropic Debye-Waller factor.

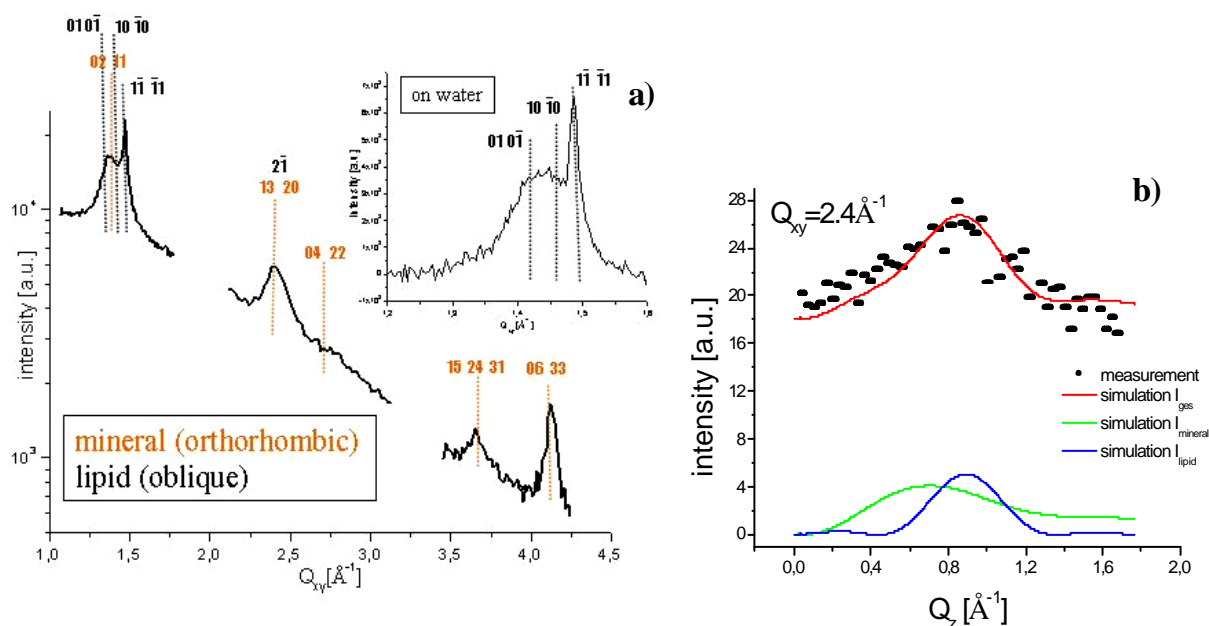


Figure 1a) integrated intensities from GID measurements for the lipid covered sol and water (inset) surface and corresponding Miller indices b) measured and simulated Bragg rod for the $(2\bar{1})$ reflection: superposition of mineral and lipid rod (red), pure lipid rod (blue) and pure mineral rod (green)

Comparison of the molecular area per lipid chain (A_0) as a function of the lateral surface pressure p for isotherms on water and sols with different mineral concentrations (see figure 2a)) show that the 2d structure of the lipid film is mapped to the structure of the mineral. In addition the tilt angle t between the lipid chain and the surface normal varies less as a function of the surface pressure compared to water. This stabilised structure is an indication for a reduced mobility of the molecules.

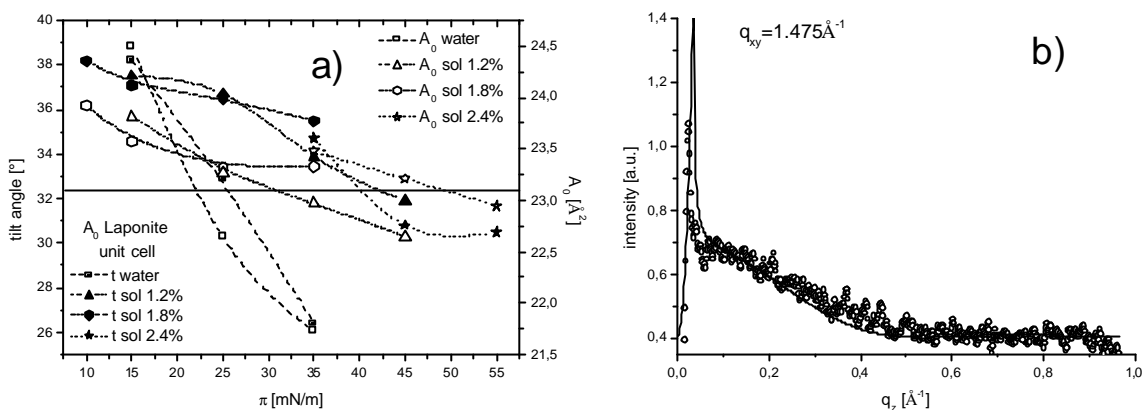


Figure 2: Tilt angle and area per molecule as a function of the surface pressure a). The black line indicates the area of a mineral unit cell. b) Lipid Bragg rod found for DMPC on a sol with 2.4wt.% mineral concentration.

As some of the major problems for crystal growth of a variety of systems from surfactant monolayers to macromolecules occur from weak molecular interactions and high mobility, the results for DPPC can be seen as a novel approach to crystal growth: nucleation and build up of 2d structures can be supported by stabilising and immobilising effects of the subphase. To demonstrate such stabilising effects on a 2d structure we performed GID on DMPC monolayers. DMPC is a phospholipid like DPPC but with shorter alkane chains (C14 instead of C16). Due to the shorter chains van der Waals interactions are reduced and hence on water no condensed phase is accessible. Measurements of pressure/area isotherms show that on a sol the accessible surface pressure is increased by about 100%. The shape of the isotherm in this high pressure region as well as the molecular densities indicate a solid like phase. Figure 2b) shows the Bragg rod for the $(1\bar{1})$, $(\bar{1}1)$ reflection of DMPC which is clearly of lipid origin. For the first time we could grow a 2d structure of an inherently non-ordering system on a liquid surface through the control of the subphase properties and the use of mineral nano-particles.

The attempt to control the structure formation of a surfactant monolayer at the air/water interface via the physical characteristics of a complex fluid goes beyond the build up of 2d structures. Crystal growth is a surface process. Our results for a phospholipid monolayer as a model system with precisely tunable physical characteristics could be a general novel approach for crystallisation of inherently non-ordering systems like polymers or proteins.

Two publications are in preparation.

[1] B. Struth, et al., Physical Review Letters **88** (2002).