EXPERIMENT I

LANGMUIR-BLODGETT FILM EXPERIMENT

1. Purpose

Some of the properties and behaviour of Langmuir films of selected compounds will be studied using a Langmuir-Blodgett Trough apparatus. Quantitative information can be obtained as to the effect of chain length on the packing size of the molecules studied as well as the effect of the sub-phase (bulk solvent) composition on the film properties.

2. Safety

This experiment requires the use of organic solvents (chloroform and toluene). Minimize as much as possible inhalation of the vapours; in particular, prepare the solutions under a fume extractor or in a ventilated fume hood. At the end of the experiment, these solutions must be discarded to the containers reserved for organic wastes.

3. Introduction

Langmuir films result from the interaction of *surfactants* trapped at the interface between two dissimilar phases (liquid-liquid or liquid-gas). For our purpose the interface is simply the contact area between an aqueous solution and air. The name surfactant is applied to molecules which carry two functional groups each having a strong preference for one of the contacting phase. The most studied surfactants are those interacting between water and air or water and water-immiscible liquids. In the particular case of water/air interface, surfactants are *amphiphilic* molecules which have both hydrophilic and hydrophobic ends. The hydrophilic group (like carboxylic acid, sulphate, amine or alcohol) is attracted to the polar aqueous medium by strong coulomb type interactions. The hydrophobic end (like hydrocarbon chain, fat and lipid group) is practically water insoluble and is subjected only to the much weaker van der Waals type of interactions.

Due to these very extreme types of bonding with each of the contacting media, the amphiphilic molecule finds itself trapped at their interface, effectively with its hydrophilic "head" group pulled into the aqueous phase and its hydrophobic "tail" group pointing into the air. In this way a stable surface monolayer may be obtained providing that the *amphiphatic* balance within the molecule happens to be of the right magnitude, *i.e.* the balance between the strength of the hydrophilic and hydrophobic interactions; too short hydrophobic tails result in the compound being soluble in water and absence of hydrophilic end results in disorganized multi-layer films.

If one reduces the surface area available by sweeping a barrier over the surface, the surfactant molecules are forced to come closer together and eventually form a compressed ordered monolayer, resulting in a so-called Langmuir film as illustrated in the schematic diagram of Fig. 1.

Further, one can transfer the Langmuir film to an appropriate solid substrate by dipping it in a controlled manner through the film. One can repeat the dipping to obtain a sequence of mono-molecular layers with various relative orientations depending whether the substrate is hydrophilic or hydrophobic. These types of organized coatings are called Langmuir-Blodgett films. For the present experiment, only monolayer Langmuir films will be produced and characterized.

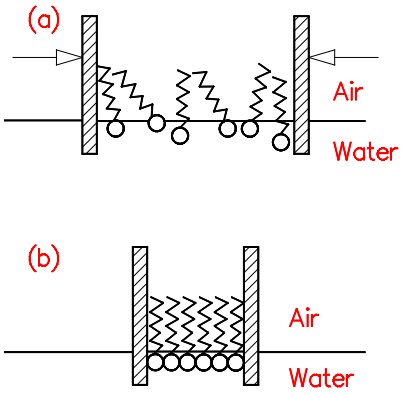


Figure 1. Conceptual representation of an expanded (a) and compressed (b) monolayer surfactant film on a water surface. The hydrophilic "head of the surfactant is symbolized by a circle while the zig-zag "tail" represents the hydrophobic carbon chain.

4. Langmuir Films

4.1. FILM FORMATION

To form a monolayer, a solution of the surfactant in a suitable solvent is deposited drop-wise on the surface of the water (the sub-phase). The solvent chosen should be very insoluble in water and evaporate reasonably quickly. As the solvent evaporates, the surfactant spreads spontaneously as a monolayer on the water surface until the "equilibrium spreading pressure" is reached beyond which no more spreading can take place and floating "lenses" of the surfactant start forming.

4.2. ISOTHERMS

Molecules in the bulk of a solution are subjected to attractive forces from the surrounding molecules; these forces are equal in all directions. On the other hand, a molecule at the interface will be subjected to unequal forces arising from each side of the interface and in the case of air/water it will be drawn towards the bulk. This effect gives rise to the *surface tension*, also defined as "the work required to expand the surface isothermally by one unit of area".

