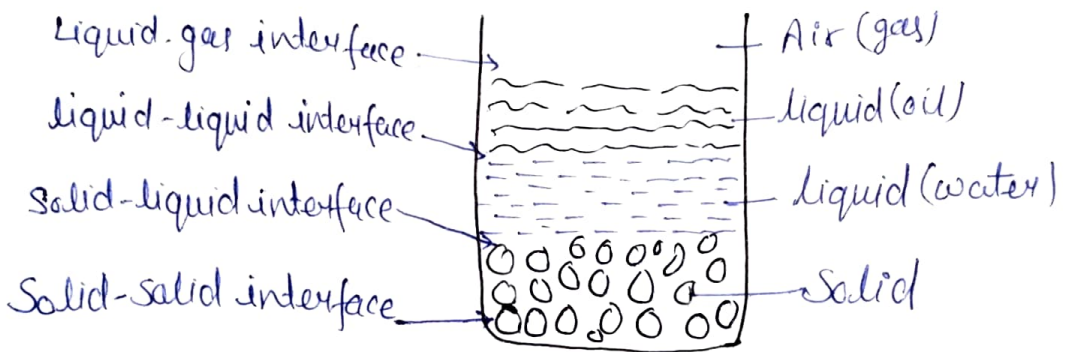


Surface and Interfacial Phenomenon

Interface :- When two phases are contact
 ↓
 the boundary b/w them is called
 ↓
 Interface.

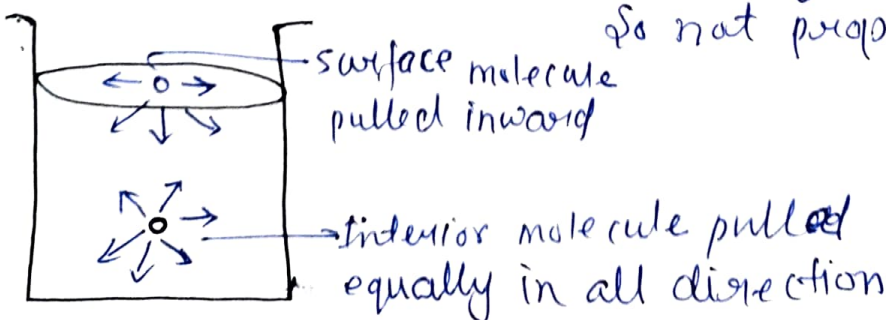
Surface :- Surface is the interface b/w two phases, one of which is gas or the vacuum.



Liquid Interfaces

- ⇒ Forces of attraction exist b/w molecules in liquid.
- ⇒ molecules in the bulk of the liquid are surrounded by other molecules have equal attraction.
- ⇒ molecules at surface → experience an inward force of attraction

↓
 So not properly balanced



⇒ Interfacial tension is force acting b/w two immiscible liquids.

Surface Tension

⇒ This property of liquid arises from → intermolecular force of attraction.

⇒ The tension of the surface film caused by the attraction of the particles in the surface layer by the bulk of liquid, which tends to minimize surface area.

"or"

⇒ Surface tension is defined as, "the force in dynes acting along the surface of a liquid at right angle to one cm in length."

$$\gamma = \frac{F}{l}$$

Unit:

In CGS system - dynes per centimeter ($\text{dyne} \cdot \text{cm}^{-1}$)

In SI system - newton/meter (Nm^{-1})

Interfacial Tension

⇒ Interfacial tension of both immiscible liquids

⇒ Interfacial tension is the force that holds the surface of particular phase together.

⇒ Interfacial tension is the force per unit length existing at interface between two immiscible liquid phases.

Units -

dynes/cm (CGS)

Newton/meter ($\text{N} \cdot \text{m}^{-1}$) (SI)

⇒ In general all tensions may be referred as interfacial tension -

- So, γ_{LL} → b/w two liquids
- γ_{SS} → b/w two solids
- γ_{LS} → b/w Liquid and solid
- γ_{LG} → b/w Liquid and gas
- γ_{SG} → b/w solid and gas.

