SURFACE TENSION and INTERFACIAL PHENOMENON

By,

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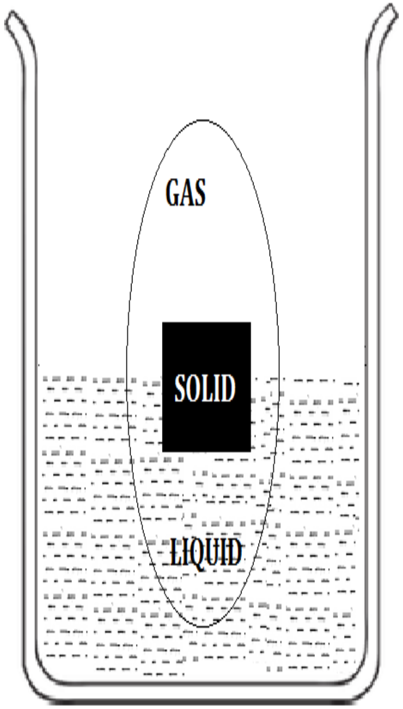
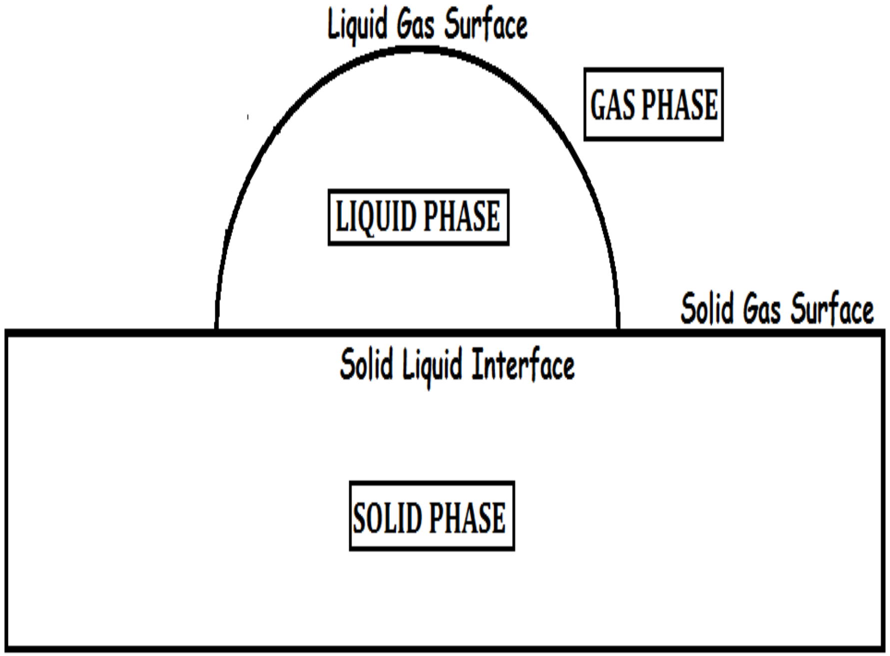
Surface Chemistry is the study of the chemical phenomena that occur at the surface or interface of two substances which can be solid-liquid, solid-gas, solid-vacuum, liquid-gas, etc.





- In the physical sciences, an interface is the boundary between two spatial regions occupied by different matter, or by matter in different physical states. When two phases like solid and solid, solid and liquid or liquid and liquid exist together the boundary between them is termed as interface.
- Out of the two existing phase, if one is air or vacuum then the boundary line separating this two phases (solid and air or liquid and air) is called as surface. The interface between matter and air, or matter and vacuum, is called as surface.
- Although surface terminology is used everywhere but every surface is an interface.

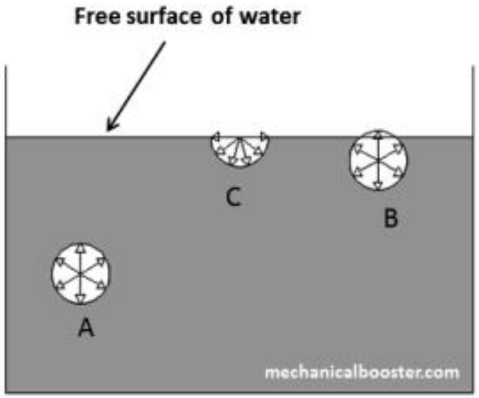
LIQUID INTERFACES

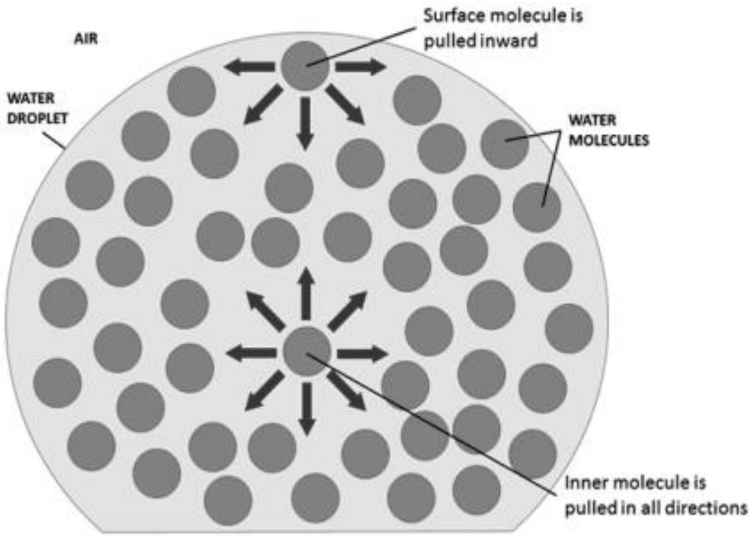
- Liquid interface is a phase boundary between two phases out of which one phase is liquid.
- Interfaces can be flat or curved.
- Depending upon adjacent phases the classification of interfaces are as follows

