PHYSICAL PHARMACEUTICS-I

UNIT 3 NOTES

SURFACE AND INTERFACE

- LIQUID INTERFACE
- SURFACE AND INTERFACIAL TENSION
- SURFACE FREE ENERGY
- MEASUREMENT OF SURFACE AND INTERFACIAL TENSION
- SPREADING COEFFICIENT
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- SURFACE ACTIVE AGENTS
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- ADSORPTION AT SOLID INTERFACES

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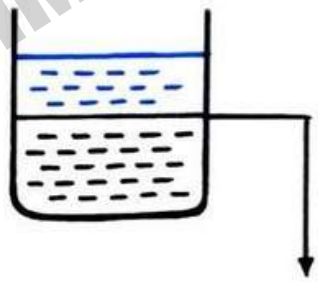
SURFACE & INTERFACE

- The term Interface is defined as the boundary present at the junction of two phases.
- There are different types of interface that can be exist depend upon the nature of phases, (i.e., Solid, Liquid, Gas).
- Different types of interfaces are as follows :-

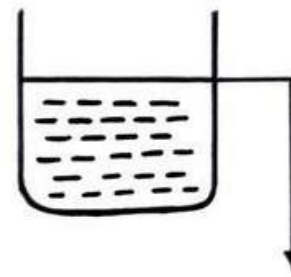
① Solid - Solid Interface
② Solid - Liquid Interface
③ Liquid - Liquid Interface
④ Solid - Gas Interface
⑤ Liquid - Gas Interface

SURFACE

- Surface is the term used to define either a Gas - Solid or Gas - Liquid Interface.
- In other simple words it is defined as outer boundary or topmost layer of a Liquid or a Solid.



LIQUID - LIQUID INTERFACE



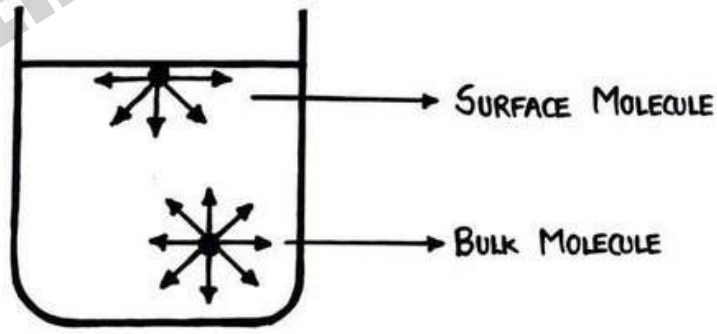
LIQUID SURFACE

Surface Tension

- Surface Tension is defined as tensile force acting at the surface of the liquid.
- The molecules in the bulk of the liquid are surrounded in all directions by other molecules, hence the net force on these molecules is zero.
- While the molecules at the surface of the liquid experiences an inward force towards the bulk.
- Now this inward force is known as Surface Tension.
- Surface Tension is defined as tendency of liquid surface to attain a minimum surface area.
- It is denoted by γ.
- Its unit is N/m.

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

- Here, γ = Surface Tension
  F/L = Cohesive Force per unit length



Interfacial Tension

- Interfacial Tension is defined as force per unit length existing at the interface between two immiscible liquids.
- Its unit is N/m
- Interfacial tension are always less than surface tension due to the presence of force of adhesion
- Greatre the adhesive force lesser will be the interfacial tension.

Types Of Intermolecular Forces

There are mainly two types of intermolecular forces.

① Cohesive Forces
② Adhesive Forces

Cohesive Forces

The intermolecular force of attraction between the similar molecules are known as Cohesive Forces.

Adhesive Forces

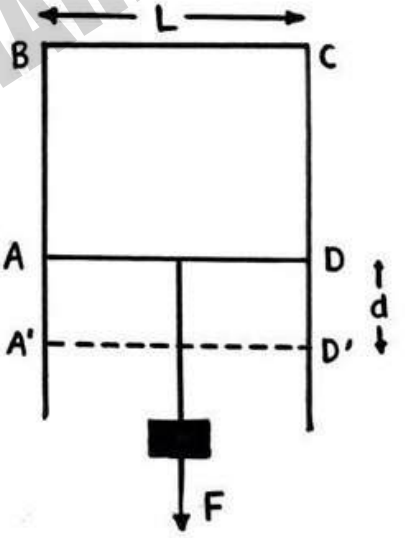
The intermolecular force of attraction between the dissimilar molecules are known as Adhesive Forces.