⇒ Natural process due to surface tension:

The phenomenon of surface tension is responsible for the following process -

- ⇒ Formation of sphericle globules in emulsion.
- ⇒ Rising of water capillary.
- ⇒ Formation of hemi-spherical surface.

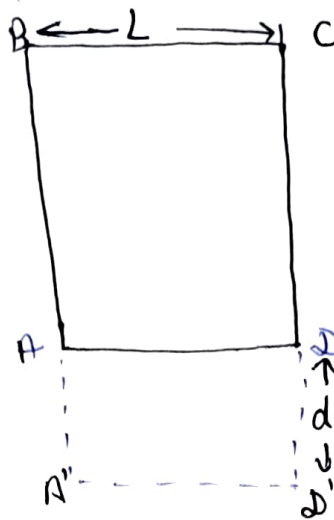
Surface Free Energy

- Surface tension maintain the minimum volume of liquid.
- Surface free energy → surface area can be increased - by the work done against the surface tension.
- The work that could be necessary to increase the surface area of phase.
- The work per unit area done by the force that create the new surface.
- "Surface free energy is defined as the work required to increase the area of a liquid by 1 square metre."

upward component
due to γ \uparrow



Downward Component due
to external force



\Rightarrow ABCD is a rectangular wire.

\Rightarrow $AD = BC = L$ and AD is movable.

\rightarrow A drop of soap solution is placed on the frame, so that it forms a film within the frame.

The side AD remains stable due to surface tension.

\Rightarrow When force is applied downward, the film gets stretched as the movable bar AD goes down until the film breaks.

If force is applied on AD (downward component), it shifts the movable wire to a distance d' to $A'D'$.

The work done W is given by:

$$W = f \times d \quad \text{--- (i)}$$

$$f = \frac{W}{d} \quad \text{--- (ii)}$$

The above force acts against the surface tension (γ) of liquid, since the surface tension tries to contract the liquid. There are two surface of each length " L " on either side of wire.

The force acting on wire is

$$F = \gamma \cdot 2L \quad \text{--- (iii)}$$

We can substitute this equation into equation (ii)

$$\frac{W}{d} = \gamma \cdot 2L$$

$$W = \gamma \cdot 2Ld$$

$$W = \gamma \cdot \Delta A$$

$\Delta A = \text{increase in surface Area}$

where, $\Delta G = \gamma \Delta A$

$\Delta G = \text{increase surface free energy}$

$W = \text{work done}$

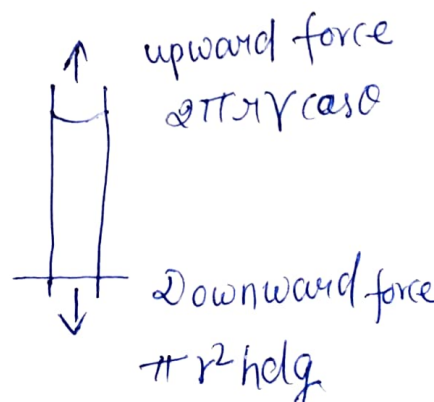
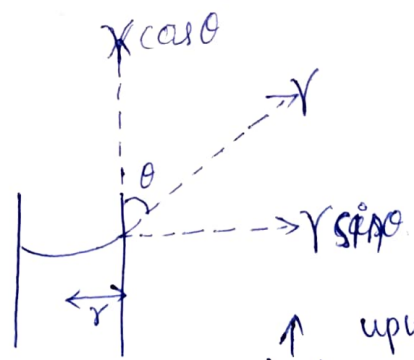
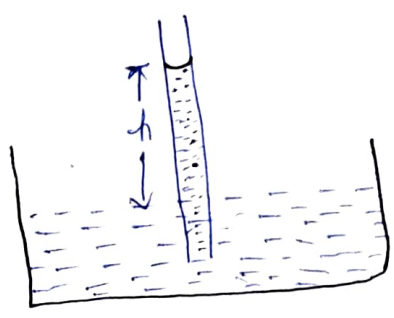
Unit - Joule or N-m

Measurement of Surface and Interfacial Tension

There are several method for S.T./I.T. Measurement.