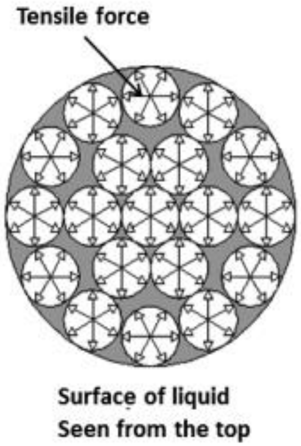
  Liquid-Liquid Interface

  Liquid-Solid Interface

  Liquid-Gas Interface


Free surface of water
C
B
A
mechanicalbooster.com


Surface molecule is pulled inward
AIR
WATER DROPLET
WATER MOLECULES
Inner molecule is pulled in all directions


Tensile force
Surface of liquid
Seen from the top

- In the liquid state the cohesive force between adjacent molecules are well developed. For the liquid molecule suspended in bulk, the cohesive forces between molecules exhibit stronger attractive forces upon their nearest neighboring molecules. On the other hand, the molecules those are on the surface, they have no neighboring molecules above and, thus they can develop adhesive force of attraction with the molecules constituting other phase. This adhesive force of attraction between liquid and gas are very small. This difference between the cohesive attractive force and adhesive attractive force tends to contract the surface and tend to pulled into a spherical shape by the cohesive forces of surface.

SOLID INTERFACES

- Solid interfaces are immobile as compared to liquid interface.
- Though the particles in solid are held with certain forces and each particle is attached with one another, the forces are not balanced at the surface because the surface particles are not surrounded by neighbouring particle.
- The perpendicular attraction to the surface tend to draw this particles inwards. The surface particle tries to overcome the imbalance of forces giving rise to adsorption.

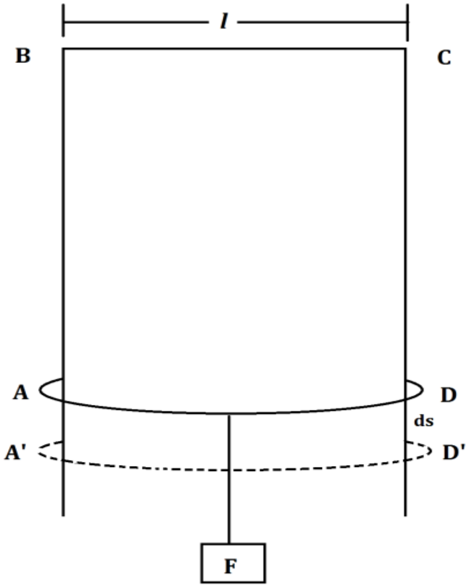
DEFINITION

- **Surface tension** can be defines as, “the forces acting at right angle to any line of unit length of the surface of the liquid”.
- **Interfacial tension** can be defined as, “the force per unit length acting at interface between two immiscible liquid”.
- **Interfacial tensions are less than surface tensions** because the adhesive forces between two liquid phases forming an interface are greater than when liquid and gas phase exist together. Therefore when two liquids are completely miscible, no interfacial tension exists between them. Surface tension measures the strength of cohesive force of liquids so surface tension is more.

SURFACE FREE ENERGY

- **Surface free energy** can be defined as the work required to increase the interface of phases.
- Surface free energy is a physical phenomenon caused by intermolecular interactions at an interface, i.e., London dispersive force, Debye inductive force, Keesom orientational forces, hydrogen bonding, Lewis acid–base interactions, and energetically homogeneous and heterogeneous interactions.
- Surface free energy can be defined as the work per unit area done by the force that creates the new surface.
- Surface free energy has the unit of erg/cm^2

SURFACE FREE ENERGY



- Consider a frame of area ABCD is placed in a soap solution. As the frame is removed from the soap solution a film ABCD is formed. The film formed is stretched by applying force F. Upon application of the force the film will displace by the distance ds and the area of soap film will now be A'BCD'.

- The applied force is equal to interfacial tension multiplied by the length of movable bar

$$\gamma\, 2l = \mathrm{F}$$

Where,

γ is interfacial tension
F is the force required to break film
l is the length of movable bar

Upon application of force F, the film area will extend by the distance ds and will shift from AD to A'D'. The work done dw can be given as

$$\mathrm{dw} = \mathrm{F} \times \mathrm{ds} \qquad \ldots\ldots\ldots\ldots (2)$$

substituting equation (1) in (2), it becomes

$$\mathrm{dw} = \gamma \times 2l \times \mathrm{ds} \qquad \ldots\ldots\ldots\ldots (3)$$

As $2l \times \mathrm{ds} = \mathrm{dA}$ i.e. change in surface area

Equation (3) can be converted as

$$\therefore \quad dw = \gamma \times \mathrm{dA} \qquad \ldots\ldots\ldots\ldots (4)$$

For finite change in the area of film equation (5) becomes,

$$\mathrm{W} = \gamma \times \Delta\mathrm{A} \qquad \ldots\ldots\ldots\ldots (5)$$