SURFACE FREE ENERGY

- Surface Tension maintains the surface area of the liquid to a minimum value, But this surface area can be increased if some work is being done against this surface tension.
- Surface Free Energy is defined as work required to increase the area of a liquid by 1 square metre.

Estimation Of Surface Free Energy

- Lets consider a rectangular wire ABCD in which the side AD is movable having length (L).
- Now side AD remains stable due to the surface tension exerted by the soap film.
- When force 'F' is applied on AD the film gets stretched to a distance 'd' at A'D'.
- Now, since the liquid (soap film) has two surfaces (one above & one below)
- Total Length = 2L



Now $\gamma = F/2L$

- or, we can say $F = \gamma \cdot 2L$
- Now Work Done = $F \times d$

$= \gamma \cdot 2L \cdot d$

- Now $2L \times d$ is equal to increase in surface area = ΔA, Hence

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

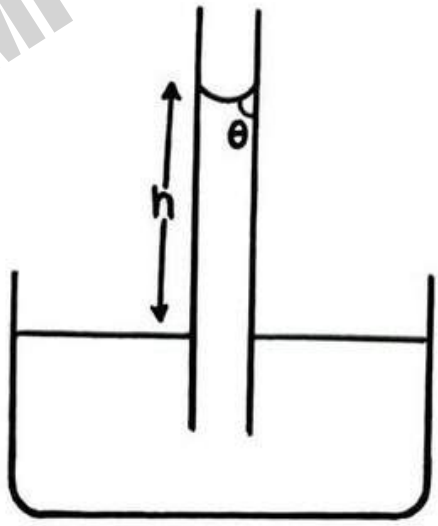
Measurment Of Surface & Interfacial Tension

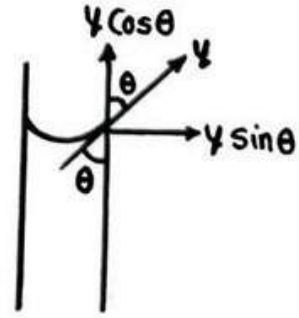
There are various methods that are used to measure the surface and interfacial tensions as follows :

① Capillary Rise Method
② Drop Weight Method
③ Drop Count Method
④ Wilhelmy Plate Method
⑤ Du Nouy Ring Method

① Capillary Rise Method

- When a capillary is placed in a container filled with liquid, the liquid rises up to a certain height in capillary.
- The rise of liquid is occurs due to adhesive force between liquid & capillary wall.
- The rise of liquid continues until the upward movement is balanced by downward force of gravity due to weight of the liquid.





CALCULATIONS

Upward Component : During the upward movement, the surface tension at any point on the circumference of the capillary tube = $\gamma \cos\theta$

- Now the total Force around the inside circumference of the capillary = $2\pi r \gamma \cos\theta$

Downward Component : The downward Force of gravity due to the weight of the liquid is given by = mg

