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Molecular Interfaces

Liquids and gases are both fluids, meaning that both flow. The characteristic that distinguishes a gas from a liquid is that the latter has a definite boundary. If you put quantities of oxygen gas and carbon dioxide gas into a container at room temperature and pressure, then even though the carbon dioxide is heavier and tends to stay at the bottom, the interface between the two is diffuse, and after a while they will mix completely. This is the case for all pairs of gases. However with oxygen gas and liquid water in the container, the water always stays at the bottom and the mixing is never complete. Even though the molecules of the water are moving at speeds even higher than those of the CO_2 molecules in the first case, the boundary between gas and liquid does not become diffuse. Another way of stating the same fact is that it takes energy to create more liquid interface. The energy required to create unit area of interface is a well-defined quantity and is called the surface tension of the liquid, symbolized g. The surface tension of common liquids ranges from about 20 mN/m for petrol to 75 mN/m for water. Although the random thermal movements of the molecules do not cause the interface to become diffuse, they do perturb it. The surface is continually distorted by millions of tiny capillary ripples. The resultant roughness is well understood and has been measured by X-rays. The amplitude of the ripples on a water surface at room temperature is approximately 0.3 nm RMS, i.e. two molecular diameters. The surface tension g, which is responsible for the existence of sharp molecular interfaces is closely connected to the existence of first-order phase transitions. If a cylinder full of steam (gaseous water) is slowly cooled, the first result is just a continuous decrease in the pressure exerted on the walls, while the contents of the cylinder remain uniform. However at a specific temperature, drops of liquid water start to appear with a density ~1000 times that of the gas phase. The molecules in the liquid droplets are in equilibrium with those in the gas and hence have the same chemical potential (free energy per molecule), although the molecular packing in the two phases have almost nothing in common. All other molecular states, including halfway stages with intermediate density, show a higher chemical potential than either stable phase. The molecules of water at the interface are in effect forced to be in such a strained halfway stage. Hence it takes energy to create more interface. The value of surface tension is inherently positive. If the g of a liquid interface ever became negative, then it would be energetically advantageous to create more interface, this is easily done by increasing the roughness of the interface. Within a short period of time, a sharp interface would cease to exist. There are a number of methods for measuring surface or interfacial tensions. Perhaps the most common is the Wilhelmy method, in which a rectangular plate is located at the interface. The force on the plate contains components from the interfacial tension, the action of gravity on the plate, and buoyancy forces. The latter two can be independently measured.

What is an amphiphile?

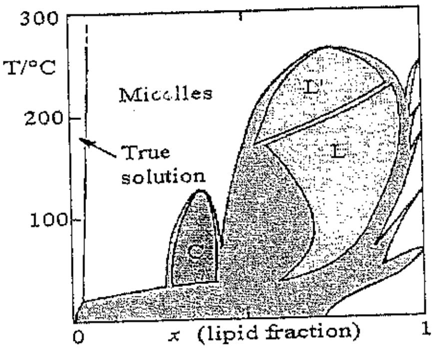
Paraffin oil and water do not mix, and this is a result of the interactions between their individual molecules. Molecules of water prefer other molecules of water, and molecules of oil prefer other molecules of oil. There are many substances showing this like prefers like behavior. Substances, which mix in water tend not to mix with oils, and vice versa.

The former are called hydrophilic (Greek for water-loving), the latter hydrophobic (Greek for water-fearing). An amphiphile is what results when you chemically link a water-fearing and a water-loving part. This apparently contradictory mixture of behaviors in the one molecule gives amphiphiles unusual properties and makes them very important both in industry and in science. The oldest known amphiphile is soap, and its cleaning action on your hands is closely related to its amphiphilic structure. All detergents are amphiphiles. Soap is made by cooking either animal fats or vegetable oils with soda. The fatty or oily substances in animals and plants are all amphiphiles, and are called lipids (Greek for fat). The fact that there are amphiphiles in living things is no mere coincidence - the properties of amphiphiles are vitally important for life, and they are what all living things make their cell membranes out of. Without a membrane, a cell could have no individual identity, and molecules required by the cell would just diffuse away into the environment.

What is self assembly?