The accumulation of surface active molecules at the interface tends to reduce the surface tension. Thus the surface tension (or *surface pressure*) is a function of the molecular surface density (number of molecules per unit area), and can be affected by "compressing" a particular monolayer. This can be observed and quantified by sweeping closed a barrier to reduce the area occupied by the film under study while the surface tension is continuously monitored. The plot obtained (surface pressure versus area occupied at a given temperature) is the *pressure-area isotherm* which has a shape characteristic of the surfactant involved in film formation. Typically for simple amphiphilic molecules, the isotherm shows usually three distinct regions (see Fig. 2).

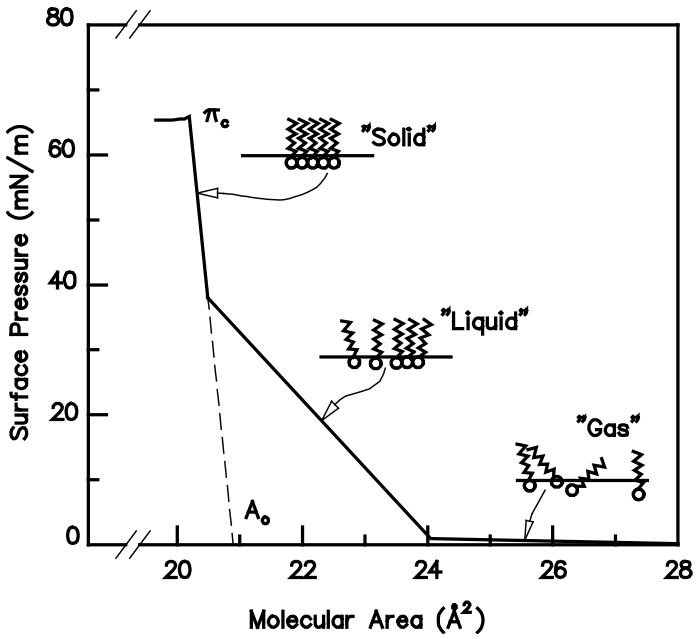


Figure 2. Idealized Langmuir isotherm of the monolayer film of a typical amphiphilic molecule. The three distinct regions of the isotherm can be associated with the different level of ordering of the film as shown schematically on the figure; π_c is the collapse pressure beyond which multilayer start forming, and A_0 is the zero pressure molecular area.

When no external pressure is applied to the monolayer, the molecules behave like a two-dimensional "gas" and obey the "state" equation

$$\pi A = KT \qquad (1)$$

where π is the surface pressure, A the molecular area, K the Boltzmann constant and T the thermodynamic temperature.

As the barrier is closing, the surface pressure increases causing first partial ordering of the film to produce a two-dimensional "liquid" and next, upon further ordering to force the film to behave like a "quasi-solid". For a clean system (no contaminants affecting the surface tension), each of these states of the film has a characteristic trace on the isotherm (see Fig. 2) with a sharp transition at the change of state.

Eventually, the collapse pressure, π_c, is reached beyond which multilayer start forming. Note that the collapse is not uniform; there still might be regions of monolayer broken up by "ridges" and aggregates. The collapse pressure can also be defined as the maximum pressure that a monolayer can sustain before expulsing molecules from the Langmuir film. The actual value of π_c depends not only on the chemical forming the film but also on the experimental conditions (temperature, compression rate, film annealing, *etc*…). Typical values are 50 to 100 mN m^{-1}.

The isotherm can provide quantitative information on the dimension and shape of the molecule under study. In particular, the *zero-pressure molecular area*, A_0, obtained from the extrapolation of the "solid phase" line to zero pressure is interpreted as the hypothetical area occupied by one molecule in the condensed phase at zero pressure; one would expect this quantity to be directly related to the average physical space occupied by a molecule in the film.

4.3. PRESSURE MEASUREMENT

The surface pressure in the present apparatus (a NIMA™ trough) is measured by monitoring the force acting on a *Wilhelmy plate*. The Wilhelmy plate consists of a strip of chromatrography paper suspended at one end of the beam of an electrobalance which measures the force acting on the plate, while the other end is just dipping into the sub-phase (see Fig. 3).