$= \rho \cdot v \cdot g$

$= \rho \cdot A \cdot h \cdot g$

$= \pi r^2 h \rho g$

Now,

UPWARD FORCE = DOWNWARD FORCE

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

- Now, For most of the liquids $\theta = 0$, hence $\cos\theta = 1$ and we get

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

$$\gamma = \frac{1}{2} r h \rho g$$

SURFACE TENSION = $\frac{1}{2} r h \rho g$

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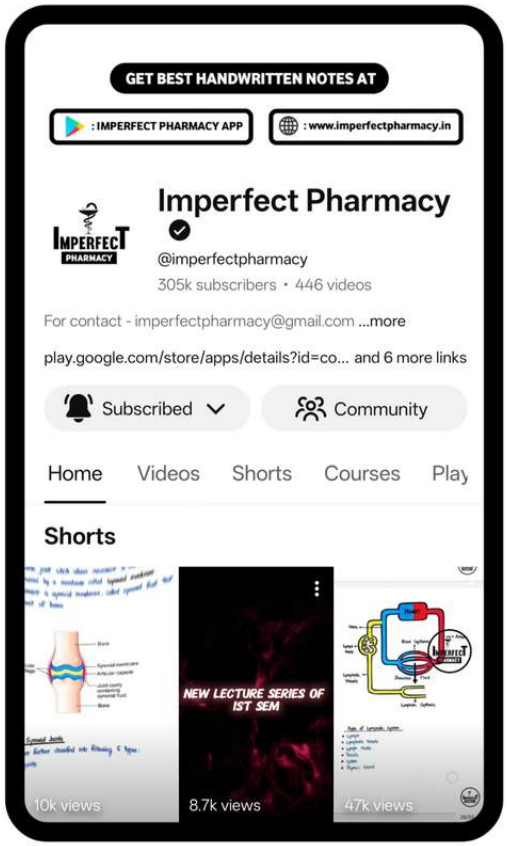

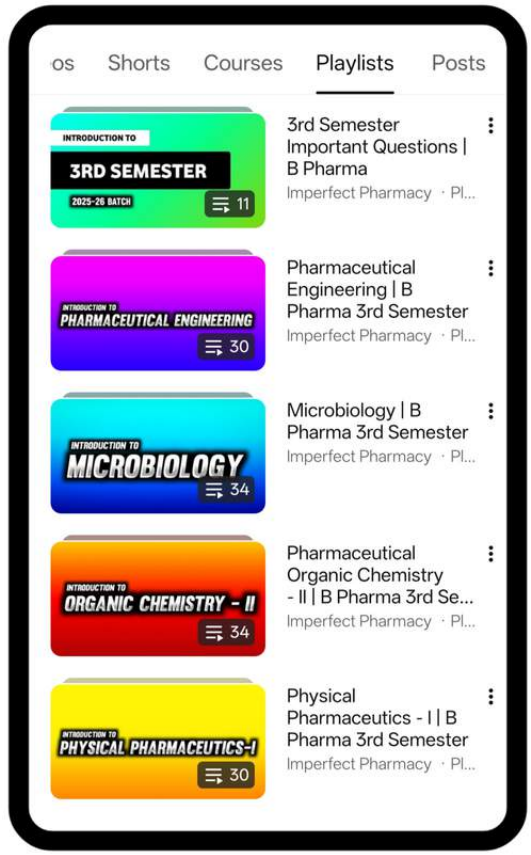

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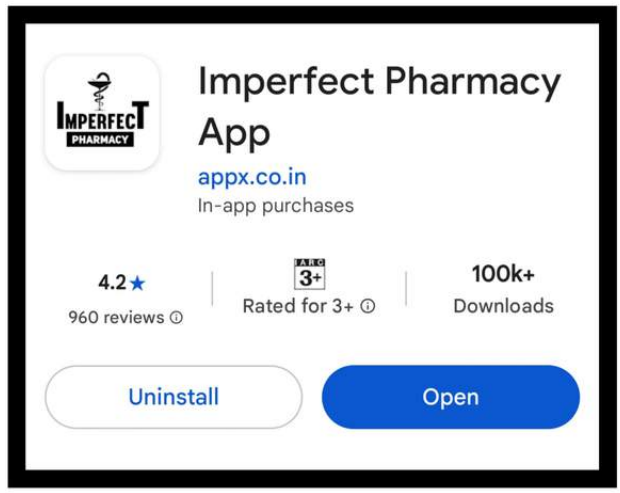
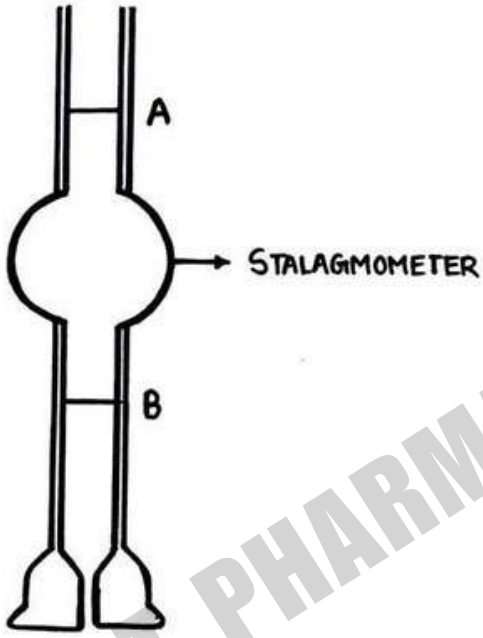