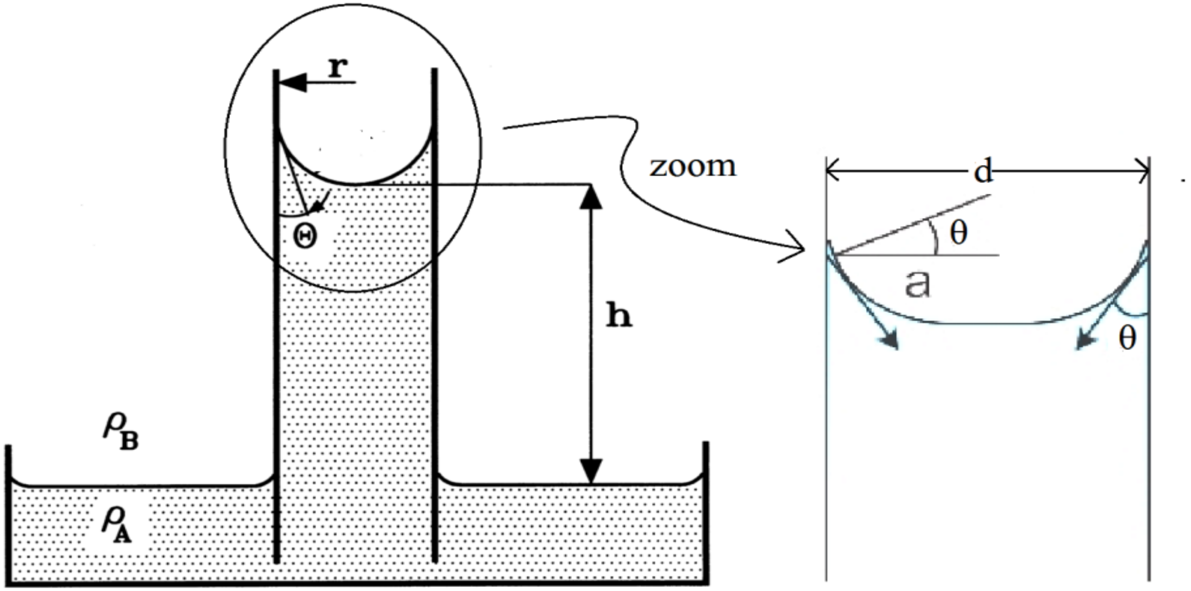
Where,
W is the surface free energy (by definition)
γ is surface tension
ΔA is increase in surface area

METHOD

- There are several methods of surface tension measurements:

  - Capillary rise method
  - Ring detachment method
  - Wilhelmy Plate Method
  - Maximum bubble pressure method
  - Stalagmometric method

Capillary rise method



When capillary is placed in the liquid contained in a beaker, the liquid generally rises up the tube to a certain distance. This is because when the force of adhesion between molecule and capillary wall is greater than the force of cohesion between liquid molecules. This is called as the wetting of the surface of capillary by the liquid, spreading over it and rising in the capillary tube.

- Consider a capillary tube of radius "r" is vertically inserted into a liquid. As the liquid wets the inner surface of capillary and rises to height "h" and forms concave meniscus. The rise in the capillary tube will continue until the upward movement is just balanced by the downward forces.
- If θ is the angle of contact between the liquid surface and capillary surface at any point on the circumference and γ is the surface tension of the liquid then upward component of force which pulls the liquid against force of gravity is $\gamma\cos\theta$ per cm

i.e upward force = $\gamma \cos \theta$ ……. (1)

- As the liquid wets total inner circumference of capillary ($2\pi r$) and spreads over it, then the total upward force becomes

$$\text{upward force} = 2\pi r\ \gamma \cos \theta \quad \ldots\ldots. (2)$$

- Now the downward force counteracting the upward movement is gravitational force

$$\begin{aligned} \therefore \quad \text{Downward force} &= \text{Gravity} \\ &= \text{mass x acceleration} \\ &= \text{(volume x density) x acceleration} \\ &= \text{(area x height) x density x acceleration} \\ &= \pi r^2 \times h \times \rho \times g \end{aligned}$$

$$\therefore \quad \text{Downward force} = \pi r^2 h\rho g \quad \ldots\ldots. (3)$$

- Since at equilibrium,

Upward force = downward force

$$\therefore \quad 2\pi r \gamma \cos\theta = \pi r^2 h \rho g \;\ldots\ldots\; (4)$$

$$\gamma = \frac{\pi r^2 h \rho g}{2\pi r \cos\theta}$$

- The angle θ is insignificant for water and some of the commonly used chemical, thus cosθ is taken as unity