Self assembly is a way of fabricating ordered molecular structures with the ultimate spatial precision. It is a phenomenon in which a number of independent molecules suspended in an isotropic (disordered) solution spontaneously come together to form an ordered aggregate which is of molecular size in at least one dimension. Whilst we have learnt to emulate Nature to some extent, the most impressive examples of self assembly are still biological. For example the ribosome is quite a complicated machine for building up a polypeptide chain according to the set of instructions encoded in a chain of messenger RNA. Just as a lathe for machining metal knobs, say, is built up from a lot of individual components themselves made out of different sorts of metal, so a ribosome is built up from a large number of different sorts of polypeptides and RNA chains. There is however a very important difference, the lathe is built up by its manufacturer from its component parts by step-by-step assembling the parts in their correct configuration and then fastening them together by welding or bolting to form the final unit. A cell does not do this. All it needs to do is to synthesize the polynucleotides and polypeptides of which the ribosome is made. The component parts then come together spontaneously into the correct configuration to form a functional aggregate. Closely related self-assembly techniques are used in many different ways by all living things to build up their internal structure. Self assembly is similar in some respects to crystallization, for example of copper sulfate from a saturated solution in water. While the concentration of $CuSO_4$ is kept above the solubility limit, crystal nuclei will slowly form and grow. The crystal aggregates certainly show much more order than the original isotropic solution. However this is not self assembly, because they eventually grow to reach macroscopic size in all directions. The size restriction is not artificial but results naturally from the requirement for functionality. The hydration of a lipid is now recognized as self assembly. Water is spontaneously taken up by an anhydrous lipid to form fantastic shapes called myelin figures. When the mixture is well agitated [illegible], the shapes become rounder and are called micelles, vesicles or liposomes. You may have heard of liposomes being used to encapsulate bioactive substances [illegible] in cosmetics and medicines for slow release.

The driving force for this self-assembly is the attempt by the molecules to hide their hydrophobic parts from the water. At very low concentrations the amphiphile dissolves completely in water to form a true solution. At higher concentrations the molecules start to aggregate together in little balls with the hydrophilic head-groups pointing outwards in contact with the water, and the hydrophilic tails hidden away from it in the interior. These are micelles, which have molecular size in all dimensions over a range of concentrations of the lipid in the surrounding solution. The phase diagram on the left of sodium oleate/water mixtures shows these two regions.



חלקן [illegible]

When there is more amphiphile and less water, the הן micelles become distorted מעוות, distending either to form a disc or a rod. Eventually they become infinitely extended [illegible]. In the region of the phase diagram marked C the micelles have stretched into threads or columns which pack in a hexagonal array. In the regions L and L' of the phase diagram the micelles have flattened into sheets, or lamellae. Since a lamella consists of two individual layers of molecules, it is also called a bilayer. דו שכבתי

What are Langmuir monolayers?

A Langmuir monolayer is a sheet שכבה of amphiphilic molecules all oriented מכוונים with their hydrophilic heads on one side of the sheet and their hydrophobic tails on the other. This means that, unlike the bilayers of biomembranes, Langmuir monolayers cannot exist stabile יציב when completely surrounded by water. Instead, Langmuir monolayers assemble and exist stably at pre-existing interfaces between phases with different degrees of hydrophilicity. The most hydrophilic molecular medium is water, whilst the most hydrophobic media are gases, (e.g. air). Hence the most extreme example of a hydrophilicity interface is a water surface. Liquid amphiphiles, for example cooking oils, spontaneously spread over such a surface until the film is just one molecule thick. The calming effect of oil on a rough sea was known to the ancients, including Pliny the Elder and Plutarch. The earliest scientific observation of this effect was reported by the great American statesman Benjamin Franklin, who on a trip to London performed a famous experiment on the pond at Clapham Common:"...the oil, though not more than a teaspoonful, produced an instant calm over a space several yards square, which spread amazingly, and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass." Simple arithmetic shows that the thickness of Ben's oil film was indeed only one molecule, although the significance of this was only realized over a century later.

