Surface film: The layer at the surface of a liquid of thickness equal to the range of molecular attraction.

Surface pressure: The surface pressure (π) is defined as the difference in interfacial tension between a clean surface and a interface in the presence of emulsifier.

Let, water in clean surface tension, γ and an
surface has

emulsifier has surface tension, γ_0. The surface pressure, $\pi = \gamma_0 - \gamma$

Langmuir experiment: When long chain of fatty acid added to the clean water surface, due to their translational motion pressure was exerted on the side of the reaction vessel illustrates the film pressure.
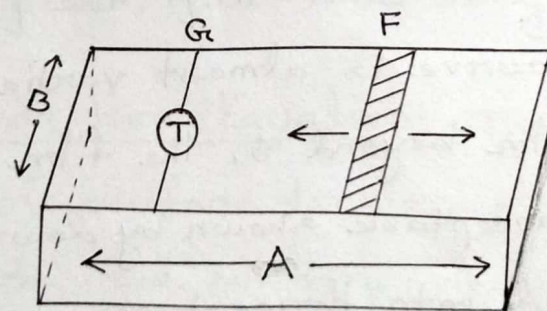
Langmuir trough

From Langmuir trough: A trough (ट्रफ़) containing clean water, where F is moveable (right or left) barrier and G is fixed barrier coupled with a torsion balance, T to measure exertor pressure on G. The trough has fixed width B and edge A. At any position of F, a definite area enclosed by F and G. When small quantity of

benzene solution of long chain fatty acid (Palmitic acid) is added to the clean water confined within two barriers, benzene evaporates leaving fatty acid behind. F is moved towards G in regular small successive steps and the pressure exerted on G, measured by T.

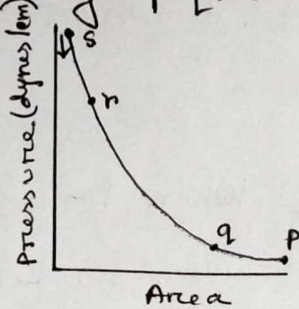Several readings are taken and pressure vs area curve shown by pqrs in fig-2.

Fig-2: Pressure – area curve.

From figure-2:

Over the region pq the pressure increases only slightly on decreasing the area. Between qr the pressure changes. Between rs the curve is almost vertical and linear. On compressing film beyond s, the film ruptures p–A curve no longer acceptable. shown by downward arrow. The film is devided into three types.
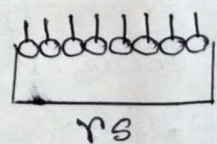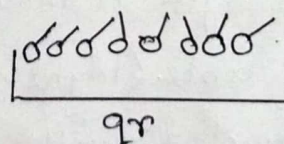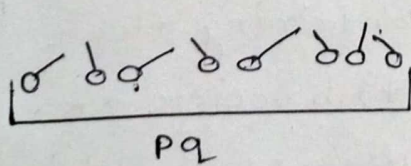
The molecule forming the film on the surface within pq area are almost lying on the surface and situated quite apart from each other.

Within the range qr, due to decreased available area, the molecules are closed to each other is called Liquid extended film.

Within the range rs, the film is said to be liquid film with low compressibility and no satisfactory relation between pressure and area is not known. If rs is extrapolated towards the area of axis, it cuts at t. This is the minimum area occupied by the molecules in a highly compressed and definitely oriented film. Thus actual number of molecules can be calculated and the area occupied by a single molecule can also be calculated.

In pq region, the film said to be gaseous since they obey $PA = constant$.

In qr region, the film obey $P(A-z) = Constant$.

Gibb's adsorption Equation: The extent of rise or reduction of surface tension depends on the concentration of solute in a solution (viz. water). If the concentration of the solute is more on the surface layer than in the bulk, the solute is said to positively adsorbed on the surface. When the concentration of the solution is more in the bulk than in the surface, the solute is said to be negatively adsorbed on the surface. Gibbs treated these phenomena from

thermodynamic principle and derived following relation

$$\Gamma = -\frac{d\gamma}{dc} \cdot \frac{c}{RT} \quad ----(i)$$

where,

γ = surface tension of the solution

Γ = The excess concentration of the solute on the surface.

c = Concentration of the solute in solution

R = The gas constant

T = Temperature in K.