$$\therefore \quad 2\pi r \gamma = \pi r^2 h \rho g \;\ldots\ldots\; (5)$$

$$\gamma = \frac{1}{2} r h \rho g \quad \ldots\ldots\; (6)$$

- Equation (6) gives surface tension of liquid by capillary rise method

Where,

γ is surface tension

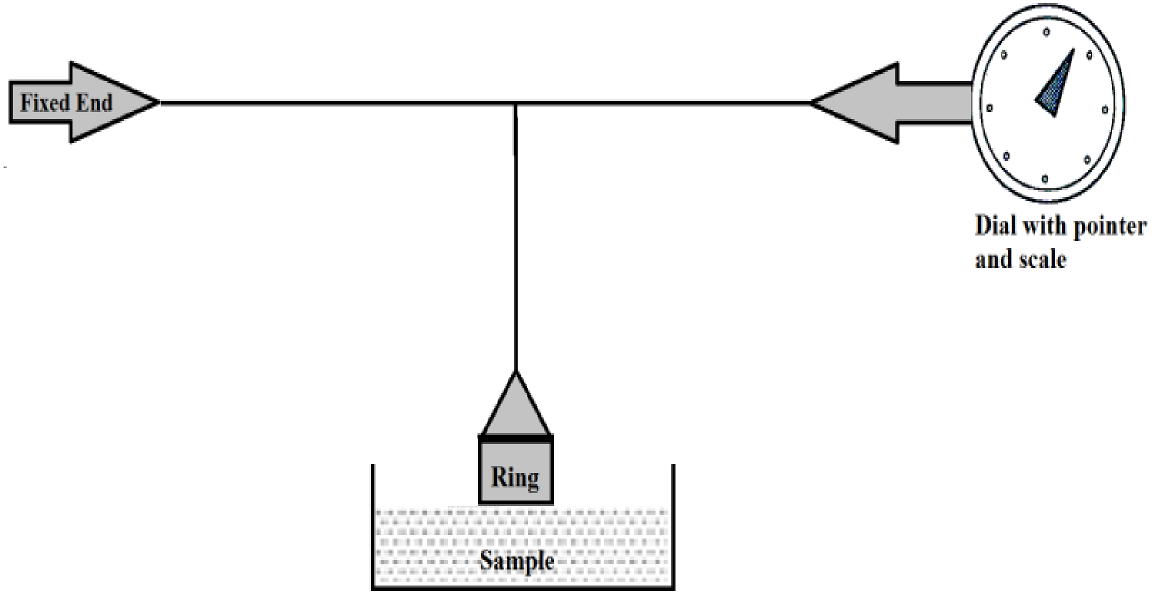
r is radius of capillary

h is height of liquid column upto the meniscus

ρ is the density of liquid

g is acceleration of gravity

Ring Detachment method



- The DuNouy method is based on pulling an object with a well-defined geometry of the surface of liquids and measuring the pull force. These techniques are also known as pull-force methods.

- The method is based on the principle that the force required to detach a ring immersed at the surface or interface is proportional to the surface or interfacial tension acting along the circumference of the ring.

- As shown in the figure the ring is attached to torsion wire whose one end is fixed while second end is attached with dial carrying a pointer. The pointer moves on fixed scale. The ring touches to sample surface kept in sample vessel. The reading displayed on the dial is the measure of the force provided to torsion wire. The force at which ring is just detached from the surface is the basis of surface tension provided by the sample.
- The surface tension is given by

$$\gamma = \frac{\text{dial reading F (dyne)}}{2 \times \text{Ring Circumference}} \times \text{correction factor} \qquad \ldots\ldots.\ (1)$$

- A meniscus correction factor is required in this method because the size and shape of the surface inside and outside the ring are not the same. Surface tension must, therefore, be corrected for the shape of the ring by a factor
- In equation (1), twice the length of the circumference is taken since the liquid is in contact with both inside and outside of the ring.

∴ Equation (1) becomes

- $$\gamma = \frac{\text{F (dyne)}}{2 \text{ x } 2\pi r} \times \text{ correction factor} \qquad \ldots\ldots.\ (2)$$

∴ Equation (2) gives surface tension by Ring detachment method

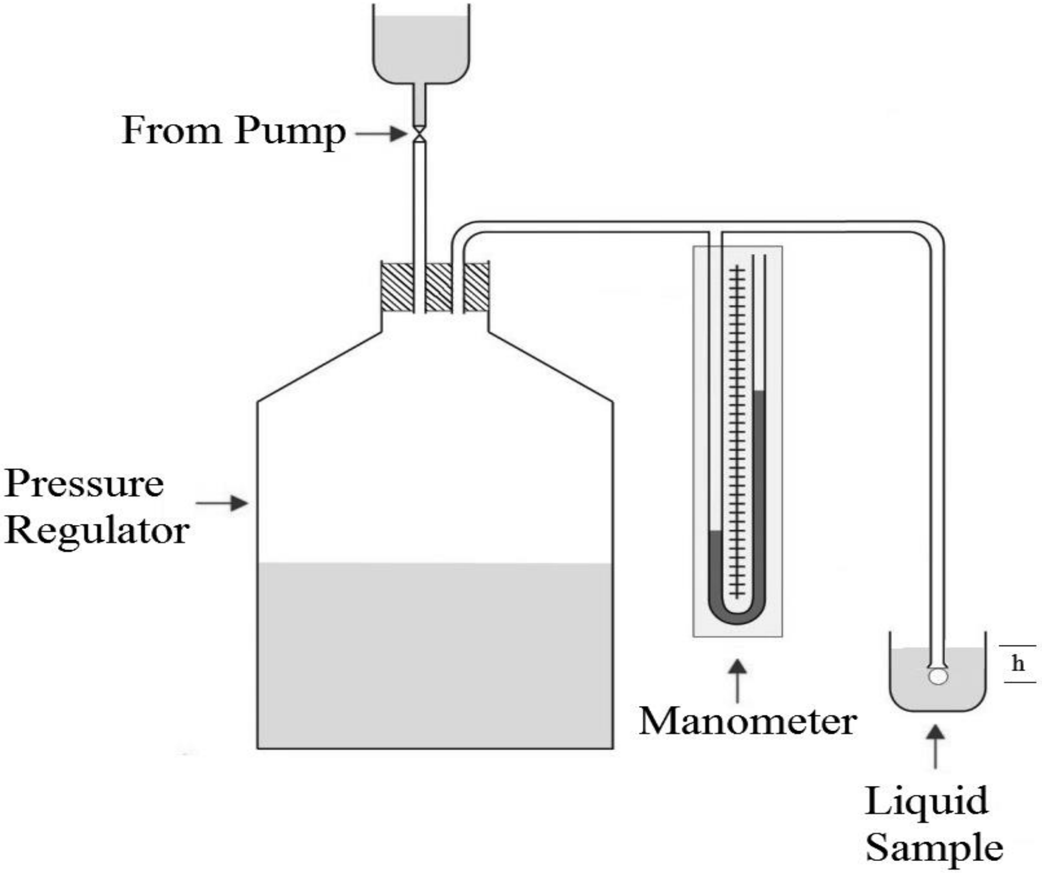
Where,

γ is the surface or interfacial tension

r is the radius of ring

F is the force required to detach the ring

Maximum Bubble Pressure method



The maximum bubble pressure method is often used to measure the dynamic surface tension, as it allows measuring the development of the surface tension at a newly created interface.