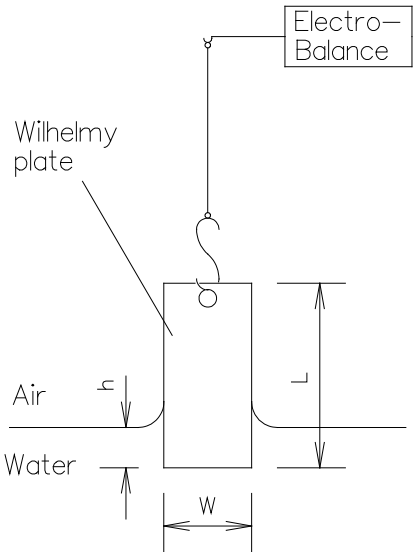


Figure 3. Principle of the *Wilhelmy plate* arrangement.

Under these conditions, the Wilhelmy plate is pulled down into the sub-phase (water) with a force depending on the surface tension.

The total forces acting on the plate are, downwards the gravity and the surface tension, and upwards the buoyancy due to the displaced water.

For a plate of dimension L × W × t (length, width and thickness, neglecting the holding hole) and density ρ, immersed to depth h, the net force F is:

F = weight − upthrust + surface tension, *i.e.*

$$F = \rho g LWt - \rho' g hWt + 2\gamma(t + W)\cos\theta \quad (2)$$

Where γ is the surface tension of the liquid, θ the contact angle of plate to liquid (0° for a completely wetted plate), *g* the acceleration of gravity (≈ 9.81 m s^{-2}) and ρ′ the density of the sub-phase.

If one measures the difference in forces experienced by the plate between immersion in pure water and in a film-covered surface, one gets:

$$\Delta F = 2(\gamma' - \gamma)(t + W) \quad (3)$$

where γ′ is the surface tension of pure water (72.8 mN m^{-1}). Further, if the thickness is small compared to the width of the plate (t << W), the Eq. 3 simplifies to:

$$\Delta F \approx 2\Delta\gamma = 2\pi \quad (4)$$

where π the surface pressure is defined as $\gamma' - \gamma = \Delta\gamma$

Table 1. Effectiveness of various functional groups to form Langmuir films.

Any carbon chain		Example of C_{16} Chain	
No film formed	Unstable films	Stable film	Chain dissolves
Plain chain	$-C_6H_4OCH_3$	$-CH_2OH$	$-SO_3^-$
$-CH_2I$	$-COOCH_3$	$-COOH$	$-OSO_3^-$
$-CH_2Br$		$-CN$	$-C_6H_4SO_4^-$
$-CH_2Cl$		$-CONH_2$	$-NR_3^+$
		$-CH{=}NOH$	
		$-C_6H_4OH$	
		$-NHCONH_3$	
		$-NHCOCH_3$	

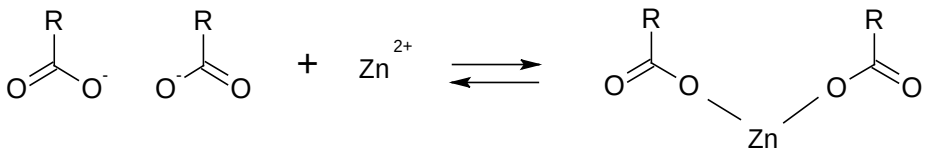
4.4. COMPOUNDS SUITABLE TO FORM LANGMUIR FILMS

As seen above, the main requirement for a molecule to form a Langmuir film is that its amphiphilic balance be of the correct magnitude. In general, long chain fatty acids and alcohols will form Langmuir films; the polar group (–COOH or –OH) has good affinity for water and effectively anchors one end of the molecule into the aqueous sub-phase, while the hydrophobic alkyl chain ($CH_3 - (CH_2)_n -$) forces the molecule to orient itself "upwards", away from the water phase into the air phase. Other hydrophilic functional groups may achieve the same result. A summary of the effectiveness of various groups to obtain a Langmuir film in shown in Table 1.

4.5. EFFECT OF THE SUB-PHASE COMPOSITION

Pure liquids other than pure water have been studied for the formation of mono-molecular films, for example, ethylene glycol, glycerol and mercury. In addition, for a given sub-phase, the properties of the monolayer can be affected by the presence of dissolved species in the sub-phase. In the case of water, the pH, dissolved ions and temperature will certainly have an effect.