② DROP WEIGHT METHOD

- In this method, Stalagmometer is generally used to measure the surface tension of the liquid.
- Stalagmometer consist of a glass tube with one marking A above the bulb and other marking B below the bulb



- It is a comparative method.
- In this method first we take a standard liquid whose surface tension is known and put into the beaker.
- Now the liquid is sucked into stalagmometer at point A & after that allowed the liquid to fall slowly through capillary & approx 20-30 drop is collected & after calculating its average mean, we get mass of one drop of liquid = m_1
- Now, the same procedure is repeated for test liquid & we get mass of one drop = m_2

CALCULATION

When a drop is formed at tip of stalagmometer, there are two forces acting on drop, 1 is upward & one is downward & when both forces becomes equal, Drop breaks & falls down.

- For Standard liquid : $m_1 g = 2\pi r \gamma_1$ ---- ①
- For Test liquid : $m_2 g = 2\pi r \gamma_2$ ---- ②

- Dividing equation ① by ②, we get

$$\frac{m_1 g}{m_2 g} = \frac{2\pi r \gamma_1}{2\pi r \gamma_2}$$

$$\gamma_2 = \frac{m_2}{m_1} \cdot \gamma_1$$

SURFACE TENSION OF TEST LIQUID = $m_2/m_1 \cdot \gamma_1$

Here in the above equation :

- m_2 = weight of 1 drop of test liquid
- m_1 = weight of 1 drop of standard liquid
- γ_1 = surface tension of standard liquid

③ DROP COUNT METHOD

Drop count method is same as Drop weight method, the only difference is in this method instead of weight, we count the number of drops of test and standard liquid using stalagmometer.

CALCULATION

- For Reference Liquid : $2\pi r\gamma_1 = m_1 g$

  $2\pi r\gamma_1 = V_1 \rho_1 g$

- Now here in the above equation V_1 is Volume of one drop of standard liquid $= \frac{V}{n_1}$
- Where, V = Total volume

  n_1 = Total number of drops
- So, We can say For Reference Liquid : $2\pi r\gamma_1 = \frac{V}{n_1}\rho_1 g$ ---- ①

- And similarly For test liquid : $2\pi r\gamma_2 = m_2 g$

  $= V_2 \rho_2 g$

  $= \frac{V}{n_2}\rho_2 g$ ----- ②

Dividing equation ① by ②, we get

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

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

$$\gamma_2 = \frac{\rho_2 n_1}{\rho_2 n_2} \cdot \gamma_1$$

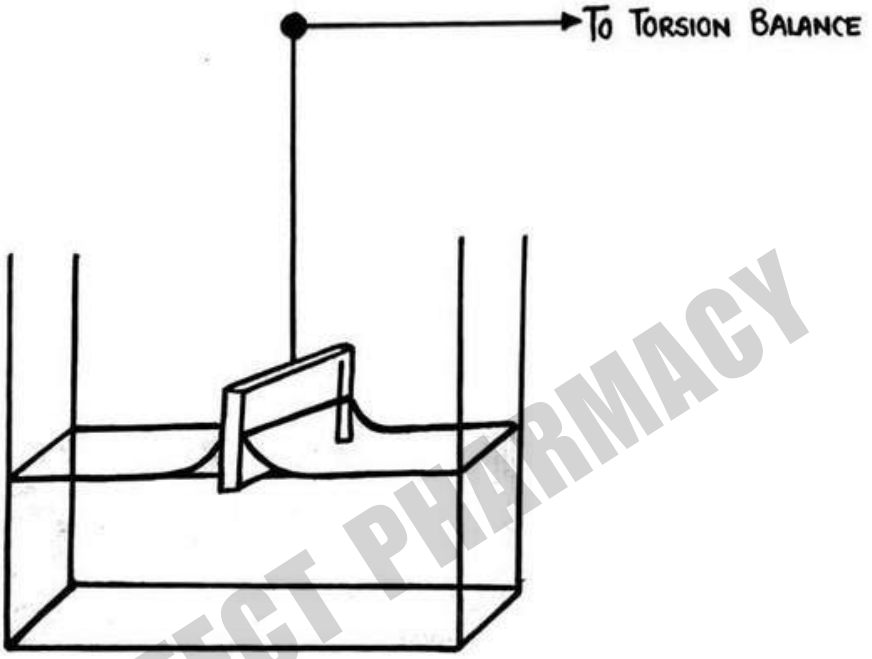
SURFACE TENSION OF TEST LIQUID = $\rho_2 n_1 / \rho_1 n_2 \cdot \gamma_1$