- In this method a capillary is immersed into the liquid to be measured, and a gas bubble is created inside the liquid using gas with controllable pressure. As the pressure increases, the size of the bubble increases until its diameter is identical to the diameter of the capillary (hemispherical bubble) and breaks in the end. In this case the Young-Laplace equation allows determining the surface tension using pressure at which bubble breaks (Laplace pressure).

$$P = h\rho g + \frac{2\gamma}{r} \qquad \ldots\ldots\ (1)$$

∴Equation (16) gives surface tension by maximum bubble pressure method

Where,

γ is the surface tension of liquid

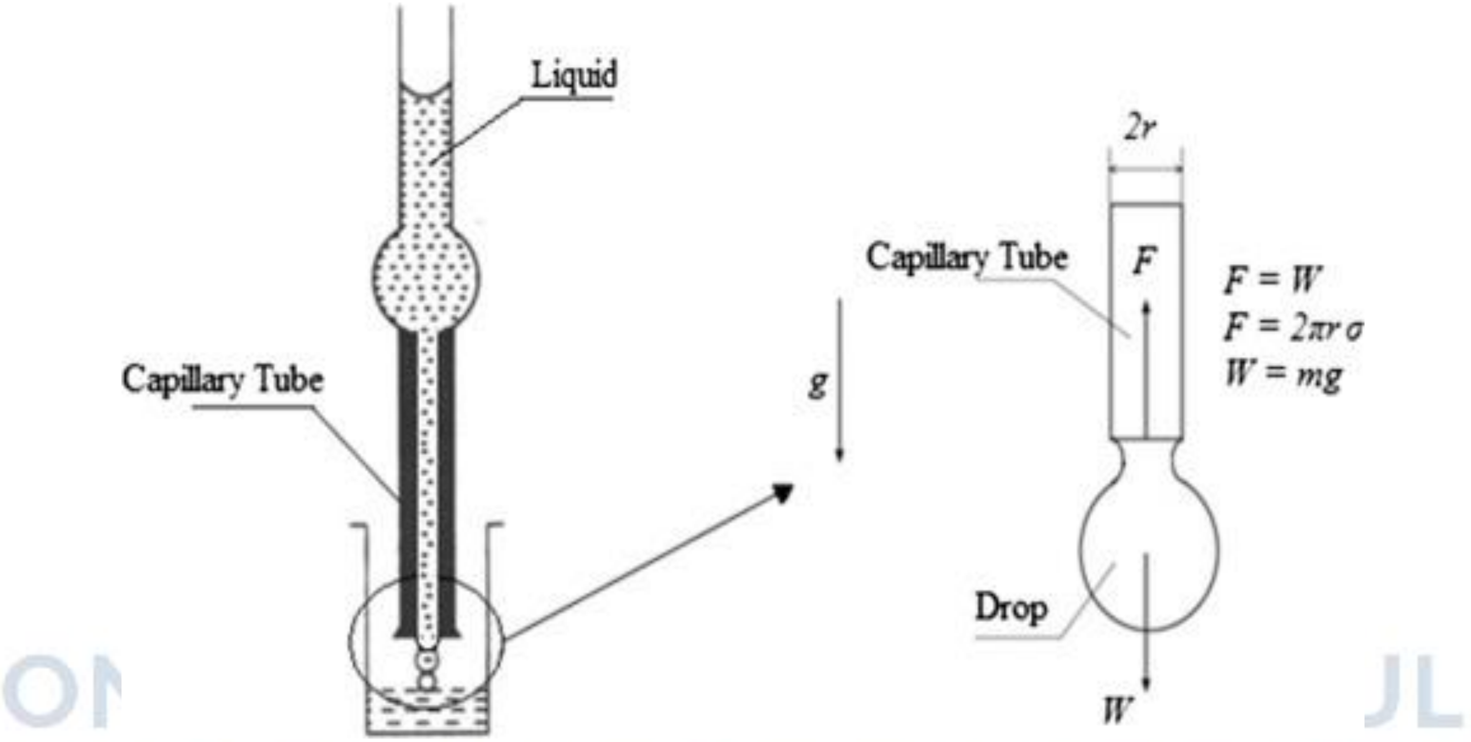
P is the maximum pressure

h is the depth of liquid

ρ is the density of liquid

r is the radius of capillary

Drop Formation method



- The weight of drop or the number of drops falling out of the tube is the determining factor for surface tension by drop formation method.
- The lower the surface tension of the liquid, the smaller the size of drop formed. Then more number of drops are formed for the given volume of liquid.

DROP COUNT METHOD:

- In this method, the clean and dry stalagmometer is filled up to the mark A (located above the bulb) with the experimental liquid. As the liquid is allowed to fall down, it will travel from mark A to mark B (located below the bulb on equal distance as of mark A) and the number of drops falling from the edge of stalagmometer is used in calculation.

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2 \rho_1}{n_1 \rho_2} \qquad \ldots\ldots\ldots (1)$$

∴ Equation (1) gives surface tension by drop count method

Where,

γ_1 and γ_2 are surface tension of two liquids

n_1 and n_2 are number of drops of two liquids

ρ_1 and ρ_2 are densities of two liquids

DROP WEIGHT METHOD:

- About 20 drops of the two liquids are received separately from the stalagmometer and weighed. The average weight is found for one drop for both the liquids.

$$M_1 g = 2\pi r \gamma_1 \qquad \ldots\ldots\ (1)$$

$$M_2 g = 2\pi r \gamma_2 \qquad \ldots\ldots\ (2)$$

Dividing equation (1) by (2)

$$\frac{\gamma_1}{\gamma_2} = \frac{M_1}{M_2} \qquad \ldots\ldots\ (3)$$

$\therefore$ Equation (3) gives surface tension by drop weight method

Where,

γ_1 and γ_1 is surface tension of two liquid

M_1 and M_2 is weight of two liquid

SPREADING COEFFICEINT

- The spreading coefficient or parameter is a measure of the tendency of a liquid phase to spread (complete wetting) on a second, liquid or solid phase.
- When two immiscible liquids with differences in their densities are bought together, spreading occurs in some cases and in some cases globule may form.
- When two liquids are analyzed, the cohesive forces and adhesive forces operating between them are considered.

