UNIT-III
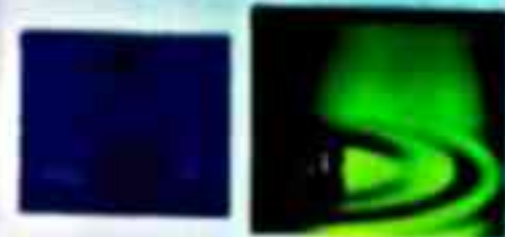
SURFACE & INTERFACIAL PHENOMENON

Points to be covered in this topic

1. LIQUID INTERFACE, SURFACE, INTERFACIAL TENSION

2. SURFACE FREE ENERGY

3. MEASUREMENT OF SURFACE & INTERFACIAL TENSION

4. SPREADING CO-EFFICIENT

5. ADSORPTION OF LIQUID INTERFACE

6. SURFACE ACTIVE AGENTS

7. HLB SCALE

8. SOLUBILISATION

9. DETERGENCY

10. ADSORPTION OF SOLID INTERFACE

❑ INTRODUCTION

❖ **Interface** is the boundary that formed between **phase** ,say **solid & liquid.**

❖ **Surface** is term used to denote interface in which one of the **phase in gas.**

Surface is the term used to describe either a **gas-solid** or a **gas-liquid interface**.
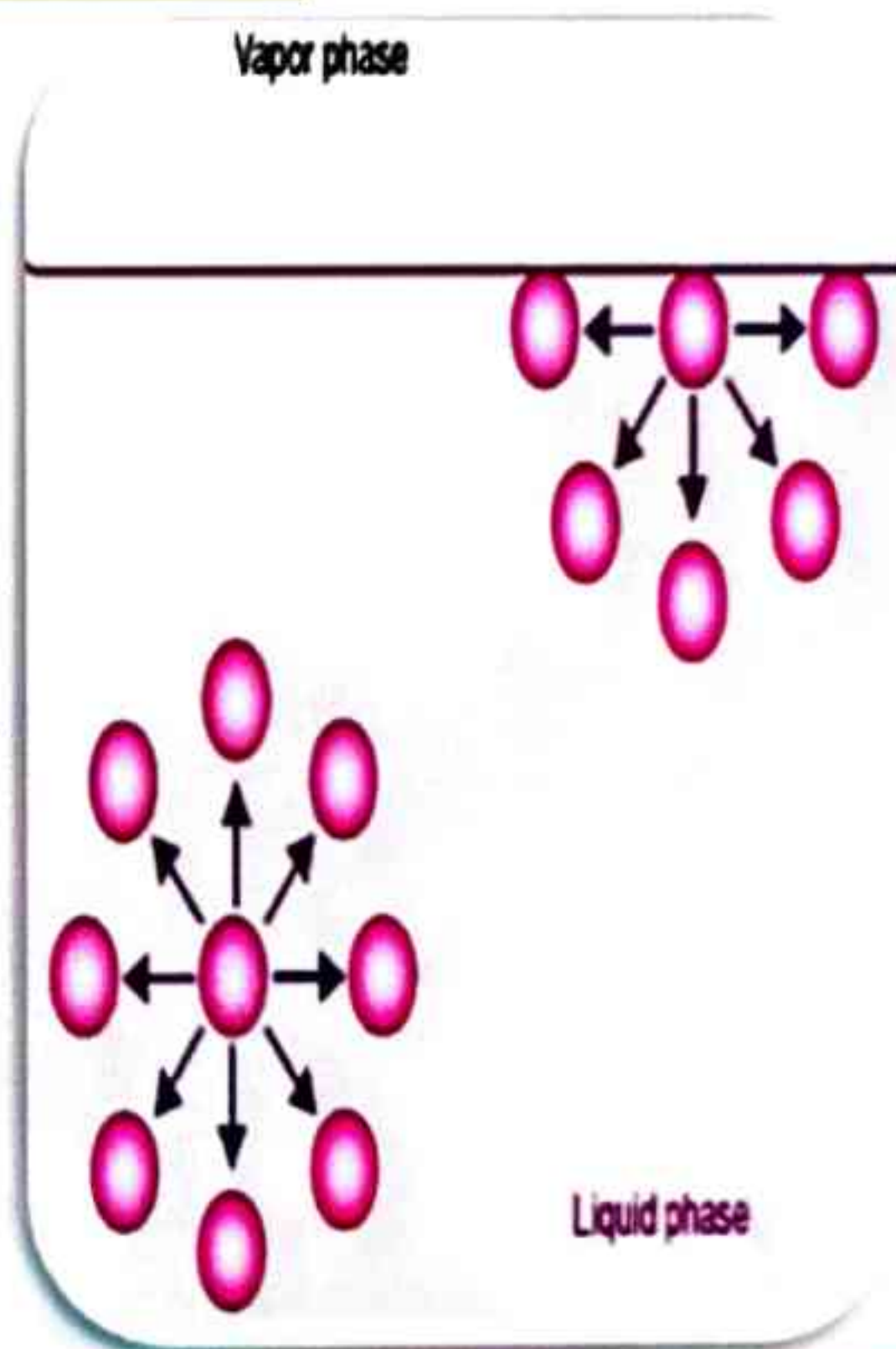