from a measurement of γ, surface tension of a series of solution of different concentration, c, a plot γ vs c is drawn. Then $\frac{d\gamma}{dc}$ is evaluated for various c. Using these values, gradient, Γ can be calculated from equation (i).
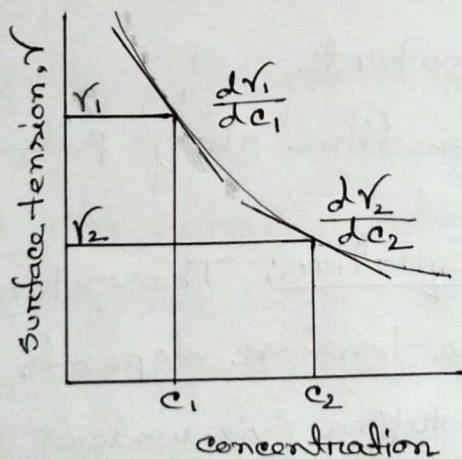

Fig: Surface tension as a function of concentration.

Derivation of Gibb's adsorption equation: A solution separated from its solvent and is kept in a close vessel in equilibrium with its vapour shown in figure 1. Let surface area, volume, surface tension, osmotic pressure of the solution be S, V, γ, π respectively.

Case-1: By pulling piston −B to a small extent, surface area increase by ds and expansion takes place aginst surface tension but volume remain constand, the work done $= -\gamma ds$.

Then osmotic pressure will be:

$$\left[\pi + \left(\frac{d\pi}{ds}\right)_v ds\right]$$

Case-2:

By piston −A, volume of the solution increased dv.

The work done:

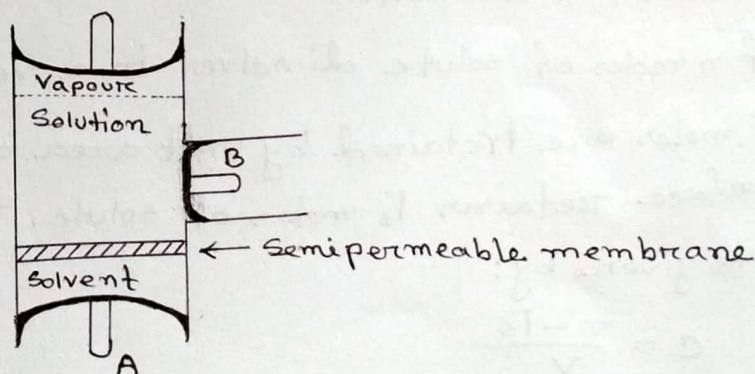$$\left[\pi + \left(\frac{d\pi}{ds}\right)_v ds\right]dv$$

Figure: 1.

The surface tension will become:

$$\left[\gamma + \left(\frac{d\gamma}{dv}\right)_s dv\right]$$

Case −3: Piston −B pushed back, so surface area decreased by ds. The work done by the system:

$$\left[\gamma + \left(\frac{d\gamma}{dv}\right)_s dv\right]ds$$

when osmotic pressure in its original value, π.

Case-4: With piston −A, the system brought back to its initial state, volume decreased by dv and work done is $-\pi dv$.

As the cycle is isothermal, the net work is zero

$$-\gamma ds + \left[\pi + \left(\frac{d\pi}{ds}\right)_v ds\right]dv + \left[\gamma + \left(\frac{d\gamma}{dv}\right)_s dv\right]ds - \pi dv = 0$$

or, $\left(\frac{d\pi}{ds}\right)_v = -\left(\frac{d\gamma}{dv}\right)_s$ $\quad$ ----- ①

As the surface tension, γ is a function of concentration i.e. of volume, $\left(\frac{d\gamma}{dv}\right)_s \neq 0$ and hence $\left(\frac{d\pi}{ds}\right)_v \neq 0$, which implies osmotic pressure is a function of surface area is realizable when concentration change will surface area.

From equation ①, surface and bulk concentration are not same of a solution.