SPREADING COEFFICEINT

- The work of adhesion is the energy required to bring out adhesion between two unlike molecule and same amount if energy is required to break the adhesive forces between unlike molecule.

$$\text{Work of adhesion (Wa)} = \gamma_{L1} + \gamma_{L2} - \gamma_{L1L2}$$

- The work of cohesion is the energy required to separate the molecules of spreading liquid so that it can flow over another layer.

$$\text{Work of Cohesion (Wc)} = 2\gamma_{L}$$

- Spreading of liquid occurs when work of adhesion is greater than work of cohesion i.e. Wa > Wc

ADSORPTION

- Adsorption refers to the collecting of molecules by the external surface or internal surface of solids or by the surface of liquids.
- Accumulation of species on higher concentration on the surface of a substance due to intermolecular force is known as adsorption.
- Solids that are used to adsorb gases or dissolved substances are called adsorbents; the adsorbed molecules are usually referred to collectively as the adsorbate.
- Adsorption can be either physical or chemical in nature. Both chemical and physical adsorption is a surface phenomenon and increase with increase in surface area.

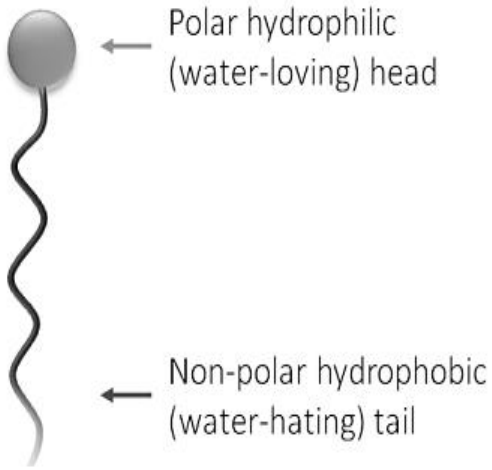
ADSORPTION

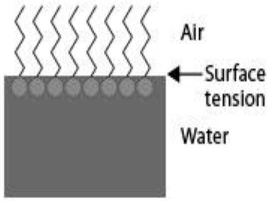
Physical Adsorption	Chemical Adsorption
Physical adsorption is reversible in nature and dependent on pressure and temperature.	The process is irreversible in nature.
There is no specificity as any gas can be adsorbed onto the surface.	The process is specific in nature; it occurs only if there is a chemical bond formation between the adsorbent and adsorbate.
Physical adsorption involves the use of weak van der waal forces	Chemical adsorption involves chemical bonds between adsorbent and adsorbate.
Increase in temperature increases physical adsorption and in the same regard, a decrease in temperature will decrease the rate of physical adsorption.	Chemical adsorption is slow at low temperature and it occurs at a higher rate with increase in pressure.
It has Low enthalpy of adsorption (20 to 40 kJ/mol).	It has high enthalpy of adsorption (40 to 200 kJ/mol)
Physical adsorption does not require energy for activation.	Chemical adsorption requires a certain level of energy for activation.
Forms multimolecular layers on adsorbent surface.	Forms unimolecular layer.

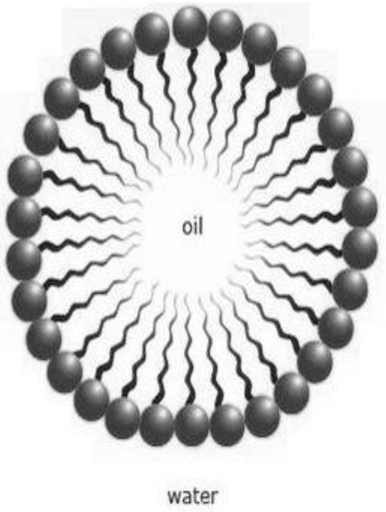
SURFACE ACTIVE AGENTS

- Surfactants are materials that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid
- In physical sense, surfactants are defines as the substances which preferentially get adsorbed at the interface and exhibit self-association in bulk of solution at specific concentration.
- In chemical sense, surfactants are defined as polymer like substances which have both polar and non-polar groups so they remain at interface.
- In the general sense, any material that affects the interfacial tension or surface tension can be considered a surfactant.

Structure







- Surfactants are amphiphilic molecules and contain a hydrophobic tail (nonpolar) that points toward the oil phase or gas phase and a hydrophilic head that point towards the aqueous (polar) phase.
- The polar head is in general unique while the nonpolar tail is made up of long hydrocarbon chain which contains ten or more carbon atoms. The reason is that the polar interaction (Debye or Keesom) are typically ten times stronger than the nonpolar ones (London).