SURFACE

INTERRFACE

●&● are two different phases
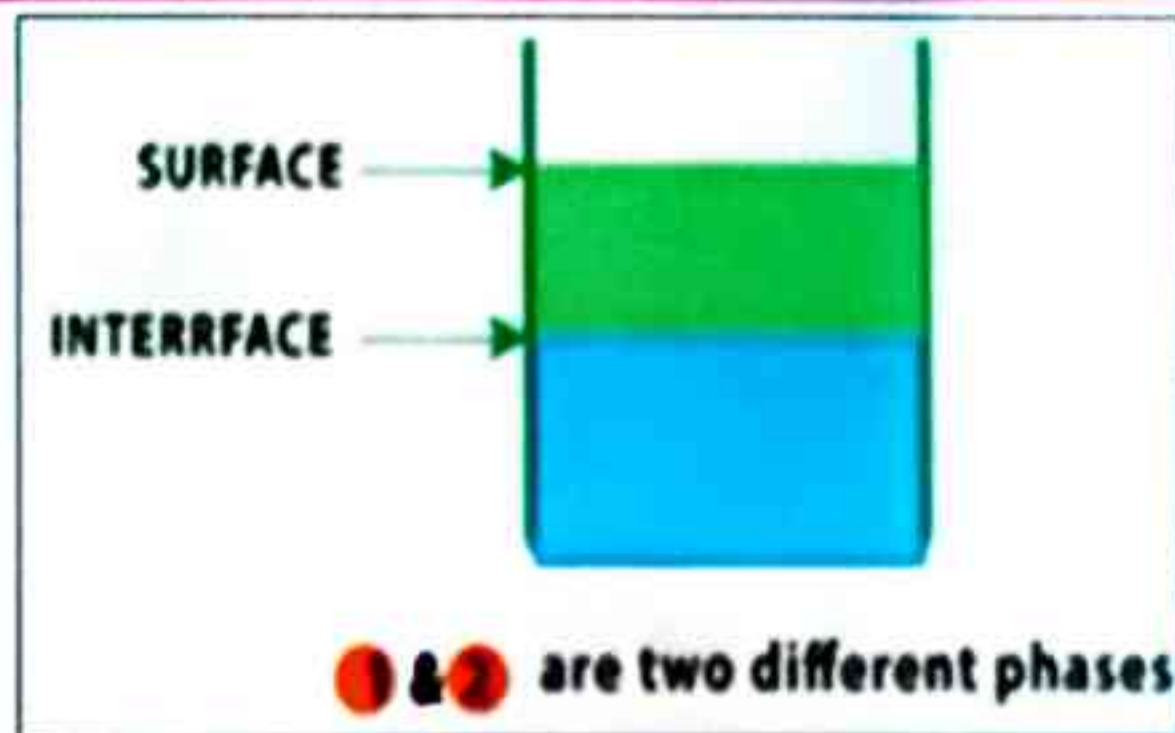
❑ LIQUID INTERFACE

- Different types of interface can exist depending on whether the two adjacent phases are in the **solid, liquid,** or **gaseous state.**

- For convenience, these various combinations are divided into two groups such as **liquid interfaces** and **solid interfaces.**

- Solid interfaces will deal with systems containing **solid–gas** and **solid–liquid interfaces.**

- The association of a liquid phase with a **gaseous** or **another liquid phase.**

❑ SURFACE & INTERFCIAL TENSION

❖ **Surface tension**

Vapor phase

- Surface tension is defined as **tensile force acting** at the **surface of liquid** which is in **contact with gas** .