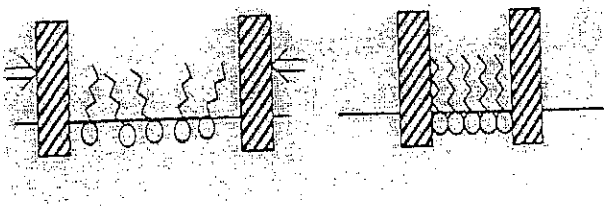
The calming of waves used by Franklin to detect the presence of a monolayer on a water surface is still studied scientifically today. However the most convenient indication that there is a monolayer on the surface is its effect on the surface tension. Pure water has a surface tension of approximately 72 mN/m, but a monolayer can cause this to drop nearly to zero.

Langmuir Films

Langmuir films consist if surface active materials or 'surfactants' trapped at the interface between two dissimilar phases, either liquid-liquid or liquid-gas.

Surfactants are molecules which are amphiphilic, that is molecules composed of a hydrophilic part and a hydrophobic one. Hydrophilic groups consist of groups such as carboxylic acids, sulfates, amines, and alcohols. These are all attracted to the polar media, as water, and the forces acting upon them are predominantly כוחות קולומביים coulomb type ($1/r^2$). Hydrophobic (or oleophilic) groups such as hydrocarbon chains, fats and lipids are much less (if at all) water soluble and the forces acting upon them are predominantly Van der חלשים יותר Waal's type ($1/r^{12}$ and $1/r^6$). Amphiphilic molecules are trapped at the interface because they posses two very different types of bonding within the one molecular structure. When surfactants dissolved in a non-aqueous נדיף volatile solvent, are introduced onto a polar liquid surface, the solvent will evaporate leaving the surfactants oriented at the liquid-gas interface. The hydrophilic 'head' groups pull the molecule into the bulk of the water and the hydrophobic 'tail' groups are pointing into the air. משטח של שכבה חד-מולקולרית A surface monolayer will only be achieved if the amphiphatic שיווי balance of the molecule is correct, that is the balance between hydrophobic and hydrophilic parts. If the hydrophobic 'tail' groups are too short (not hydrophobic enough), the molecule will be dragged into the water and dissolve. While if there is no hydrophilic part, the molecule may form thicker multi-layer films on the surface, or even להתאדות evaporate.

Sweeping the קיר, מחסום barrier over the water surface causes the molecules to come



closer together and eventually to form a compressed, ordered mono-layer- much like forcing together balls on a billiard or pool table. The film produced by such a method is known as Langmuir film.

פיזור

Spreading

[illegible]

The monolayer is formedon the surface of the sub phase by dissolving the amphiphilic substance (חומר) in a suitable solvent, and spreading the resulting solution dropwise onto the water surface.

The spreading solution is best applied (מוצע) to the surface by allowing small drops to fall from the syringe (מזרק) while it is held a few millimeters above the sub-phase. Each drop should be allowed to evaporate before the next is applied. An alternative procedure that is used for molecules known to form more rigid films, involves distributing (מחלק ?) the drops equally over the entire surface of the sub-phase.

The process of spreading once the drop of the solution is on the sub-phase surface can occur in a number of ways. Usually a thin film is formed by the spreading solution while the Langmuir film forming material attains (מגיע) its favored configuration at the air-water interface. The solvent evaporates and leaves behind only the monolayer. In some cases the deposited droplet does not spread over the sub-phase, but instead a thin film of dilute (מדולל) solution of monolayer forming material spreads from the droplet ([illegible]) (as most solvents used are slightly soluble in water. Depletion of the spreading solvent will not be due to exclusively to evaporation, but also to some dissolution of it into the sub-phase).

Spontaneous spreading will continue until the surface pressure of the monolayer is equal to the 'equilibrium spreading pressure'. At this point, all of the available surface is covered in monolayer and any further droplets of solution remain embedded (משובצים) in the monolayer as floating lenses, as no more spreading out can take place. Any undispersed (לא מפוזר) material must be removed otherwise it may be deposited as bulk (נפח) (גושי) aggregates on substrates (מצע (ויפר סיליקון)) dipped into the monolayer.

Isotherms

Molecules in a solution are subject to attractive forces; in the bulk of the solution these forces are equal. However, the forces at a surface or interface are unequal and the net effect is to pull the peripheral molecules into the bulk of the solution. This effect gives rise to surface tension. The surface tension can be defined as 'the work required to expand the surface isothermally by unit area' (i.e. Newton-meters per meter squared). The tendency of surface-active molecules to accumulate at the interfaces favors expansion of the interface and hence lowers the surface tension. Such behavior makes it possible to monitor the surface pressure as a function of the area occupied per molecule provided that the number of molecules deposited is known.