- ① Capillary Method
- ② Drop count method by using stalagmometer.
- ③ Drop weight method by using stalagmometer.
- ④ Wilhelmy plate Method
- ⑤ Ring detachment Method or Du-Nuoy tensiometer.

① Capillary Method :-



→ Total surface tension along circular contact is $2\pi r$ times.

So, upward force = $2\pi r \gamma \cos \theta$

• The downward force on liquid^{is} due to its weight

So, Downward force = $\pi r^2 h d g$

↓
mass × gravity

But,

Upward force = Downward force

$$2\pi r \gamma \cos \theta = \pi r^2 h d g \quad \left\{ \begin{array}{l} \text{for most liquids} \\ \theta = 0^\circ \text{ and} \\ \cos \theta = 1 \end{array} \right.$$

$$2\pi r \gamma = \pi r^2 h d g$$

$$\gamma = \frac{\pi r^2 h d g}{2\pi r}$$

$$W = 2\pi r \gamma$$

$$\boxed{\gamma = \frac{r h d g}{2}} \text{ dynes/cm.}$$

Where,

r = Radius of capillary

h = Height of rise in level of liquid in capillary

d = Density of liquid

g = Acceleration due to gravity.

2) Drop Count Method :-

It is used to measure the surface tension of liquid.

In this method, we find out surface tension through comparing.

i) firstly take known liquid, which we know the surface tension.

ii) then fill stalagmometer with that liquid at point A, then stalagmometer closed from bottom from or with the help of finger.

iii) Now, Release liquid slowly - slowly dropwise from capillary untill liquid reached at point B - and continuously count no. of drop, then note it.

iv) Now, Do same with other liquid, which we have to find its surface tension.

v) So, on comparing both, by using formula we find out surface tension (γ).

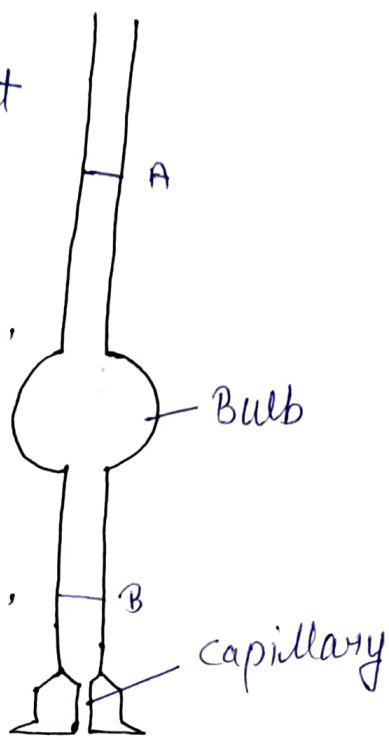


Fig. Stalagmometer

⇒ Derivation :-

We know that

$$w = 2\pi r \gamma$$

Where, $2\pi r$ = circumference of capillary.

1st case → when we take water (known surface tension)

$$w_1 = 2\pi r \gamma_1 \Rightarrow \gamma_1 = \frac{w_1}{2\pi r \cdot n_1} \quad \text{--- (1)}$$

2nd case \rightarrow when we take unknown surface tension .

$$W_2 = 2\pi r \gamma_2$$

$$\gamma_2 = \frac{W_2}{2\pi r \cdot n_2} \text{--- (ii) } \left\{ \text{where } n = \text{no. of drop} \right\}$$

Now,

we know that

$$W = m \cdot g \quad \& \quad \rho = \frac{M}{V} \Rightarrow m = \rho \cdot V$$

$$\Rightarrow W = \rho V g$$

where,

ρ = density of liquid

V = volume of liquid

g = acceleration due to gravity.