For long chain alkaloid acids, the pH affects the degree of ionisation, and as a consequence the net repulsion experienced between adjacent acid groups. Still with alkanoic acids, if divalent ions, like Zn^{2+} are present, the following ionic interactions occur:



(5)

while the pH controls the equilibria

$$Zn^{2+} + 2\ OH^{-} \leftrightarrows Zn(OH)_2 \qquad (6)$$

and

$$R\text{-}COOH \leftrightarrows R\text{-}COO^{-} + H^{+} \qquad (7)$$

5. Experimental

Langmuir films will be prepared and characterized for a series of amphiphilic compounds; the effect of sub-phase ionic composition will not be studied due to time constraint.

5.1. SOLUTION PREPARATION

In order to obtain meaningful results, all surfaces coming in contact with the solution under study must be as free of contamination as possible (greases, organics and dust particles). Wear the plastic gloves provided (no latex) when preparing solutions, handling glassware and the any part of the NIMA trough. Lift off the trough cover only when necessary. Try to avoid too much vibration.

IMPORTANT NOTE

It is also critical that the glassware used to prepare the samples and that the syringes used to inject the samples on the trough be clean and free of any trace of left-over compound from previous trials. Rinse several times the volumetric flasks and the micro-syringes with small amount of chloroform, toluene and/or acetone.

5.1.1. Sub-phase

The sub-phase will consist of water containing $ZnSO_4$. Prepare accurately 500 ml of a 10^{-4} M $ZnSO_4$ solution using ultra-pure water (obtained from the Millipore apparatus in the lab).

5.1.2. Samples

Using chloroform as the solvent, prepare in 5 ml (or 10 ml) volumetric flasks, solutions of at least three different long-chain fatty acids taken from Table 2 below; the concentration should be ≈1 mg ml^{-1} but accurately measured on the analytical balance.

Table 2. List of common fatty acids and some of their properties..

Fatty Acid	Chain length	Alternate Name	Remarks
Stearic	C18	Octadecanoic	Saturated
Arachidic	C20	Eicosanoic	Saturated
Docosanoic	C22	Behenic	Saturated
Oleic[1]	C18 cis-9	Cis-9-octadecenoic	Unsaturated
Elaidic	C18 trans-9	Trans-9-octadecenoic	Unsaturated

Prepare also 10 ml of a solution of cholesterol in toluene (2 mg in 10 ml).

5.2. TROUGH PREPARATION

Using Kimwipes moistened with chloroform, clean the teflon surfaces and the barriers. Use a pasteur pipette attached to the aspirator to remove extra droplets. With the barriers open (≈ 3/4 open), fill the trough with the most dilute $ZnSO_4$ solution until the solution is brimming over the edge. Attach a new Wilhelmy plate and adjust the height so that it is dipping into the liquid without touching the bottom of the trough; cover the trough.

On the computer,

1. set the barrier speed to 500 (**b**, **500** - see manual for instructions on software commands),
2. zero the trough (**z**),
3. start to run a blank isotherm (**Enter** key). The barriers will start closing and unless stopped will keep closing until the minimum separation allowed is reached (**Barrier A/B too close** message on the computer screen).
4. Stop the barriers by hitting **space bar**. If the liquid surface is clean, the blank isotherm should be flat with a zero surface pressure. Any deviation from zero indicates that some contamination is present on the surface and must be cleaned. Gently touch the surface of the liquid, particularly next to the barriers, with the pasteur pipette attached to the aspirator to skim off the contaminants (to avoid

[1] Oleic acid may be a delicate sample to use; select this compound only if there is no other choice.

cross-contamination from previous samples, use a new pipette tip for each new sample).

5. Open the barrier (**o**) and repeat the run until a flat isotherm is obtained. If too much liquid has been aspirated, more $ZnSO_4$ solution must be added in order to keep the liquid brimming over the edge of the trough.

5.3. RUNNING THE EXPERIMENT

On the computer screen, set up the run parameters, *i.e.*,

1. logging interval of 50 cs,
2. autosave off (**m, I, i**),
3. *x*-axis units in area per molecule (**a**),
4. enter the operating conditions (**m**, **o**): exact concentration for each compound and injection volumes (30 µl for stearic, arachidic and behenic acid, 20 µl for oleic acid and elaidic acid, 40 µl for cholesterol).

