

## What and why: Langmuir films

This note describes the basic theory, measurements and applications of Langmuir films.

### Langmuir films

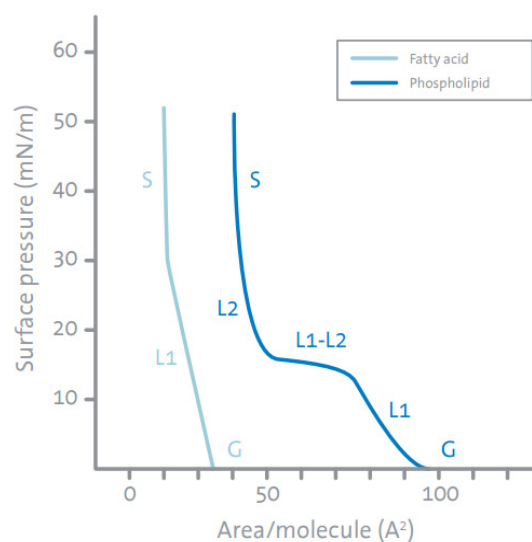
When molecules possess hydrophobic (water-hating) and hydrophilic (water-loving) parts, they orientate themselves in a predictable way on water surface. A vast range of molecular materials are well suited to forming monolayers at the air-water interface. These include lipids, nanoparticles, polymers, proteins and many other biomolecules. Modern chemical engineering has made it possible to synthesize almost any type of functional molecule in such a way that it can be used for creating monolayers.

Many amphiphilic substances are insoluble in water and can with the help of a suitable solvent easily be spread on a water surface to form an insoluble monolayer. In these monolayers, also called Langmuir (L) films, all molecules are concentrated in a one molecule thick layer at the interface. The amphiphilic nature of the molecules dictates the orientation at the interface (air/water or oil/water) in such a way that the polar head group is immersed in water and that the long hydrocarbon chain is pointing towards air, gas or oil. The name Langmuir film originates from the name of the pioneer of these films, Irving Langmuir, who extensively studied these insoluble monolayers in the early 20th century. Irving Langmuir ultimately won the Nobel Prize in Chemistry 1932 for his research on surface science.

### Surface pressure – area isotherm

The most important indicator of the monolayer properties of an amphiphilic material (usually used to create Langmuir films) is given by measuring the surface pressure as a function of the area of water surface available to each molecule. Usually an isotherm is recorded at constant temperature by compressing the film (reducing the area with the barriers) at a constant rate while continuously monitoring the surface pressure.

A number of distinct regions, called phases, are apparent on examining the isotherms. The phase behavior of the monolayer is mainly determined by the physical and chemical properties of the amphiphile, the subphase temperature and the subphase composition. A simple terminology used to classify different monolayer phases of fatty acids has been proposed by W.D.



[Figure 1]: Isotherms of a fatty acid with a single hydrocarbon chain and a phospholipid with two hydrocarbon chains.

Harkins as early as 1952. At large the monolayers exist in the gaseous state (G) and can on compression undergo a phase transition to the liquid-expanded state (L1). Upon further compression, the L1 phase undergoes a transition to the liquid-condensed state (L2), and at even higher densities the monolayer finally reaches the solid state (S). If the monolayer is further compressed after reaching the S state the monolayer will collapse into three-dimensional structures. The collapse is generally seen as a rapid decrease in the surface pressure or as a horizontal break in the isotherm if the monolayer is in the liquid state.

Figure 1 presents the isotherms of a fatty acid with a single hydrocarbon chain and a phospholipid with two hydrocarbon chains. In this example, one can see that the fatty acid has three distinct regions; gas (G), liquid (L1) and solid (S), while the phospholipid has an additional almost horizontal transition phase (L1-L2) between the two different liquid phases. This is very common for phospholipids.

## Key application areas

The possibility to synthesize organic molecules and the development of novel new inorganic materials with desired structures and functionalities enable the production of electrically, optically and biologically active materials on a nanometer scale. KSV NIMA Langmuir Troughs can be used to form monolayers of amphiphilic molecules, different surfactants and specialty chemicals. During the last decade the Langmuir film concept has also been used for the preparation and study of highly organized monolayers of colloidal and nanoparticles at the air/water interface.