Put these value in equation (i) and (ii)

$$\gamma_1 = \frac{\rho_1 V g}{2\pi r n_1}$$

$$\gamma_2 = \frac{\rho_2 V g}{2\pi r n_2}$$

On comparing both-

$$\frac{\gamma_1}{\gamma_2} = \frac{\frac{\rho_1 V g}{2\pi r n_1}}{\frac{\rho_2 V g}{2\pi r n_2}}$$

$$\boxed{\frac{\gamma_1}{\gamma_2} = \frac{\rho_1}{\rho_2} \times \frac{n_2}{n_1}}$$

③ Drop weight Method

It is same as drop count method, in which we use same capillary or stalagmometer. Difference is that,

In which we weight the drop (one drop), firstly that liquid which we know surface tension, then weight the other liquid's drop which we have to find out the surface tension.

1st case →

As we know —

$$W = 2\pi r \gamma$$

1st case → know liquid

$$W_1 = 2\pi r \gamma_1$$

$$\gamma_1 = \frac{W_1}{2\pi r}$$

2nd case → Unknow liquid

$$W_2 = 2\pi r \gamma_2$$

$$\gamma_2 = \frac{W_2}{2\pi r}$$

On comparing both,

$$\frac{\gamma_1}{\gamma_2} = \frac{\frac{W_1}{2\pi r}}{\frac{W_2}{2\pi r}}$$

$$\boxed{\frac{\gamma_1}{\gamma_2} = \frac{W_1}{W_2}}$$

where,

γ = surface tension

W = weight of drop.

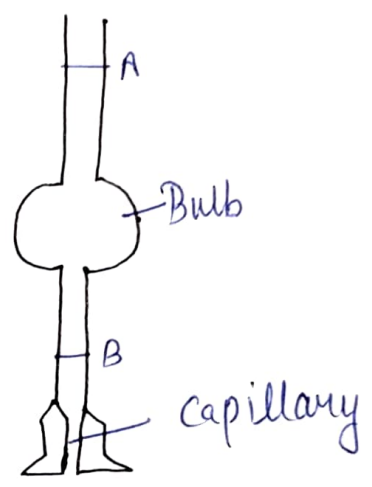
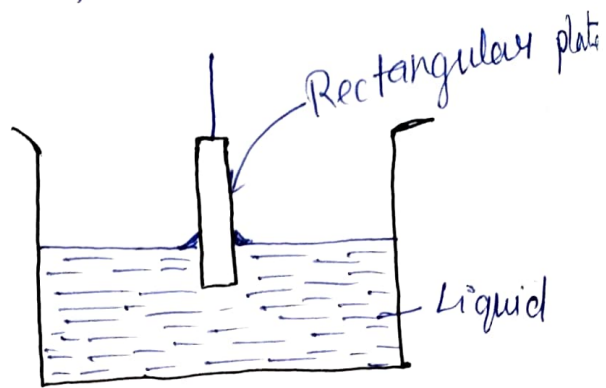


Fig. Stalagmometer

④ Withelmy Plate Method :-

↳ used for measure surface or Interfacial tension.

⇒ Firstly we put the rectangular plate in that liquid, which we have to find out the surface tension.



⇒ test liquid is taken in container

↓
the plate immersed into it

↓
container gradually lowered till plate detached from liquid surface

↓
reading on the balance noted just prior to the detachment.

So,

$$W_L - W = 2(L+T)\gamma$$

OR

$$\gamma = \frac{W_L - W}{2(L+T)}$$

where,

W_L = reading on balance prior to detachment

W = weight of plate in air.

L = Length of plate

T = Thickness of plate

⑤ Ring detachment method or Du-Nuoy tensiometer (51)

It is used for measure both surface and interfacial tensions:

→ In this method, A slowly lifting ring, often made up of platinum it attached from the surface of liquid.