- The **net effect** is that the molecules at the surface of the liquid experience an inward force toward the bulk.

- Such a force pulls the molecules of the **interface together** and, as a result, **contracts the surface**, resulting in a surface tension.

Liquid phase

- The surface tension, has the units of **dynes/cm** in the **CGS** system and of **N/m** in the **SI system.**
- The term surface tension is reserved for **liquid–vapor (γ_{lv}), and solid–vapor (γ_{sv}) tensions.**

❖ Cohesive forces:

- The **intermolecular attraction** between the **similar molecules** is called the **cohesive force.**
- **For example:-** Molecules of water in bulk are surrounded the similar types of molecules and the **intermolecular forces** between them are the force attraction.

❖ Adhesive forces:

- The force between the **unlike molecules** is called the **adhesive force.**
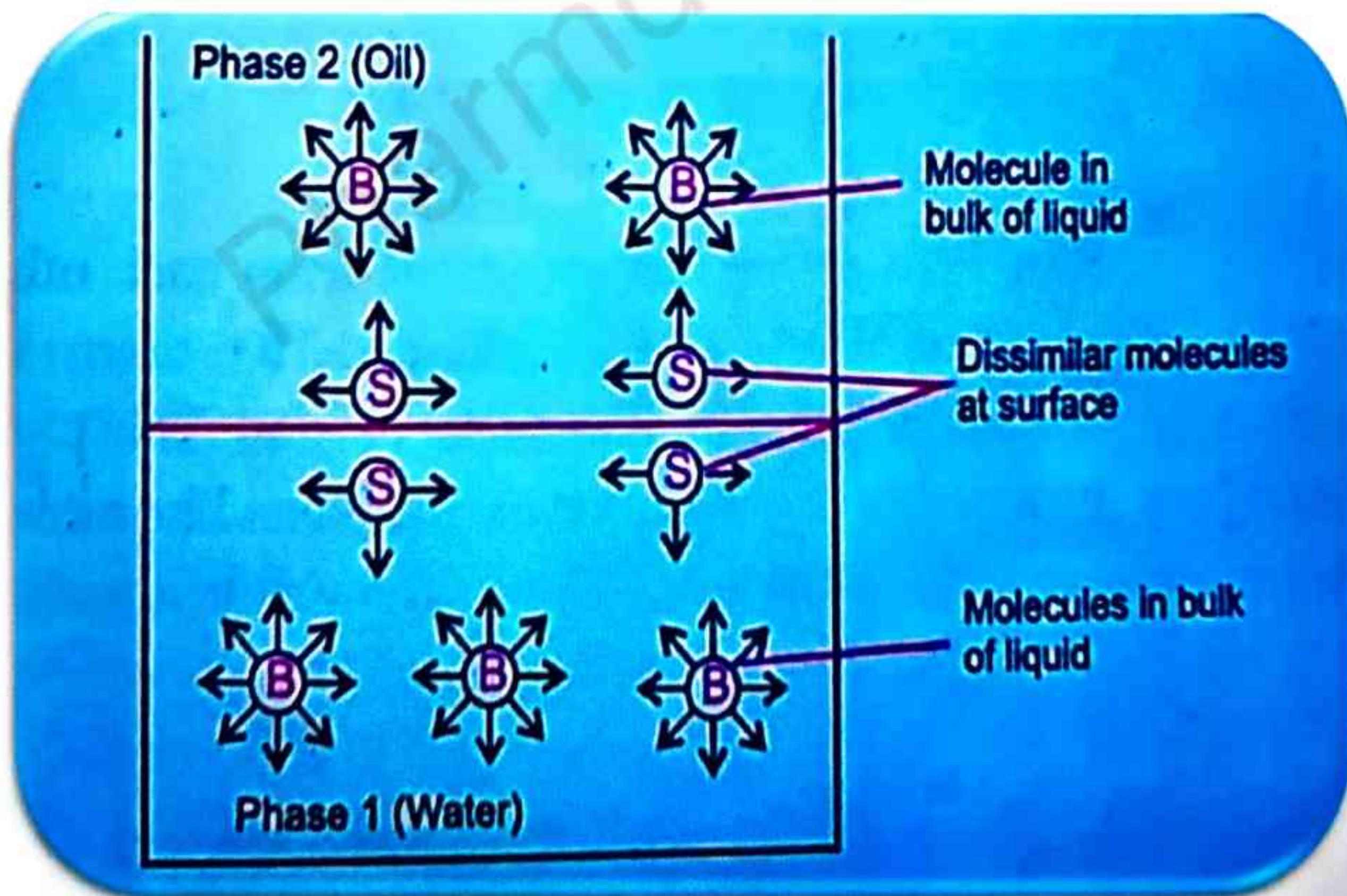- **For example:-** Molecules of water at the surface behave differently than the **molecules** in the bulk.