### Modelling of biomembranes and biomolecular interactions

Different lipids are the main components of mammalian plasma and cell membranes. Langmuir films offer a powerful research tool to examine the behavior and role of these lipids in biological membranes such as:

- Cell membrane model structures
- Drug delivery and behaviour
- Protein interactions

### Fundamental chemical research

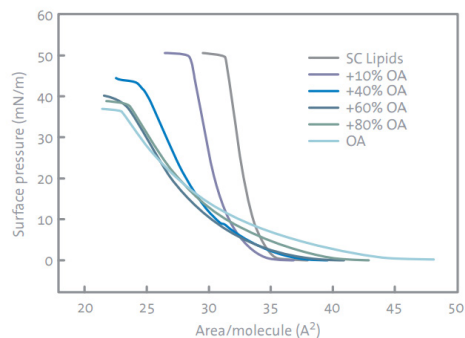
Surface processes of monolayers at controlled packing densities can be examined using Langmuir films. From the experiments, information can be obtained on:

- Optical, electrical and structural properties
- Surface adsorption and desorption
- Polymerization

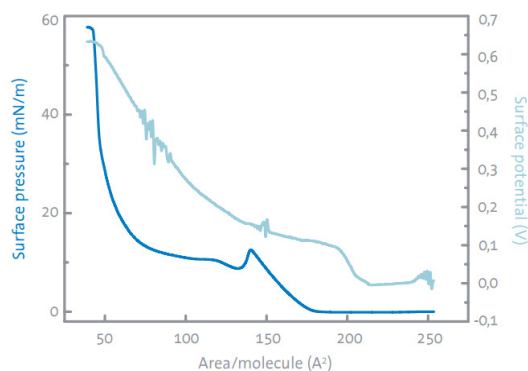
### Surfactants in food, cosmetic, petroleum and pharmaceutical industry

In the fabrication process of food products, cosmetics, pharmaceutical products and oil, surfactants and dispersing agents are used as stabilizers at liquid/liquid and liquid/air interfaces. Using Langmuir troughs, it is possible to examine:

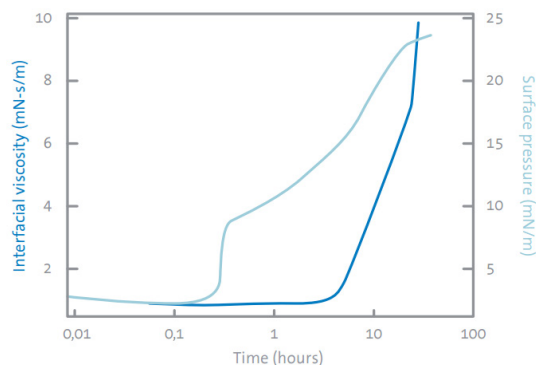
- Emulsion stability
- Dispersions
- Froths and foams
- Crude, fuel and lubricant oils



[Figure 2]: Skin lipid interactions. Oleic acid (OA) is commonly used as a texture modifier in many skin care products. The graph displays the isotherm of model stratum corneum (SC) lipids consisting of ceramide, cholesterol, and palmitic acid. With increasing levels of OA the films became more fluid and more compressible. Brewster angle microscopy studies with KSV NIMA BAM showed that lower concentrations of OA preferentially mix with the ceramide-enriched domains, but at higher concentrations OA starts to disrupt the palmitic acid enriched, more ordered domains. With permission from Langmuir 2013, 29 (15), pp 4857–4865. Copyright 2013 American Chemical Society.



[Figure 3]: Structural characterization. The graph displays the surface pressure-area (blue) and surface potential-area (light blue) isotherms of an antiparasitic drug monolayer at an air-buffer solution interface. An unusual surface pressure-area transition was observed at mean molecular area of 140 Å<sup>2</sup>, but no transition was shown in the surface potential-area isotherm. This suggests that the transition is not a phase transition but instead the drug could undergo aggregation, dimerization or conformational change at this mean molecular area.



[Figure 4]: Enzyme monolayers. The graph illustrates the evolution of the interfacial viscosity (blue) of a protein monolayer (lysozyme) residing between water and decane plotted as a function of time. The surface pressure (light blue) of the layer is also plotted. The change in surface pressure shows the evolution of the adsorption, interfacial viscosity and the crosslinking of the protein as a viscoelastic "skin" develops at the interface as a function of time. The surface pressure data complements the interfacial rheology data.