Here, in the above formula :

- ρ_2 = ~~surface~~ Density of test liquid
- n_1 = number of drops of standard liquid
- ρ_1 = Density of standard liquid
- n_2 = number of drops of test liquid
- γ_1 = surface tension of standard liquid.

④ WILHELMY PLATE METHOD

- This method is used for measuring both Surface & Interfacial Tension.
- In this method, a rectangular plate made of Glass, Platinum or thin micra is suspended vertically into the liquid which is attached with a torsion balance.



CALCULATIONS

When plate is suspended into the liquid then it is stretched downwards due to the surface tension of the liquid and in response we apply a force in upward direction that will be equal to the surface tension of the liquid.

$$F = 2(Ltd)\gamma \cos\theta$$

- Now if liquid completely wets the plate $\theta = 0$, $\cos\theta = 1$

$$F = 2(L+d)\cdot\gamma$$

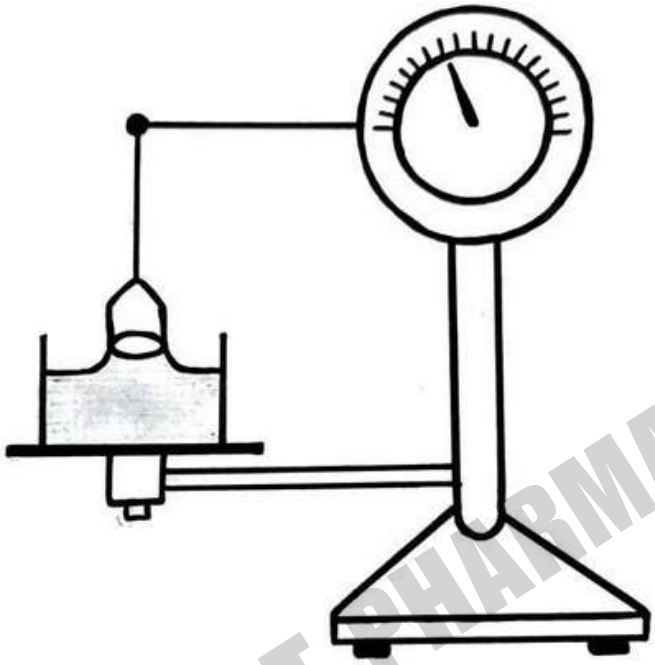
$$\gamma = \frac{F}{2(L+d)}$$

SURFACE TENSION = F / 2(L+d)

Here,
- F = Applied Force
- L = length of Plate
- d = Width of Plate

⑤ Du Nouy Ring Method

- This method is also known by the name of Ring Detachment Method. or Du Nouy Tensiometer.
- The liquid whose surface tension is to be measured is put into a containes & a platinium - iridium ring is suspended in the liquid.