Fig :- Adhesive & cohesive force

❖ Interfacial tension

- It is the force per unit length existing at the **interface between two immiscible liquid phase** .

- If two liquids are **completely miscible** , **no interfacial tension** exist between them.

- **CGS = dynes/cm**

- When phases exist together, the boundary between two of them is known as an interface.

- Interfacial tension for the force between **two liquids(γ_{ll})** , between **two solids(γ_{ss})** and at a **liquid–solid interface (γ_{ls})**
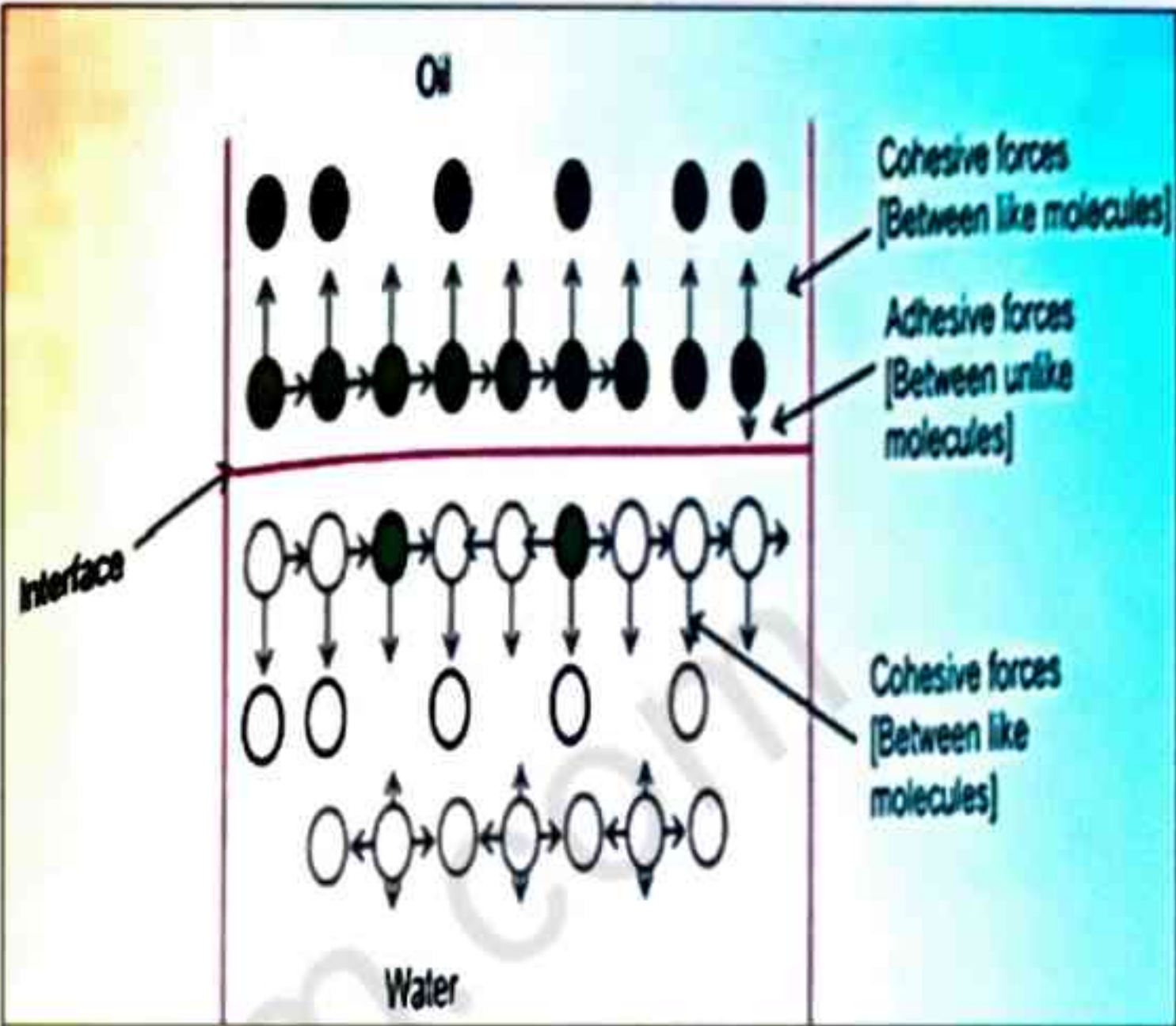