Types

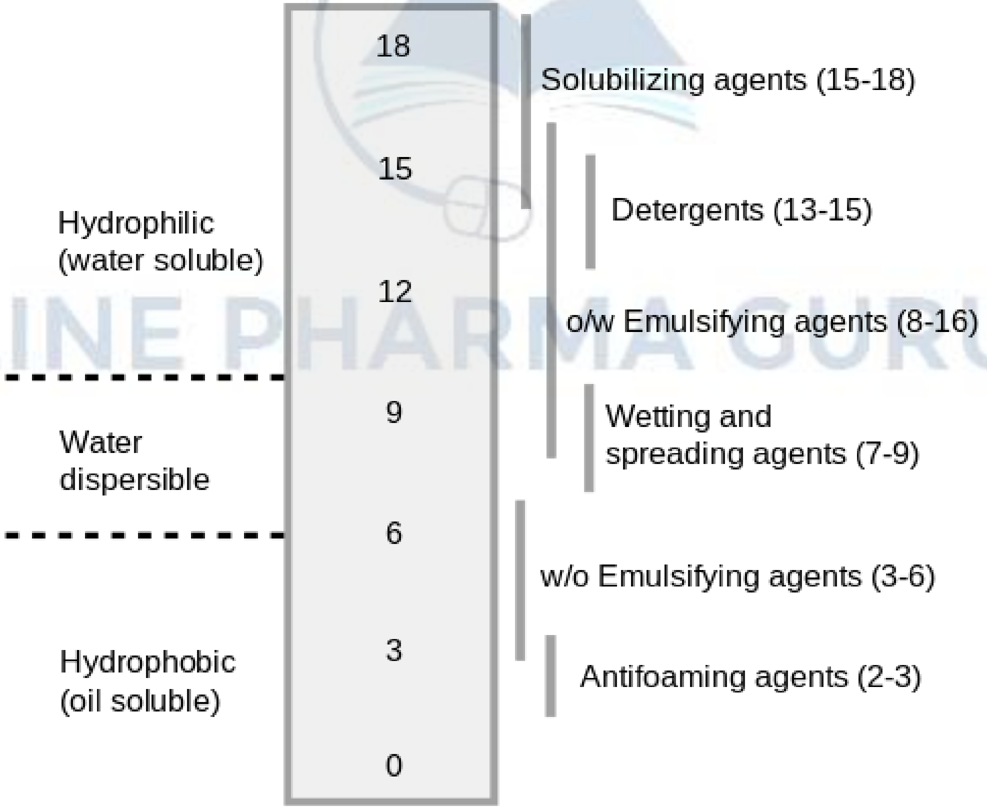
- **NON IONIC SURFACTANT:** These are surfactants that have no ions.
- **ANIONIC SURFACTANT:** These have a negatively charged end of the molecule that gives it the hydrophilic part of the molecule.
- **CATIONIC SURFACTANT:** These are positively charged molecules usually derived from nitrogen compounds.
- **AMPHOTERIC (ZWITTERIONIC):** Those surfactants that change their charge with pH. They can be anionic, nonionic, or cationic depending on pH.

Working

- When used in low concentrations, surfactants adsorb onto the surface or at interfaces between phases, and the adsorption of surfactant lowers the interfacial tension between the phases.
- When used in high concentration, some of the concentration gets adsorbed at the surface and remainder of them goes into the bulk of solution. In the bulk aqueous phase, surfactants form masses, such as micelles, where the hydrophobic tails form the core and the hydrophilic heads are immersed in the surrounding liquid. Other types of structures can also be formed, such as spherical micelles or lipid bilayers. The shape of the molecules depends on the balance in size between hydrophilic head and hydrophobic tail.
- Three parameters, i.e., hydrophilic-lipophilic balance (HLB), critical micelle concentration (CMC) and surfactant packing parameter influence the type of surfactant aggregates that are formed.

HYDROPHILIC LIPOPHILIC BALANCE

- The HLB concept, proposed by Griffin in 1949, is the best-known method to select a surfactant suitable for an application. This semi-empirical method assigns the surfactant a HLB number according to its chemical structure.



Hydrophilic
(water soluble)

Water
dispersible

Hydrophobic
(oil soluble)

Solubilizing agents (15-18)

Detergents (13-15)

o/w Emulsifying agents (8-16)

Wetting and
spreading agents (7-9)

w/o Emulsifying agents (3-6)

Antifoaming agents (2-3)

Determination of HLB

a) GRIFFIN METHOD:

- In 1949, Griffin derives equation for the HLB value of non-ionic surfactant containing polyoxyethylene chain

$$\therefore \qquad HLB = \left(\frac{E + P}{5}\right) \qquad \ldots\ldots\ldots (1)$$

Where,

E is the percent by weight of polyoxyethylene chain

P is the percent by weight of polyhydric alcohol group

- The limitation of equation (1) was polyoxyethylene chain and thus not applicable for other type of emulsifier. Therefore for most polyhydric alcohol fatty acid esters approximate values may be calculated with the formula

$$\therefore \qquad HLB = 20\left(\frac{1 - S}{A}\right) \qquad \ldots\ldots\ldots (2)$$

Where,

S is the Saponification number of the ester

A is the Acid number of the acid

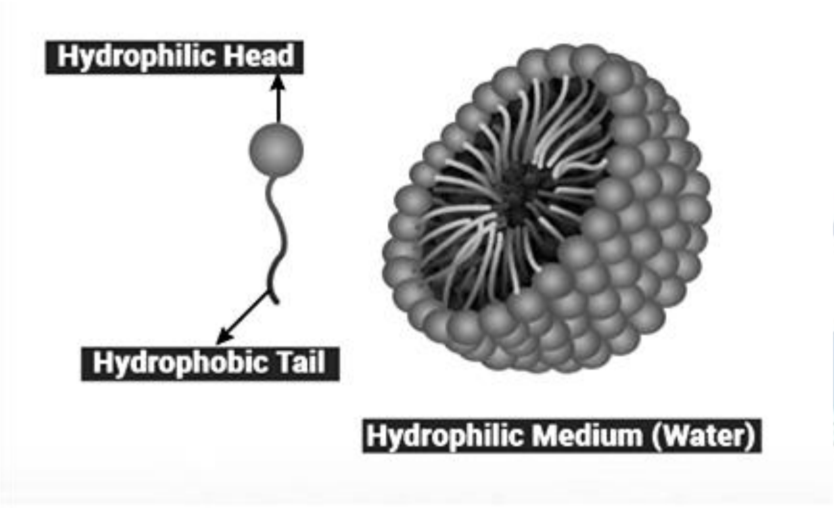
Determination of HLB

b) DAVIES METHOD:

- In 1957, Davies suggested a method based on calculating a value based on the chemical groups of the molecule i.e. splitting the group into hydrophilic and lipophilic groups.

$$\therefore \text{HLB} = \sum (\text{Number of hydrophilic group}) - \sum (\text{number of lipophilic group}) + 7 \qquad \ldots\ldots\ (3)$$

CRITICAL MICELLE CONCENTRATION



- Critical micelle concentration (CMC) can be defined as the minimum concentration of the surfactant at which micelle formation takes place.