The characteristics of a monolayer on the water surface are studied by measuring the changes in surface tension upon compress of the monolayer. The reduction of surface tension is known as 'surface pressure'. Pressure readings are made by means of Wilhelmy plates attached to microbalance. The plot of surface pressure versus area occupied per molecule is known as a 'pressure-area isotherm', isotherm because compression takes place at constant temperature. The shape of the isotherm in characteristic of the molecules making up the film and hence provides a two-dimensional 'finger-print'.

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Forces at the Sub-Phase Surface

The forces affecting the polar head groups submerged שקועים in the aqueous sub-phase במים של- are ionic and proportional to $1/r^2$, whilst the forces between the hydrocarbon chains are due to Van der Waals interactions and proportional to $1/r^6$ and $1/r^{12}$. Hence, the intermolecular actions in the sub-phase are of longer range than those רחוק קרוב in the super-phase עליון. The isotherm can usually be seen to consist of three distinct regions.

1 → After the initial deposition הפקדה onto the sub-phase, when no external pressure is applied to the monolayer, the molecules behave as a two-dimensional ממדי gas , which can be described by:

$\pi A = KT$

π– surface pressure

A- molecular area

K- Boltzmann constant

T- thermodynamic temperature

2 → On further נוסף compression דחיסה some ordering סידור of the film takes place and it behaves as would be expected of a two-dimensional liquid.

With continued closing of the barrier, the increase in pressure causes additional ordering סידור, the monolayer behaving as a quasi-solid (מוצק-כמעט). The solid state is characterized by a steep תלול usually linear relationship between the surface pressure and the molecular area.

3 → Eventually the collapse pressure, $\boxed{\pi_c}$ is reached at which the film is irretrievably ללא חזרה loses it's mono molecular form. The forces exerted הופעל upon it become too strong for confinement כליאה in two-dimensions and molecules are ejected נפלט מתמוטט out of the monolayer plane into either the sub-phase (more hydrophilic molecules) or the super-phase (more hydrophobic molecules). However, collapse התמוטטות is not uniform אחיד across מעבר the monolayer, but is usually initiated מתחיל near the leading edge שפה of the barrier or at discontinuities in the trough גיגית- such as corners of the Wilhelmy plate לוחית. Usually a collapsed film

will consist of large areas of uncollapsed monolayer interspresed with 'mountain ridges' where monlayers have been crushed together to form bulky aggregates.

The collapse pressure can be defined as the maximum to which a monolayer can be compressed without a detectable expulsion of molecules from the Langmuir film. It depends on the chemical substances used, the temperature, the rate at which the film is compressed and procedures to which the film has been subjected to. The value of the collapse pressure for a simple saturated fatty acid can be in excess of 80mN/m which could be equivalent to about 200 atmospheres if extrapolated to 3-D. When the monolayer is in the two-dimensional 'solid' or 'condensed liquid' phase, the molecules are relatively well oriented, and the closely packed and the zero-pressure molecular area (A_0) can be extrapolating the slope of the solid phase to zero-pressure- the point at which this line crosses the X-axis is hypothetical area occupied by one molecule in the condensed phase at zero pressure (22-25 Å^2). The area corresponds to the cross sectioned area of a hydrocarbon chain, suggesting that the compressed monolayer consists of close packed vertically oriented chains.

Who first discovered monolayers?

Pliny the Elder and Plutarch observed some characteristic effects of monolayers in antiquity ימי קדם, and Benjamin Franklin even performed experiments on them. However, none of them recognized them for what they were, and they could scarcely בקושי have had a realistic idea of the true nature of what they were seeing. Because they did not have the scientific concept of atoms and molecules which we now know is necessary to put monolayers into a comprehensible מובן) framework מסגרת. This framework was developed throughout the 19th century, and major contributions תרומות? were still being made at the beginning of the 20th. The first person to make worthwhile, reproducible measurements on monolayers was Agnes Pockels who lived in Braunschweig, Germany. Agnes Pockels was the original housewife superstar. She performed her first experiments on monolayers in her kitchen in her home, starting in about 1882.