Fig:- Formation of interface between oil & water

- Interfacial tensions are **less than surface tensions** because the **adhesive forces between two liquid phases** forming an interface are **greater than when a liquid and a gas phase** exist together.

➢ Classification of interfaces

Phase	Interfacial tension	Types	Examples of interfaces
Gas-gas	----------	No interface possible	------------------
Gas-liquid	γ_{LV}	Liquid interface	Body of water exposed to atmosphere
Gas- solid	γ_{SV}	Solid surface	Table top
Liquid- liquid	γ_{LL}	Liquid-liquid interface	Emulsion
Liquid –solid	γ_{LS}	Liquid-solid interface	Suspension
Solid-solid	γ_{SS}	Solid –solid interface	Powder particles

☐ SURFACE FREE ENERGY

- To **move a molecule from** the **inner layers** to the **surface, work** needs to be done **against** the **force of surface tension.**

- Each molecule near the surface of liquid **possesses** a certain **excess of potential energy** as compared to the **molecules** in the **bulk of the liquid.**

- The **higher** the **surface** of the **liquid**, the **more molecules** have this **excessive potential energy.**

- Surface of the **liquid increase, energy of the liquid** also **increase.**

- Energy is proportional to the size of the free surface is called **surface free energy.**

- To evaluate the **amount of work** in **increasing the surface area.**

- Equation may be written as $\gamma \times 2L = f$
- Surface tension maintains the surface area of a liquid to a **minimum value.**

- Surface free energy is defined as the work required to **increase** the area of a **liquid** by **1 square meter.**

- Surface free energy is **equal** to the surface tension.

- The mass is added to extend the surface by a distance **ds** the work **dw** [force x distance] can be written as