→ The force, required to raise the ring from the liquid's surface is measured and related to the liquid's surface tension

$$\gamma = \frac{f}{2\pi(r_1 + r_2)}$$

Where,

γ = surface tension

f = applied force

r_1 = radius of outer surface

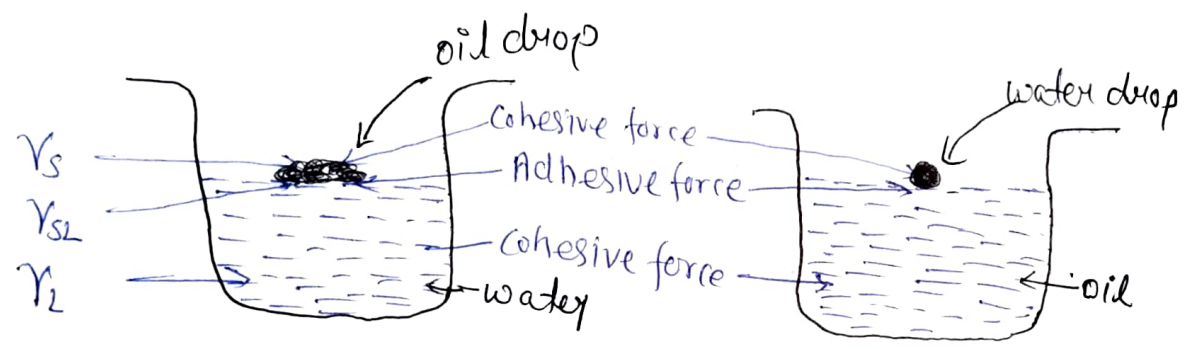
r_2 = radius of inner surface

Spreading Coefficient

In two immiscible liquid, when we placed first's liquid drop on the surface of other, it will spread as a film.

And the ability of one liquid to spread over another liquid is calculated as spreading coefficient.

eg- Emulsion- o/w etc.



if we want spreading then ↑ the adhesive force -

$$W_A > W_C$$

So,

$$S = W_A - W_C \quad \text{--- (1)}$$

where,

S = Spreading Coefficient

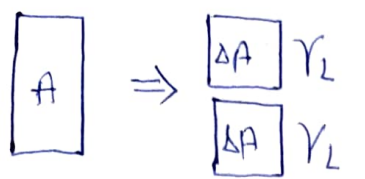
W_A = work done of adhesive force

W_C = work done of cohesive force

- Adhesive force - It applied on two different nature's liquid.
- Cohesive force - It applied on the same nature's liquid.

Derivation:-

1st step - Work done for cohesive force -



Same nature liquid

$$W_c = \gamma_L \Delta A + \gamma_L \Delta A \quad \left\{ \because \gamma_L = \text{surface tension of water} \right.$$

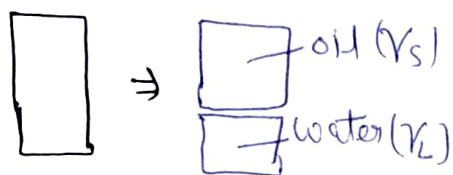
$$W_c = 2\gamma_L \Delta A$$

if $\Delta A = 1 \text{ cm}^2$, then

$$\boxed{W_c = 2\gamma_L} \quad \text{(ii)}$$

$\Delta A = \text{Area of drop}$

2nd step - Work done for Adhesive force -



$$W_A = \gamma_s \Delta A + \gamma_L \Delta A - \gamma_{Ls} \Delta A$$

if $\Delta A = 1 \text{ cm}^2$, then.

$$\boxed{W_A = \gamma_L + \gamma_s - \gamma_{Ls}} \quad \text{(iii)}$$

Now, put the value of eqn (i) and (iii) into (1)