She used her bowls קערות? as the water container (now called Langmuir trough שוקת) and a button as a du Noüy ring to measure the surface tension of the liquid in it. She sent an account of her work to Lord Rayleigh, who recommended its publication in Nature. She introduced many of the basic concepts of amphiphilic monolayers including the use of a spreading solvent to deliver a small quantity of material rapidly במהירות and accurately במדויק to the surface, and her isotherm of a stearic acid monolayer is now recognized to be essentially correct. Lord Rayleigh was inspired by this contact to make his own experiments, from which he concluded that these layers were just a single molecule thick.

While Einstein's explanation for Brownian motion and Bragg's X-ray structure determinations of crystals were also important, the isotherm studies performed by Pockels, Rayleigh and their successors provided the most direct access to molecular dimensions. The equipment was simple, and no sophisticated mathematics were required for its interpretation. It played a major part in convincing the body of scientists of the time of the reality of atoms and molecules, and that they were more than just a convenient hypothesis.

Who was Langmuir?

Irving Langmuir was an industrial research scientist early this century. He was employed by the US General Electric Company in Schenectady in northern New York. In spite of the earlier investigations of amphiphilic monolayers not only by Pockels and Rayleigh but also by many other physicists in France and England. These systems are now named after him because he was the first to give essentially the modern understanding of their structure at the molecular level, in particular the fact that the molecules show a preferential orientation. Langmuir was also the first to show that monolayers can be transferred from the air/water interface to solid substrates for further study. Together with his assistant,. Katherine Burr Blodgett, he showed that it was possible to go further and to deposit many monolayers onto the same substrate, thus building up a multilayer stack of any required thickness. Deposited monolayers of whatever thickness are now known as Langmuir-Blodgett films.

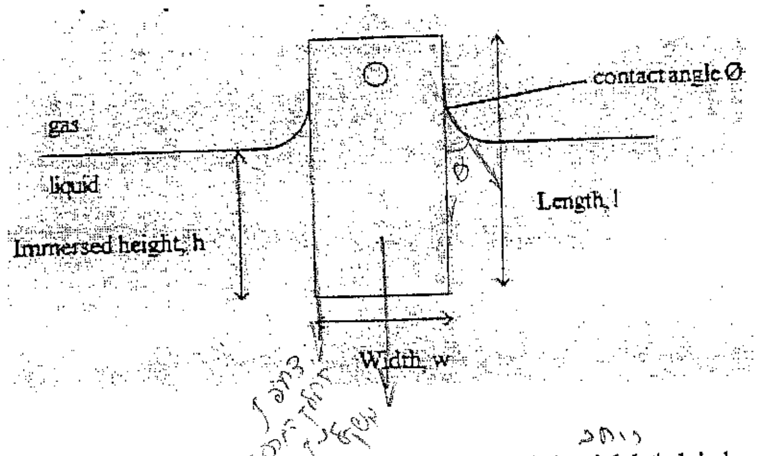
Langmuir's work in this area followed his trail-blazing study of electron emission from metal surfaces in a vacuum, which he showed was strongly influenced by monolayers of gases. In the course of this work he invented the ubiquitous tungsten-filament incandescent lamp. He was a prolific and creative scientist, and in 1933 was awarded the Nobel Prize for his work.

Basic Tensionmetry Theory

לוחית מושעה

Consider a plate suspended at the liquid-gas interface. The forces on the plate consist of:

1. The weight of the plate.
   מכוסה מים
2. The upthurst on the submerged part of the plate.
3. The surface tension of the liquid on the plate.



עובי

מושקע

If the dimensions of the plate are l*w*t (length*width*thickness) and it is submerged at height, h, the forces acting on the plate can be expressed as:

$$Force = (\rho_P l \cdot w \cdot t) \cdot g - (\rho_L h \cdot w \cdot t) \cdot g + 2((w+t) \cdot ST) \cdot \cos\phi) \quad \text{(eq.1)}$$

Force = weight- upthurst + surface tension

ρ_p= density of the plate

ρ_L= density of the liquid

ST= surface tension of the liquid

ϕ= The contact angle of the liquid to the plate

תאוצה

g= acceleration due to gravity

Before making any measurements, the control unit is zeroed, there by

לקזז מונח

eliminating the weight term from Eq. 1:

$$Force = -(\rho_L h \cdot w \cdot t) \cdot g + 2(w+t) \cdot ST \cdot \cos\phi \quad \text{(Eq.2)}$$