If n moles of solute dissolves in a volume, v of which Γ moles are retained by unit area of surface, total surface retains Γs moles of solute. Then bulk concentration c is given by:

$$c = \frac{n - \Gamma s}{v}$$

or, $\left(\frac{dc}{dv}\right)_s = -\frac{n - \Gamma s}{v^2} = -\frac{c}{v}$

and $\left(\frac{dc}{ds}\right)_v = -\frac{\Gamma}{v}$

The osmotic pressure, $\pi = cRT$

So, $\left(\frac{d\pi}{dc}\right)_v = RT$

From equation ①:

$$\left(\frac{d\pi}{dc}\right)_v \cdot \left(\frac{dc}{ds}\right)_v = -\left(\frac{d\gamma}{dc}\right)_s \cdot \left(\frac{dc}{dv}\right)_s$$

or, $RT\left(-\frac{\Gamma}{v}\right) = -\left(\frac{d\gamma}{dc}\right)_s \cdot \left(-\frac{c}{v}\right)$

or, $\Gamma = -\frac{c}{RT} \cdot \frac{d\gamma}{dc}$ $\quad$ ----- ⑪

The above equation is known as the Gibb's adsorption equation.

<u>Math:</u>

Langmuire film: A langmuir film can be defined as an organized monolayer of amphiphilic molecules at a liquid-gas interface.

Langmuir - Blodgett film: A Langmuir-Blogett film (L.B. Film) can be defined as one or more monolayers of material deposited from a liquid surface onto a solid substrate by dipping the substrate through a floating monolayer at a constant molecular density.
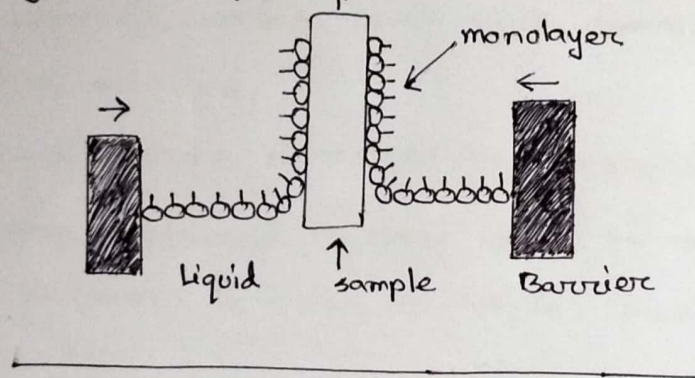

Application of Langmuir - Blodgett film:

① For creating highly organized and controlled nano-particle coating on solid substrate.

② The glucose biosensor can made of poly LB films.

③ LB films can be used as biological membrane.

④ LB films can be used as passive layers in MIS (Metal-insulator- semiconductor).

⑤ LB films are used to transfer high quality molecular layers of a variety of materials in electronic industry.

⑥ Anti reflective glass can be produced by successive layers of fluorinated organic film.

⑦ LB films is an effective technique to produce ultra thin films.

Preparation of LB films:

① Langmuir-Blodgett films are prepared by first a small quantity of amphiphilic compound dissolved in a volatile solvents onto the surface of purified water.

② When the solvent has evaporated, the organic molecules may be compressed to form floating two dimensional solid. →>*

③ If the surface pressure of the monolayer is held constant in condensed phase, then the film may be transferred from the water surface onto a suitable solid substrate simply raising and lowering the latter through the monolayer/air interface.
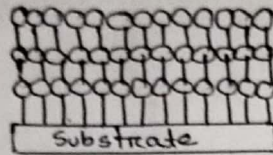→>*

The sequential isothermal compression changes the structure of monomolecular film, which passes through a series of two dimensional states reffered to gas phase, liquid phase and solid
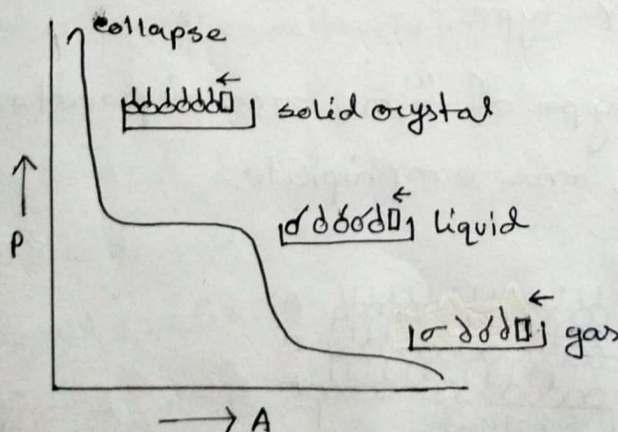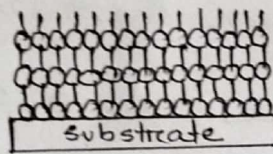