$$S = W_A - W_c$$

$$S = \gamma_L + \gamma_s - \gamma_{Ls} - 2\gamma_L$$

$$S = \gamma_s - \gamma_L - \gamma_{Ls}$$

$$\boxed{S = \gamma_s - (\gamma_L + \gamma_{Ls})}$$

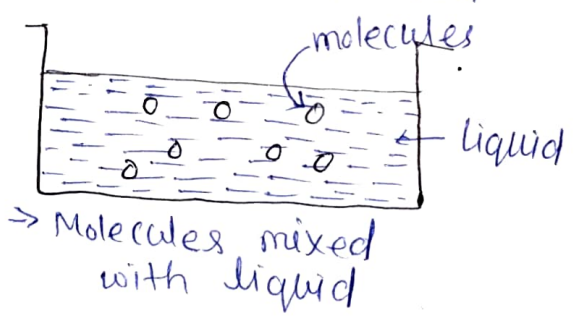
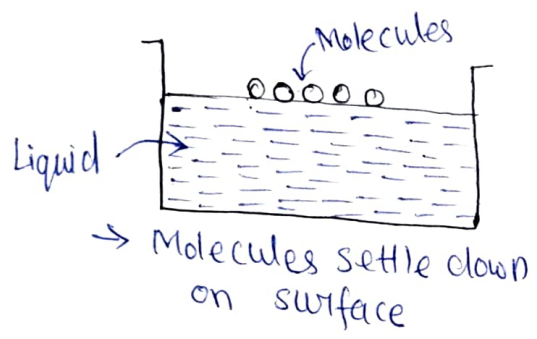
If, $\gamma_s > (\gamma_L + \gamma_{Ls})$, then spreading possible.

and $\gamma_s < (\gamma_L + \gamma_{Ls})$, then spreading not possible.

Adsorption at liquid interfaces

Adsorption is defined as the deposition of some molecules or ions (molecular species) onto the surface of liquid-

- Positive adsorption
 - ⇒ Molecules deposit on the surface of liquid
 - ⇒ surface free energy & surface tension decreased
- Negative Adsorption (Absorption)
 - ⇒ molecules do not deposit on the surface. it mix with the liquid
 - ⇒ surface free energy & surface tension increased.

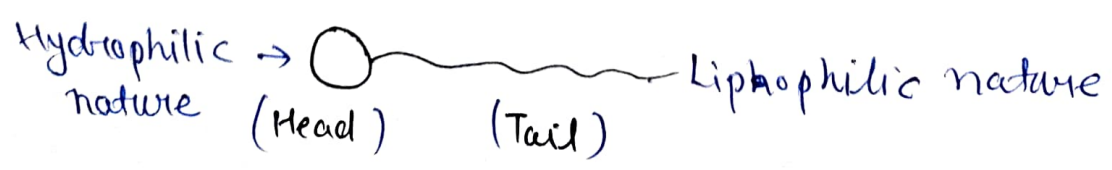


Surface Active Agents (Surfactants) :-

In physical term, surface active agent is defined as substances which get adsorbed at the interface and exhibit self association in the bulk of solution, therefore, these substance reduce the surface tension.

Detergents, soaps, emulsifiers etc.

⇒ It help in mixing of oil into water...