Calculation

When ring is suspended in the liquid it is stretched downwards and in response we apply a force to detach the ring which will be equal to the surface tension of the liquid :

$$F = 2\pi(r_1 + r_2)\gamma.$$

$$\text{Surface Tension} = F / 2\pi(r_1 + r_2)$$

Here, • F = Applied Force

• r_1 & r_2 = Inner & Outer radius of disc

SPREADING COEFFICIENT

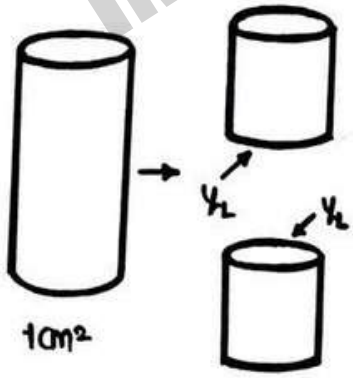
- When a drop of Oleic Acid is placed on the surface of water, it spreads as a film on the surface of waters.
- The ability of one liquid to spread over another liquid is known as Spreading.
- Generally Spreading occurs when Adhesive Force is more than Cohesive Force.
- Now Spreading Coefficient is the measure of tendency of spreading.
- Spreading Coefficient (S) is defined as difference between Work of Adhesion and Work of Cohesion.

$$S = W_a - W_c$$

Here S = Spreading Coefficient
W_a = Work of Adhesion
W_c = Work of Cohesion

WORK OF COHESION

Work of cohesion can be defined as energy required to separate a column of pure liquid into two sections.

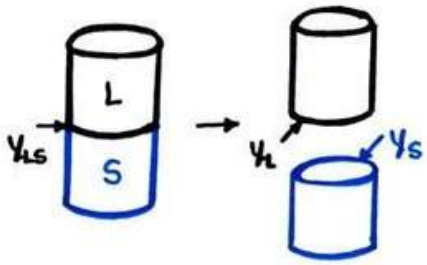


$W_c = \gamma_L \Delta A + \gamma_L \Delta A$
$= 2\gamma_L \Delta A$
Now if area = 1 cm²

$$W_c = 2\gamma_L$$

Work Of Adhesion

Work of adhesion can be defined as energy required to separate a column of two immiscible liquids into two sections.



$W_a = \gamma_L \Delta A + \gamma_S \Delta A - \gamma_{LS} \Delta A$

Now if $\Delta A = 1 cm^2$

$$W_a = \gamma_L + \gamma_S - \gamma_{LS}$$

Now Spreading Coefficient = $W_A - W_c$

$= \gamma_L + \gamma_S - \gamma_{LS} - 2\gamma_L$

$= \gamma_S - \gamma_L - \gamma_{LS}$

$$S = \gamma_S - (\gamma_L + \gamma_{LS})$$

- Here
  - S = Spreading Coefficient
  - γ_L = Surface tension of Spreading liquid
  - γ_S = Surface tension of Sublayer liquid
  - γ_{LS} = Interfacial tension

- If $\gamma_S > \gamma_L + \gamma_{LS}$, S is positive & spreading will occur
- If $\gamma_S < \gamma_L + \gamma_{LS}$, S is negative & spreading will not occur

Application

- Absorbtion of medicament from Cream, Lotions
- Stabilization of Emulsions, Coating of Tablets etc.

ADSORPTION AT LIQUID SURFACES

- The deposition or adhesion of some molecules or ions into the surface of the liquid is defined as Adsorbtion at Liquid Surfaces.
- It is a surface phenomenon.
- It is of two types

① Positive Adsorbtion
② Negative Adsorbtion

POSITIVE ADSORBTION

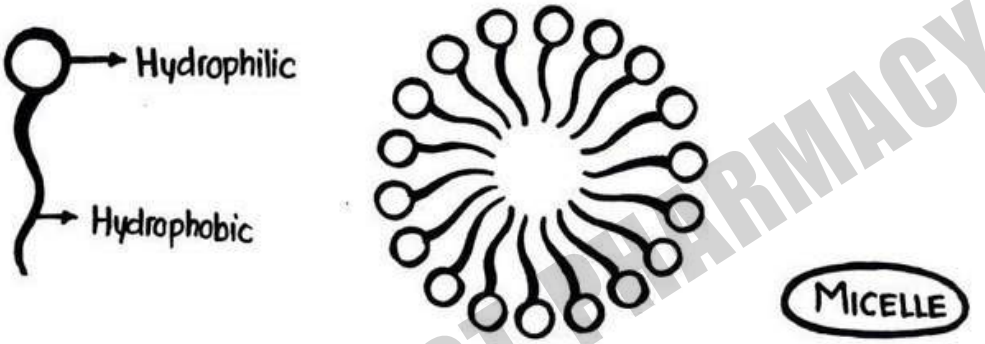
- When molecules deposits on the surface of the liquid, then it is known as Positive Adsorbtion.
- In case of positive adsorbtion, Surface Tension & Surface Free Energy get decreased.