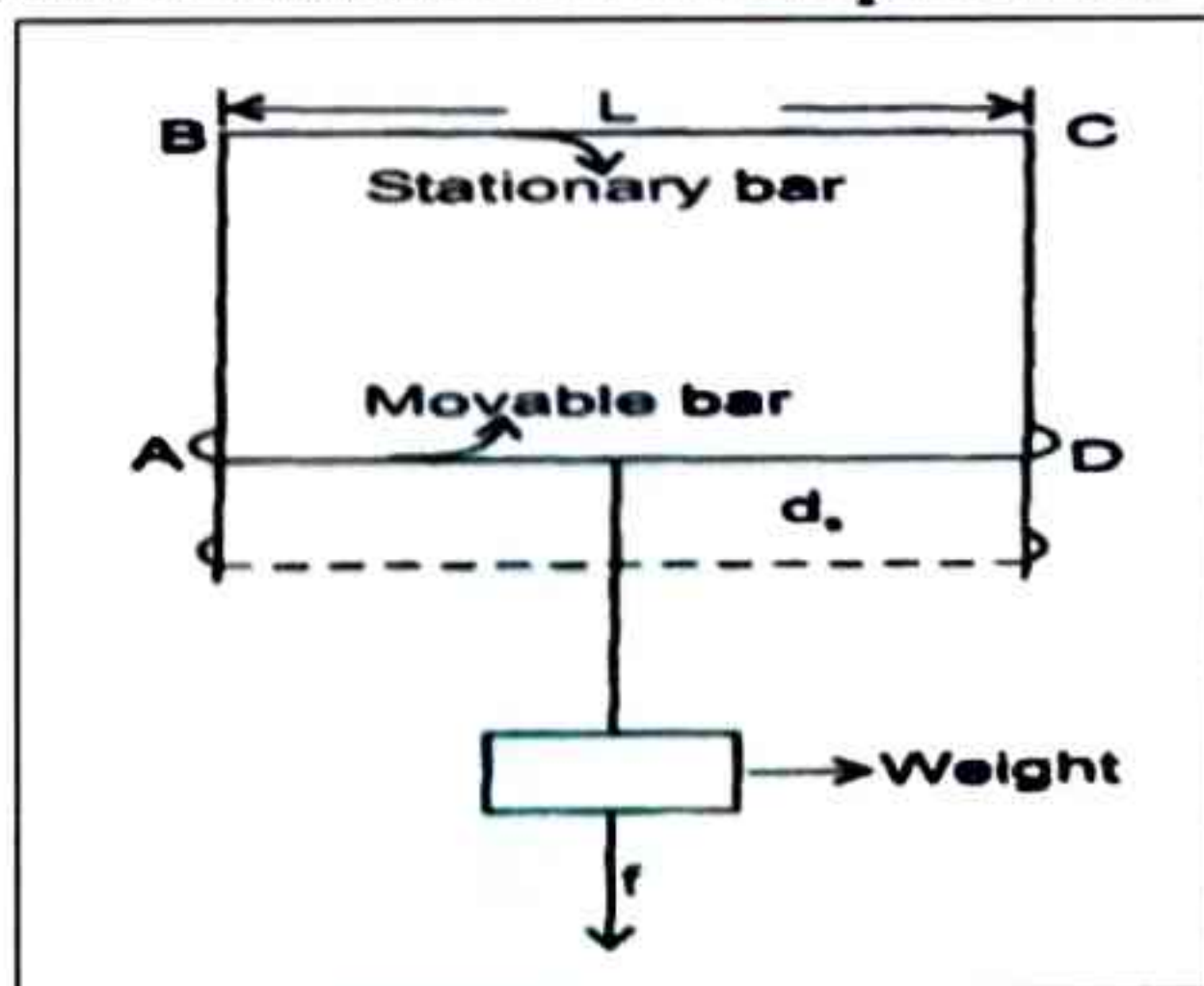$$dW = f \times d_s = \gamma \times 2L \times ds$$

- and ,since $2L \times d_s$ is **equal** to the increase in surface area dA produced by extending the **soap film**

$$dW = \gamma dA$$

- For a **finite change**

$$W = \gamma \Delta A$$

B —— L —— C
Stationary bar

A —— Movable bar —— D
d_s

→ Weight
f

Fig :- Wire frame apparatus used to demonstrate the principle of surface tension

- ✓ **W**= Work done, or surface free energy increase, expressed in **ergs,**
- ✓ **γ**= Surface tension in **dynes/cm**
- ✓ **ΔA**= Increase in area in **cm** .

❑ MEASUREMENT OF SURFACE & INTERFACIAL TENSION

- Surface and interfacial tension is very important **physio-chemical property** which affects the surface chemistry of the substances whether solid, liquid or gas.
- There are many methods for the measurement of surface and interfacial tension

Methods for measurement of surface & interfacial tension

Sr.No.	Name of method	Measurement
1	Capillary rise method	Surface tension
2	Drop formation method (stalagmometer)	Surface tension
3	Bubble pressure method	Surface tension
4	Wilhelmy plate method	Surface tension & interfacial tension
5	DuNouy ring method	Surface tension & interfacial tension

1. Capillary rise method

❖ Principle

- When a capillary tube of **radius 'r'** is vertically inserted into a liquid, the liquid rises to a **height 'h'** and forms a concave meniscus.
- This is because of the **adhesive forces** between **liquid molecules** and glass are **stronger** than **cohesive forces** between liquid molecules.

- The liquid is said to wet the capillary wall, spreading over it, and rising in the tube.