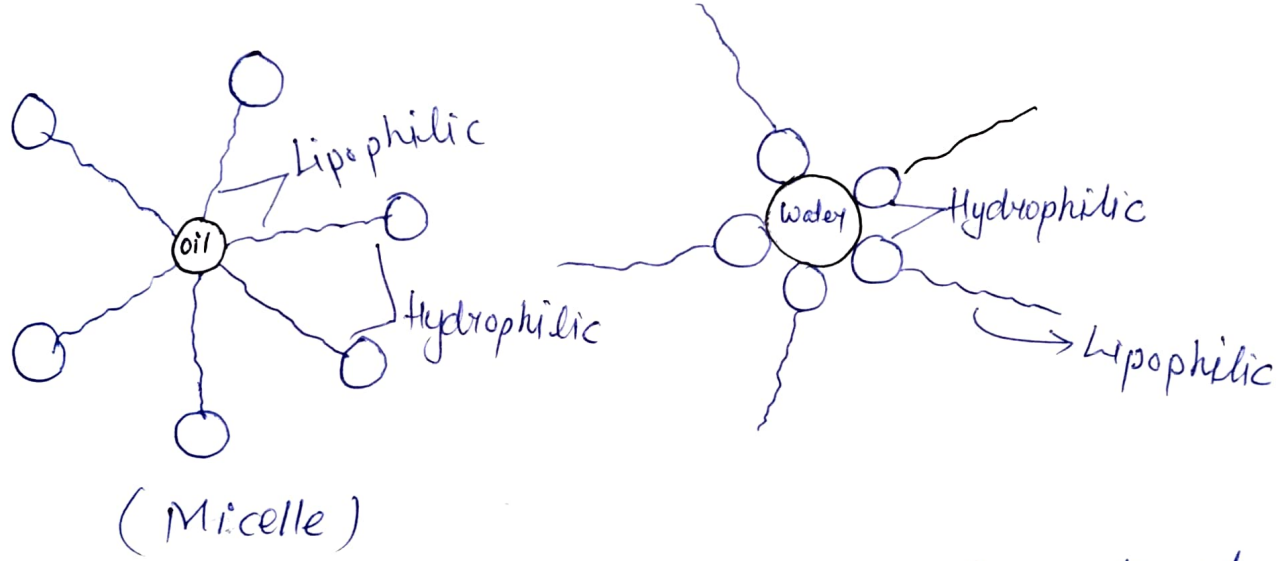


Depending on the number and nature of polar and non-polar groups present

the amphiphile may be predominantly

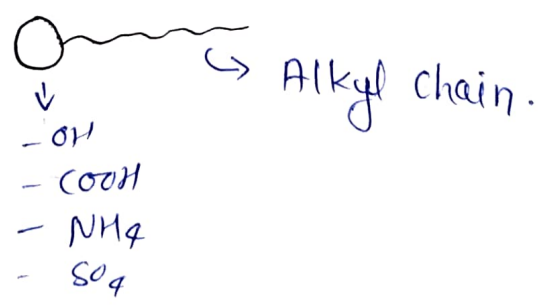
hydrophilic (water loving)
"or"
Lipophilic (Oil loving).

⇒ If we add oil and water in any container, then it is immiscible, so we used surfactants to reduced interfacial tension ~~between~~ and helps to mix them.



⇒ oil (lipophilic), so attached with lipophilic part of surfactants.

⇒ water (hydrophilic), so attached with hydrophilic part of surfactants.



Classification of Surfactants

Depending on functional groups:

- ① Anionic - sulphate, sulpho notes
- ② Cationic - Cetyltrimonium bromide, Benzalkonium chloride.
- ③ Amphoteric (zwitterionic) phosphatidylserine
- ④ Non-ionic - Tween & Co, Tween 80, glycerol

HLB System (Hydrophilic Lipophilic Balance)

Griffin developed an arbitrary scale of values to serve as a measure of the hydrophilic, lipophilic balance of surfactant.

⇒ The high HLB value of surfactant indicates the surfactant is hydrophilic and if surfactant has low HLB value it will be a hydrophobic one.

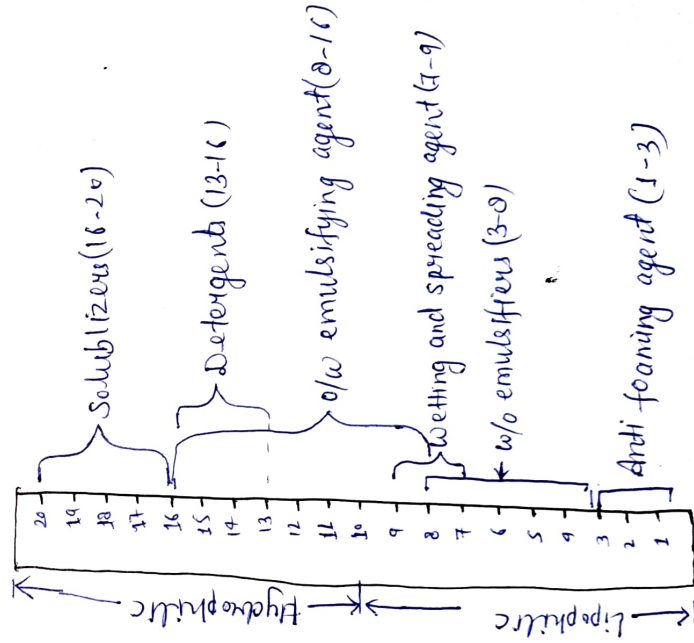


Fig. HLB Scale.