Force =- upthrust + surface tension

When making an absolute measurement, the plate is drawn up and out of the liquid so that's it's lower edge is level with the liquid surface. This eliminates the upthrust reducing Eq. 2 to:

$Force = 2(w + t) \cdot ST \cdot \cos\phi$ (Eq.3)

Finally, if the contact angle of the liquid to the plate is 0° then the expression further reduces to:

1 $Force = 2(w + t) \cdot ST$ (Eq.4)

Hence for a plate, the surface tension is :

2 $$ST_{plate} = \frac{Force}{2(width + thickness)}$$

Where surface tension is in units of milli-Newton/meter. the force in units of milliNewtons and the perimeter in units of meters. Generally therefore, the surface tension is given by:

ST = Force/Perimeter

Thus for a ring, the surface tension is given by:

3 $$ST_{ring} = \frac{Force}{(\pi d + \pi(d - 2t)}$$

Where "d" is the outer perimeter of the ring and "t" is the thickness of the wire in meters. When determining surface tension, there are always three unknowns that have to be identical:

a) The perimeter of the plate.

b) The contact angle of the liquid of the material to the plate.

c) The surface tension it self.

Only when the perimeter and the contact angle are known, can the surface tension be measured. Hence the dimensions of the plate, it self must be ascertained that zero contact angle exists between the plate and the liquid. It is therefore recommended that paper plates are used, as the liquid can completely soak into the paper, thus ensuring zero contact angle.

Trough cleaning

The cleanliness of a trough is very important for obtaining reproducible results. There are three basic categories of cleaning agent which have been used for this purpose[3]:

A. Solvents: alcohols, chlorinated

B. Detergents: potassium octanoate, Decon90®, Helmanex®

C. Aggressive chemicals: fuming nitric acid, chromic acid, hydrofluoric acid Solvent Cleaning. The most rapid procedure for trough cleaning is to empty the trough using the suction tool and to wipe it over with a paper tissue moistened with solvent and held in a gloved hand. Suitable solvents are the lower alcohols, such as ethanol or 2-propanol, and chlorinated solvents such as chloroform ($CHCl_3$) or 1,1,1-trichloroethane (CCl_3CH_3). The solvents should be the purest available, spectroscopic or analysis grade, and the tissues should be checked out for surface-active contamination — perfumed tissues are unsuitable. Check that the plastic or rubber gloves are resistant to the solvent.

Solvent cleaning is quick and convenient for removing low-molecular-weight contamination, and can be employed when changing substances. However it does not remove polymeric contamination, often of biological origin. Detergent cleaning is now recognized as the all-round best method for thorough trough cleaning. It should be performed roughly once a week. Use only a detergent suitable for the purpose. Do not use normal detergents. Nima recommends the use of the pure generic detergent potassium octanoate. The contaminants which are troublesome in an LB trough are the surface-active ones. Most of them are only weakly surface active, not introduced on purpose, and present in only microgram quantities. Normal detergents will remove contaminants, but being highly surface active themselves, leave a trough useless for further work. The only detergents which you can use to clean your trough are ones which can be completely rinsed away afterwards. The logic of detergent cleaning is that the micelles of the detergent present the contaminant with an enormous area of surface with a hydrophilic-hydrophobic gradient. By the law of mass action, any material with the slightest of tendencies to accumulate at the air-water interface will also incorporate itself into the micelles, which are then removed. The technique was first used over a decade ago in Switzerland and Germany and has proved itself, in spite of its mildness, to be extremely effective against both low-molecular-weight and polymeric contamination.

Aggressive Chemicals. Fuming nitric acid, used undiluted, oxidizes most organic contaminants within 5 minutes. So-called chromic acid also works by oxidation and produces far fewer fumes. However its action is slower and it leaves a residue of trivalent chromium cations which may be problematic for carboxylic monolayers. It is in fact a mixture of potassium dichromate, water and sulfuric acid. The dichromate is dissolved in the minimum amount of water and then an equal volume of sulfuric acid is carefully added. Polysiloxanes are only removed very slowly by these two reagents, and for these materials HF diluted to 1% is more effective. Because of the hazards both to you and to your equipment associated with the use of all these chemicals, Nima does not recommend them. The modern detergent cleaning procedure described above is equally effective in removing surface-active impurities and poses considerably fewer hazards.