NEGATIVE ADSORBTION

- When the solute molecules reaches on the bulk of the liquid, then it is known as Negative Adsorbtion.
- In case of negative adsorbtion, Surface Tension & Surface Free Energy get increased.

SURFACE ACTIVE AGENTS

- Surface Active Agents are those agents that acts on surface of the liquid.
- They are also known as Surfectants.
- These are the agents that are used to lower the surface tension of the liquids and also used to reduce the interfacial tension between two immiscible liquids.
- Surfectant contains both Hydrophilic (Water Loving) and Hydrophobic (Water Hating) Groups.
- When surfectants are placed in water, the hydrophilic group dissolves in water while hydrophobic group forms Micelles.



CRITICAL MICELLE CONCENTRATION

The concentration of surfectant molecules above which surfectant molecules starts to form Micelles is known as Critical Micelle Concentration.

CORE

The vacant space inside the Micelle is known as Core.

Types Of Surfectants

① Anionic Surfectants
② Cationic Surfectants
③ Ampholytic Surfectants
④ Non-Ionic Surfectants

Anionic Surfectants

- These are most common type of surfectants
- It contains organic tail with negative charge head & small +ve molecule like NH_4^+.
- It consist of soaps of Alkali, Amines, Metals, Alkyl Sulphates etc.
- They have unpleasant taste.
- They are not suitable for internal use due to irritant action on internal mucosa.

Cationic Surfectants

- It contains organic tail with positive charge head and small negative molecules like chloride etc.
- They are more costly than anionic surfectants.
- Example : Cetrimide, Benzalkonium Chloride

Ampholytic Surfectants

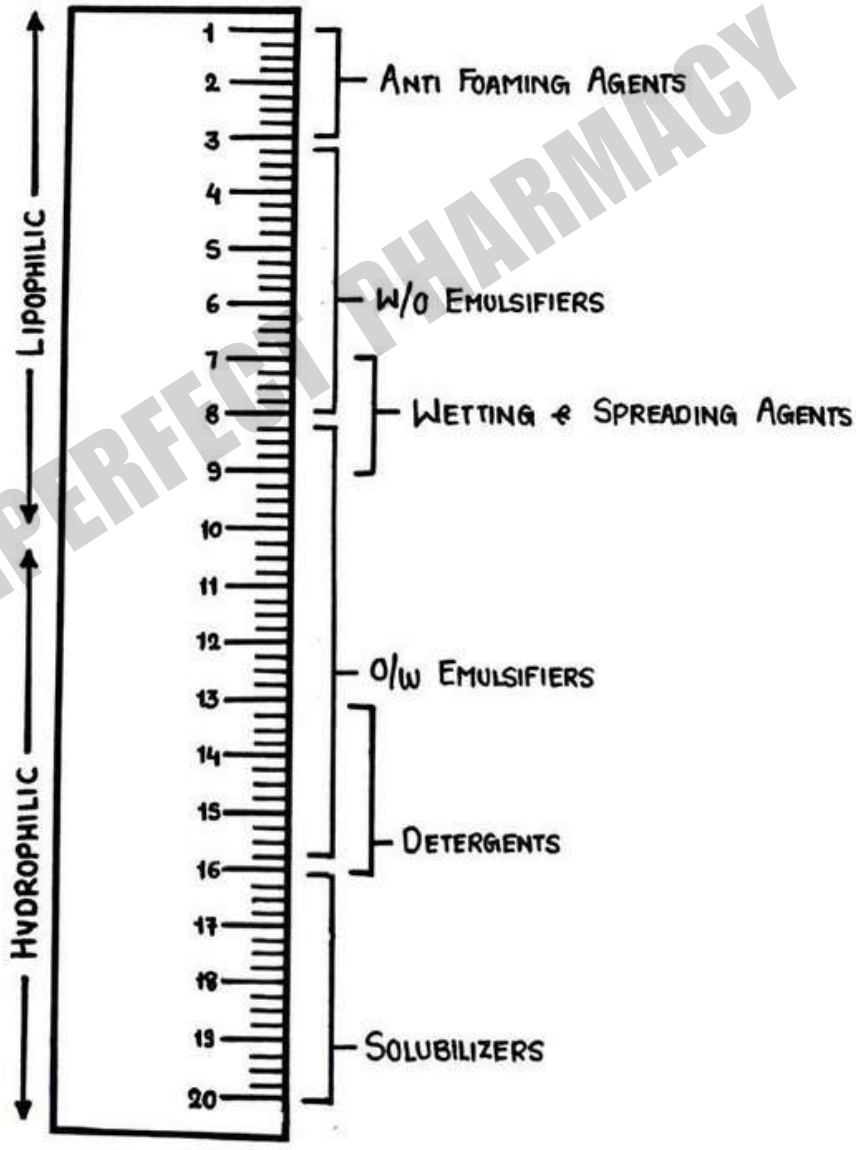
- These surfectants depends on the pH of the system.
- Below a certain pH, they are cationic while above a certain pH they shows anionic behaviour
- At intermediat pH they act as a Zwitterion.
- They are used in cosmetic products, detergents, toothpaste, shampoos etc.