Solubilization → Mc Bain in 1937

The ability of micelles to increase the solubility of materials that are normally insoluble or slightly soluble in dispersion medium is called as solubilization or micellar solubilization.

→ It is used in many industries for the mixing of two immiscible liquid & help in mixing of drugs.

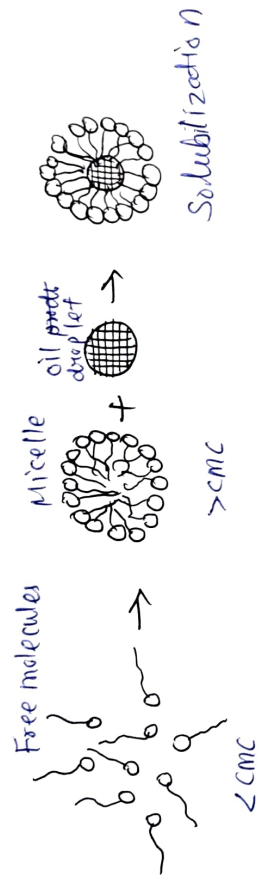


Fig. Micellar solubilization

→ Concentration of surfactant at which micelle form called Critical Micelle Concentration (CMC)

Detergency

Detergency is a complex process involving the removal of foreign matter from surfaces. The surfactant possessing such property is called detergent.

→ The term detergency is mostly used in the cleaning, removing of grease, oil and dirt.

This process needs many actions-

→ The surfactant requires good wetting properties to ensure good contact with the solid surface.

- ⇒ If should also have ability to remove dust into the bulk liquid.
- ⇒ The surfactants having HLB value 13 to 16 are used effectively as detergents.

Adsorption at Solid Interface

- When substance (material) deposits on the surface of solid is called as adsorption at solid interfaces.
- ⇒ The material which deposits on the surface of solid is called adsorbate.
- ⇒ The material on whose surface the process takes place is called adsorbent.



⇒ A number of drugs such as

dyes, alkaloids, fatty acids and organic acid and base

↓
capable of getting adsorbed from solutions onto solids such as alumina or charcoal.

Principles of Adsorption

① Freundlich Isotherm :-

Freundlich established the relationship as,

$$\frac{w}{m} = Kp^{1/n}$$

where, w = mass of gas adsorbed

m = mass of adsorbent

K and n = constant \rightarrow depends on nature of gas and adsorbent and on temperature.

Taking log on both side

$$\log \frac{w}{m} = \log k + \frac{1}{n} \log p.$$

② Langmuir Adsorption Isotherm :-

The theory of Langmuir is based on some assumptions:

- (i) The surface of solid possesses a fixed number of active sites for the adsorption of gases.
- (ii) The thickness of adsorbed gas layer is one molecule.
- (iii) The rate of adsorption is proportional to number of sites unoccupied.
- (iv) The rate of desorption is proportional to the number of occupied sites.

Let, θ ν_1 = rate of adsorption

ν_2 = rate of desorption

θ = occupied site (filled site)

$(1-\theta)$ = unoccupied site (vacant site)

P = pressure

So,

$$r_1 \propto (1-\theta)p$$

$$r_1 = k_1(1-\theta)p$$

{ according to assumption (ii) }

and

$$r_2 \propto \theta$$

$$r_2 = k_2\theta$$

{ according to assumption (iv) }

At equilibrium,

$$r_1 = r_2$$

∴

$$k_1(1-\theta)p = k_2\theta$$

$$\Rightarrow k_1p - k_1\theta p = k_2\theta$$

$$\Rightarrow k_1p = k_2\theta + k_1\theta p$$

$$\Rightarrow \boxed{k_1p = \theta [k_2 + k_1p]}$$

∴ this is Langmuir equation.

$$\theta = \frac{k_1p}{k_2 + k_1p}$$