- Micelles are formed by a cumulative formation of amphiphilic molecules in an aqueous solution.
- In a micelle, ionic heads form an outer shell in contact with water, while nonpolar tails are sequestered in within.
- Critical micelle concentration (CMC) is a measure of surfactant efficiency. A lower CMC indicates less surfactant is needed to saturate interfaces and form micelles.

ADSORPTION AT SOLID INTERFACE

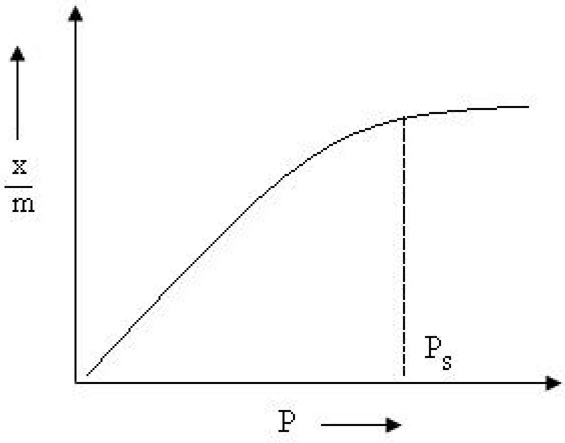
- Solid interfaces are immobile as compared to liquid interface. The average lifetime of a molecule at water/gas interface is about 01 microsecond whereas at non-volatile metallic solid it may have 10^{37} seconds.

- Though the particles in solid are held with certain forces and each particle is attached with one another, the forces are not balanced at the surface because the surface particles are not surrounded by neighbouring particle. The perpendicular attraction to the surface tend to draw this particles inwards. The surface particle tries to overcome the imbalance of forces giving rise to adsorption.

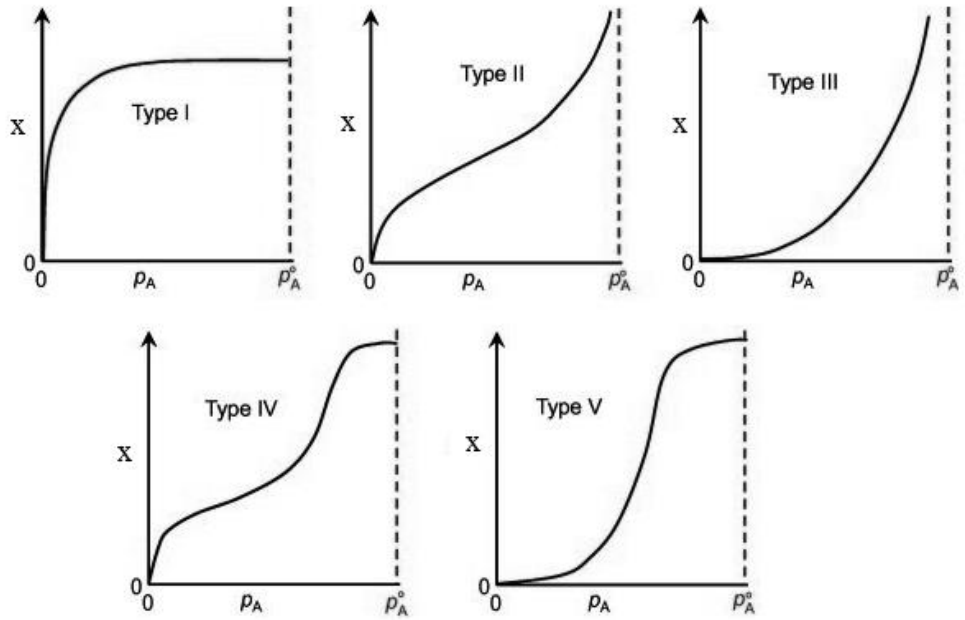
- The adsorption of material at solid interface may take place from either an adjacent liquid or gas phase.

ADSORPTION AT SOLID INTERFACE

- The relationship between the amount of gas physically adsorbed on a solid and the equilibrium pressure or concentration at constant temperature yields an adsorption isotherm.
- An adsorption isotherm is a graph that represents the variation in the amount of adsorbate(x) adsorbed on the surface of the adsorbent (m) with the change in pressure at a constant temperature.



ADSORPTION AT SOLID INTERFACE



- **Type I**: This graph represents increase in adsorption with increasing pressure following by levelling off.
- **Type II** :This is the sigmoidal in shape and occurs when gas undergoes physical adsorption onto nonporous solid to form monolayer and when pressure is increased further multilayer is formed.

- **Type III** : refers to multilayer adsorption by weak interactions with low energy between adsorbed molecules and the adsorbent having macropores.
- **Type IV adsorption isotherm** represent the multilayer adsorption together with capillary condensation to the mesoporous adsorbents. This represents the adsorption of gas on porous solids.
- **Type V adsorption isotherm** describes the stepwise formation of a multilayer on the surface of nonporous adsorbent.

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