Non Ionic Surfectants

- These are those surfectants that do not contains any ions.
- They doesn't ionize in water because its hydrophilic part contains non-dissociable molecules.
- They are pharmaceutically important.
- They are resistant to pH change.
- Example : Glycerol, Polyether etc.

HLB Scale

- HLB stands for Hydrophilic - Lipophilic Balance.
- HLB system consist of an scale that is designed to differentiate surfactants according to their nature.
- HLB scale was introduced by Sir Griffin in 1949.
- The values in HLB scale ranges from 1-20 that indicates whether the surfactant is Hydrophilic or Lipophilic in nature.
- Higher HLB value indicates that Surfactant is Hydrophilic while Lower HLB value indicates that surfactant is Lipophilic.



Types Of Surfectants

- HLB Value 1-3 represents Anti Foaming Agents.
- HLB Value 3-8 represents W/O Emulsifying Agents.
- HLB Value 8-16 represents O/W Emulsifying Agents.
- HLB Value 7-9 represents Spreading & Wetting Agents.
- HLB Value 13-16 represents Detergents.
- HLB Value 16-20 represents Solubilizing Agents.

$$HLB = \frac{\text{Hydrophilic}}{\text{Lipophilic}}$$

Determination Of HLB Value

HLB Value can be determined by using following Formulas :

- Method 1 :

$$HLB = \frac{E + P}{5}$$

Here E = % w/w Ethylene Oxide Chains
P = % w/w Polyhydric Alcohol Groups

- Method 2 :

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

Here S = Saponification Value
A = Acid Value

Applications Of HLB Value

- HLB used in formulating Creams, Lotions & other cosmetic products.
- It's employed in various pharmaceutical formulations.
- It is used in Food emulsifiers.
- It is used to identify the nature of surfectant.
- In agriculture it is used in the formulation of Herbicides & pesticides.

Limitations Of HLB Value

- Emulsion stability can be affected by Temperature changes that is not addressed by HLB Value.
- It doesn't define the stability of complex formulations involving multiple surfectants.
- It doesn't define the concentration of surfectants.

SOLUBILIZATION

- Solubilization is simply defined as the process of increasing the solubility of a poorly water-soluble substances with the help of Surface Active Agents.
- The mechanism involves entrapment of molecules in micelles.
- Non-Polar molecules are dissolved in Non-polar core of micelles while Polar molecules gets adsorbed at micellar surface.
- Solubilization plays an important role in various fields including pharmaceuticals where it improves the absorption & bioavailibility of drugs.

DETERGENCY

- Detergency is defined as the phenomenon in which dirt or Foreign particles removed from the surfaces with the help of Surfactants.
- Surfactant in detergents act by reducing adhesion forces between dirt and the surfaces and dirt gets removed.
- After removing the dirt surfactant gets adsorbed to the particle surface and develop charge there that prevents the deposition of dirt on solid surfaces.
- Detergents are mainly used in Household cleaning, Food Industry & Industrial cleaning.

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