Trough cleanliness

The most basic check of trough cleanliness is to compress rapidly to as small an area as possible, until the barriers are nearly touching the Wilhelmy plate. Any pressure rise indicates trough contamination. Since many amphiphiles do not develop any surface pressure until the molecules are nearly densely packed, and since the maximum feasible area compression ratio is usually not greater than 10:1, this technique detects only gross contamination. Another quick check of contamination is to observe the receding contact angle of water on the Teflon of the trough. It should be visibly greater than 90°. When you are sucking water out of your trough, the receding puddle should show gray edges, and should only show a tendency to stick to visible features (grooves, etc.) of the Teflon surface. A third check taking only a couple of minutes is to measure the surface tension of the trough water. A more time-consuming but much more sensitive check is to take the isotherm of stearic acid. When comparing with the literature, beware of the many papers giving contaminated isotherms! The 'liquid-condensed' region should be absolutely straight. The extent, in pressure, of the curved regions near lift-off and the tilt transition <u>should not exceed 2 mN/m</u>. Any deviation in these respects is indicative of organic contamination. The lift-off area should be in the range 24-25 Å^2. The tilt transition pressure should be 26 mN/m, essentially independent of temperature. Normally, this pressure is affected most by ionic contamination of the subphase.

The isotherm of behenic acid is even more sensitive to organic contamination. In addition to the features at lift-off and the tilt transition, the swivel transition should be visible as a small kink in between. The surface pressure of the swivel transition is very sensitive to temperature.

Substances

Pure water requirements

It is difficult to keep water in an ultrapure state for any length of time, and by far the best solution is to purchase a water purification unit producing freshly- deionised water directly in your laboratory. In order to keep a trough clean, there is no alternative to using significant quantities of ultrapure water, equivalent to many changes of trough water per day. For the container used to transport ultrapure water, perfluorinated polymers (Teflon, FEP) are the best but rather expensive. Polypropylene is almost as good and considerably cheaper, and becomes very clean with repeated use. Glass has very little organic contamination, but dissolves quite appreciably to give a 10 μM silicate solution.

If you want to check the pH of the water, you must use a pH meter specifically designed for use with ultrapure water. When water has had had plenty of time to equilibrate with the air, its true pH lies in the vicinity of 5.5. Cadmium starts to work its magic at pH 5, so that it is not necessary to add buffer.

Quick check of surface tension

With practice, the following procedure will give you a value for the surface tension of your water correct within about 1 mN/m. It is a good and quite quick check of the quality of your water. (It can also be used to measure the surface tension of any liquid).

1. Using tweezers, fit a clean filter-paper Wilhelmy plate to your pressure sensor. Turn the knob on the pedestal to lower it completely into the liquid in the trough and leave it there a second or two to soak. If the range of height available from the knob is insufficient, add another S-hook to the chain.

2.Raise the plate slowly until the bottom edge is just at water level, still attached to the meniscus. The higher the better, but if the meniscus detaches wind the plate down again to touch the surface. Wait about a minute for excess liquid to drain.

3.Raise the plate slowly until the meniscus breaks. Check that there is no excess water hanging down. If so, lower the plate to touch the water surface and let it drain, then raise it again gently.

4.Press ' Z ' to zero the value of surface pressure displayed on the screen.

5.Lower the plate slowly, stopping as soon as it hits the water and the meniscus sticks to the paper.

6.Wait for the displayed value to stabilize and note it. Its negative is the surface tension. At 20°C, the surface tension should be 72.4 mN/m.