Types of LB films:

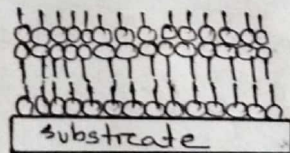X-type: These films are with all heads facing away from the substrate.

x—type

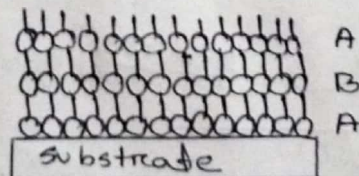**Z-type:** These films are with all heads pointing towards the substrate.

z—type

Y-type: These films orienting monomolecular layer in a head-to-head and tail-to-tail configuration.

Y—type

A-B-A type: These-type of films are deposited when there is more than one amphiphile.

A—B—A type.

Characteristics of LB film:

① They are extremely thin films.

② They have high degree of structural order.

③ The films have different optical, electrical and biological properties which are composed of some specific organic compound.

④ LB-layers may not be stable for long period of time or harsh environment.

⑤ Specialized equipment is needed to create them.

⑥ Special care must be taken to ensure reproducible and well-ordered films.

Self Assembled Monolayer:

A SAM (self assembled monolayer) is defined as the assembly of molecules without guidence from an external source to make itself into an organized monolayer on a surface.

In some cases, molecules that forms monolayer do not interact strongly with substrate. In other cases the SAM molecule possess a head group, tail and funetional end group and head group has a strong affinity to the substrate. Common head groups include thiols, silanes etc. SAMs are created by chemisorption of 'head groups' onto a substrate from either the vapoure or liquid phase followed by a slow organization of 'tail groups'. Initially at small density on the surface absorubater are in a disordered mass or 'laying

down phase, but at higher molecular coverage, begin to form crystalline or semi crystalline form.

Absorbate molecules are adsorbed readily and are stable due to strong chemisorption of 'head group' than the physisorbed bonds of Langmuir- Blodgett films. The monolayer of SAMs packs tightly due to vander Waals intraction. The 'head groups' assembled on the substrate and 'tail groups' assembled far from the substrate.
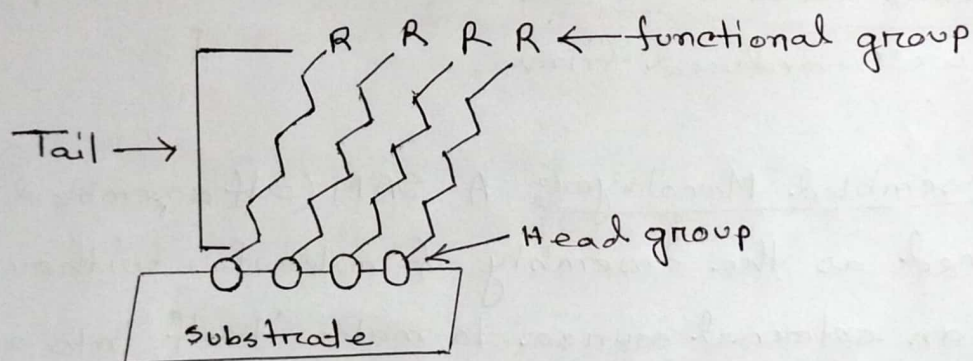

Figure: Representation of SAM structure.

A simple alkanethiol molecule which have sulfur binding group for the attachment to a noble metal surface, a alkane chain, head group. The head group provides a platform where any desired group can be used to produce surfaces. The sulfur group link the molecule with gold surface. By changing head groups a surface can be hydrophobic and hydrophilic.
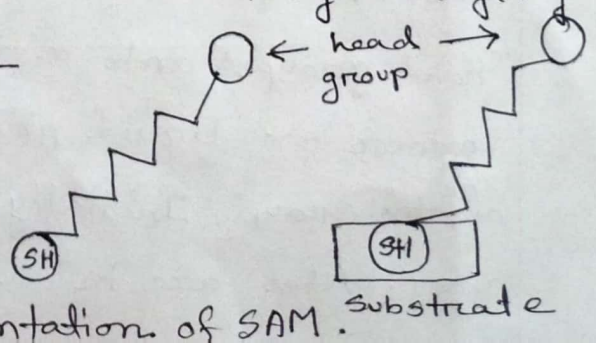

Fig: Representation of SAM.