Move the barriers to ≈3/4 open. Clean well the micro-syringe provided, first with some solvent, then with some of the solution to be injected before filling the syringe with the required volume. Wait for the pressure reading to be stable before zeroeing the trough (**z**). To spread the sample on the sub-phase, inject drop-wise slowly from a height of ≈1cm the required volume. As the solvent evaporates, one can observe the spreading of the film; in the case of chloroform, evaporation is almost immediate, but one should wait for a few minutes to let toluene evaporate completely.

With a barrier speed of **25** (**b 25**), zero the trough then start scanning for an isotherm (**Enter**). The isotherm is displayed on the screen as it builds up.

Stop the run (**space bar**) when the critical pressure (π_c) is reached, corresponding to a sudden drop or a prolonged horizontal portion on the isotherm.

Save the data (**S** *filename*) on the computer (*don't forget to say "yes" after being prompted*).

Clear the display memory (**v**), then clear the screen (**m**, then **Q**)

In principle, the barriers could be opened and the run repeated. In some cases, the film may be "annealed", i.e., the barriers are closed partially (well before the critical pressure) then opened, and then closed again until the critical pressure is reached.

Before running another sample, the sub-phase surface must be rid of the previous film by aspirating the surface of the liquid; use the *Easy-clean* feature of the system (**e**). Under this mode the barriers keep closing to maintain a constant surface pressure as the film is skimmed off the surface. Check the cleanliness of the surface by running a blank isotherm as described earlier.

Obtain at least one isotherm for each of the compound prepared.

Once all the data have been collected, drain the trough, rinse once with ultra-pure water, drain then clean with Kimwipes tissues and chloroform. Before leaving, transfer your data to you own diskette, drain, clean, cover the trough and sign the log book.

6. Data analysis

The data are stored in a text format (ASCII) and can be easily examined with a text editor or can be imported into any spreadsheet program. The data are stored as four columns of numbers representing, in order, pressure A, area A, pressure B, area B. A and B refer to pressure sensor A or B; only sensor A is used in the present set up, so effectively only the first two columns are of interest; note that the *first column represents the y-variable* (surface pressure) and *x-variable is in the second column* (area). The units of area are the units chosen in the initial set up (absolute area, or area per molecule).

First generate a plot corresponding to each of the isotherm collected. Then, determine the corresponding molecular area (zero pressure molecular area, A_0). This can be done graphically by extrapolating the fast rising linear part of the isotherm to zero pressure (see Fig. 2), or performing a linear fit on this portion of the curve and using the values of the slope and intercept to calculate A_0. If the area unit is in absolute area, calculate the area per molecule from the number of molecules of compound injected to form the film. Report the results in tabular form. Estimate quantitatively the various source of errors and report the errors on the results.

7. Discussion

Find first the formula and the structure of the different compounds used.

Compare the molecular area obtained from the experimental data within the series of fatty acid studied and relate the values to the geometry of the molecules. Using a simple "stick and ball" model and standard bond length and atomic sizes, rationalize the results obtained. In particular be aware that the molecules are constantly "wriggling" and that for long carbon chain the stretched out conformation is only one of the numerous other possible conformations, which may be sampled to various degree by the molecule. Then, any observed quantity related to the size of the molecules represents an average value of the corresponding dimension. What can you deduce about the average orientation of each acid in the compressed film? What effect would you expect on the packing of the film if a triple bond were to replace the double bond in some of these acids? What is the purpose of adding $ZnSO_4$ to the sub-phase?

For cholesterol, assuming that the monolayer has the same density as cholesterol crystals, calculate the approximate thickness of the film. Again, using a simple stick and ball model, estimate the size of a cholesterol molecule. From the above result and estimate, is it possible to deduce the orientation of the cholesterol molecule within the compressed film?

Simple computer molecular modeling can be used to obtain some of the size parameters relevant to this discussion; for this purpose ACD Chemsketch, a free software available on the web has been loaded on one of the Pchem lab computer; HyperChem may be used also.

More generally, can you think of some application of this technique, or use of the information obtained from this type of measurements?

8. References

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Report: Langmuir-Blodgett Films

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