Trough Temperature Control

Many experiments require precise control of the trough temperature. All Nima troughs are constructed with the Teflon in intimate contact with a metal baseplate through which thermostatted water can circulate. This is the optimum configuration for good thermal control. Unfortunately, while Teflon has been found by the vast majority of groups to be the optimum trough material, its thermal conductivity is not high. Even though, we machine the Teflon on the bottom of the trough as thin as possible. The thermal resistance of this layer is not much lower than the convective thermal resistance of the air above the trough. So that there can be a temperature difference of several degrees between the subphase water and the trough baseplate when the trough is operated near 0°C or 40°C. To minimize this difference, the only feasible way is to improve the thermal isolation of the top of the trough. In the first instance, this is best achieved by putting the trough in a cabinet which restricts the possibilities for convection. If the heat differentials are too large even when the trough is in a cabinet, the next step is either: to insulate the cabinet, or by means of a heater or cooler, perhaps using the thermostatted water also fed to the trough baseplate, to establish a temperature profile preventing convection.

Isotherm technique

When taking isotherms of common materials such as stearic acid, variations of up to 1 Å^2 in the area measurements are typical. This range of error must be compared to the total area per molecule, which is about 25 Å^2, i.e. it corresponds to a relative error of ±2% or so. With practice it is possible to get this error down below ±1% with isotherms of fluid monolayers. There are four areas of isotherm technique, which can often be improved:

1. accuracy of the area measurement
2. accuracy of the spread volume
3. correction for material already on the trough
4. choice of material

Meniscus Area: It is normal to do trough work with the water a couple of millimeters above the level of the trough edges. The curvature of the meniscus then means that the actual trough area is typically 2% greater than the projected area, which is what is displayed as the isotherm abscissa. --> [illegible]

However it is perfectly possible to work with the water surface completely flush with the trough edges, and then there is no correction required. This requires more frequent topping up of the water level after cleaning, but there is a trick to minimize the extra effort. Once you've made the surface flush once, and zeroed the pressure for a clean water surface, then rather than getting down with your eyes at trough level to check visually while topping up with water, keep your eye on the pressure reading. When the water level is correct, the reading will be zero again.

Syringe dead volume: Before spreading, dispense a drop into the bin or onto a spare bit of absorbent tissue without touching it, and then touch the tip of the needle lightly onto the water surface on the other side of the barrier. Then, after having dispensed the desired amount of material onto the working side of the barrier, touch the tip of the needle lightly on the water surface, this time on the working side of the barrier. This procedure minimizes the effect of dead volume in the hypodermic, and ensures that the amount of spreading solution, which is pushed out from the cylinder by the piston actually ends up on the working water surface. It's also an idea to get a bit of emery paper and sand the end of the hypodermic needle square.

Differential Isotherms: It is almost impossible to clean a trough completely. If you just rely on the servomechanism moving the barrier down to its minimum area and then suction from there, you typically leave a few percent of material behind. Even the procedure in which the barrier is unclipped from its holder and used as a broom to 'sweep' the monolayer into a corner does not remove everything from the water surface, although it is considerably better. And don't forget the material on the Wilhelmy plate! As a result of these unavoidable difficulties, 'differential' isotherms are considerably more precise. First of all, spread and suck off the desired material a couple of times, to ensure that, even if the trough is not 'clean', the monolayer on the trough is the one you want. For the last suction before the measurement, remove material only to the point that the monolayer is developing a significant pressure m at minimum barrier area. m must not so high that there is any risk of collapse, but high enough to ensure that all holes of expanded monolayer have closed up. It might, for example, be just below the tilt transition. Record the isotherm of this amount of material. Then expand to maximum area and spread carefully a measured amount Vc of spreading solution. Finally take the isotherm again.

Now compare the preliminary area A0 before and the final area A1 after spreading, both at m . The true amount of material on the water surface for the final isotherm must then correspond to the volume Vc*A1/(A1-A0) . In the Nima trough program, leave the display in cm2 up to this point, enter the compensated spread volume, and then toggle to the display in Å2, which will now be correct.

Monolayer Fluidity: Finally, taking an isotherm doesn't make much sense if the monolayer is not fluid. There are inherent problems of this sort working with fatty acids when there is iron, copper or aluminium in the subphase, or with a number of polymeric materials. It is perfectly possible in solid monolayer systems to get pressure gradients which have no tendency to decrease with time.Usually you get high pressures near the barrier and low pressures at the other end of the trough, so that the 'isotherm' which you record depends on where you put the Wilhelmy plate. If you must work with these materials, then perhaps the least bad of the solutions is to add a small quantity of amphiphile which you know to completely demix from the desired material, and whose monolayer stays fluid. For aliphatic systems perfluoroacids might be one such choice.