- The rise in the tube continue until the upward movement is just balanced by the downward force of gravity due to the weight of the liquid.
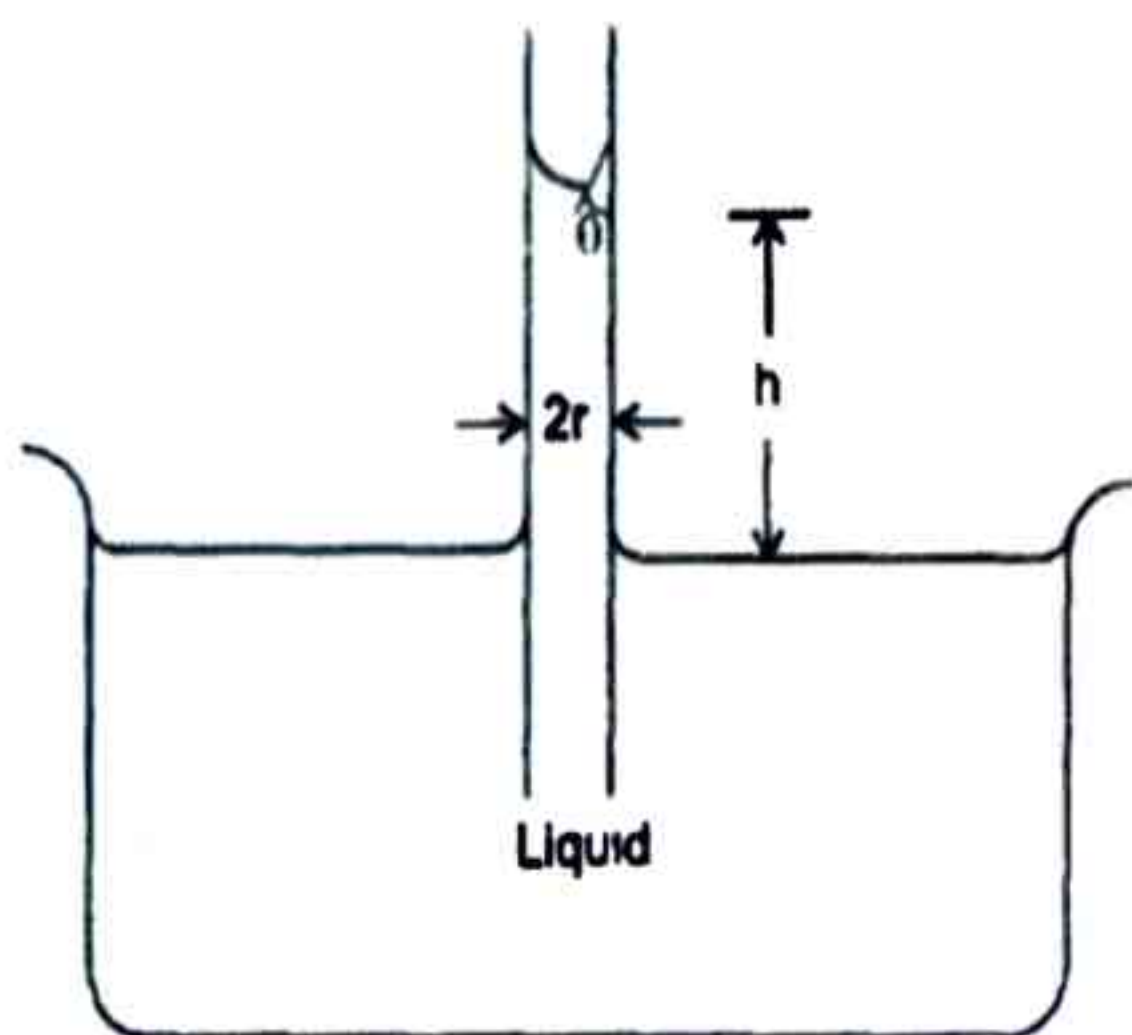

Fig A :- Measuring surface tension by means of the capillary rise principle.
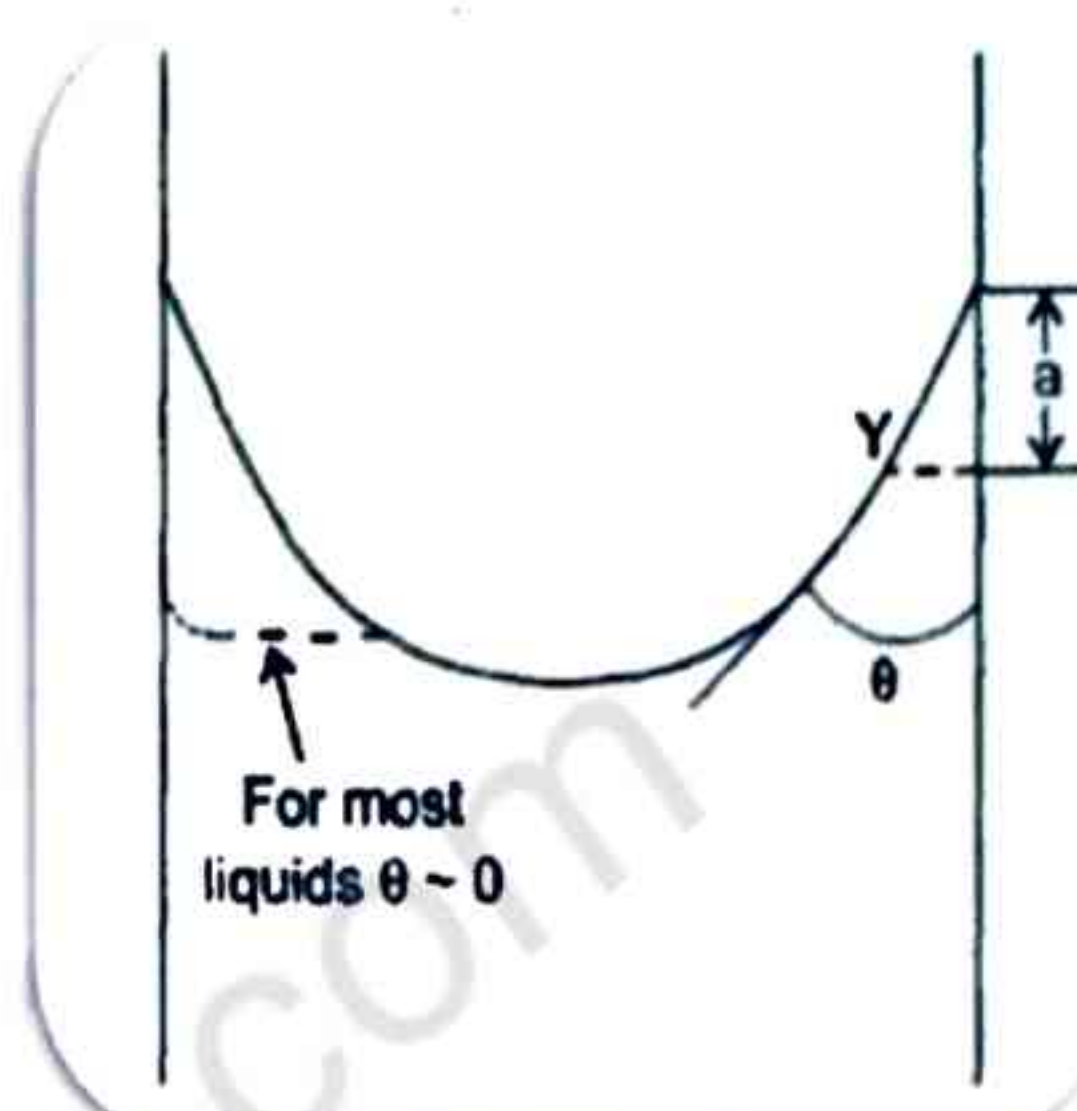

Fig B:- Force components and contact angle at the meniscus of a liquid.

- The upward vertical component of the force resulting from surface tension on the circumference is given by

$$a = \gamma \cos\theta$$

- The total upward force around the inside circumference of the tube is

$$2\pi r \gamma \cos\theta$$

- Where, θ = contact angle between surface of liquid and the capillary wall.

Fig :- Travelling microscope

- $2\pi r$ = Inside circumference of the capillary

- For water θ is insignificant as shown in Fig. (B).

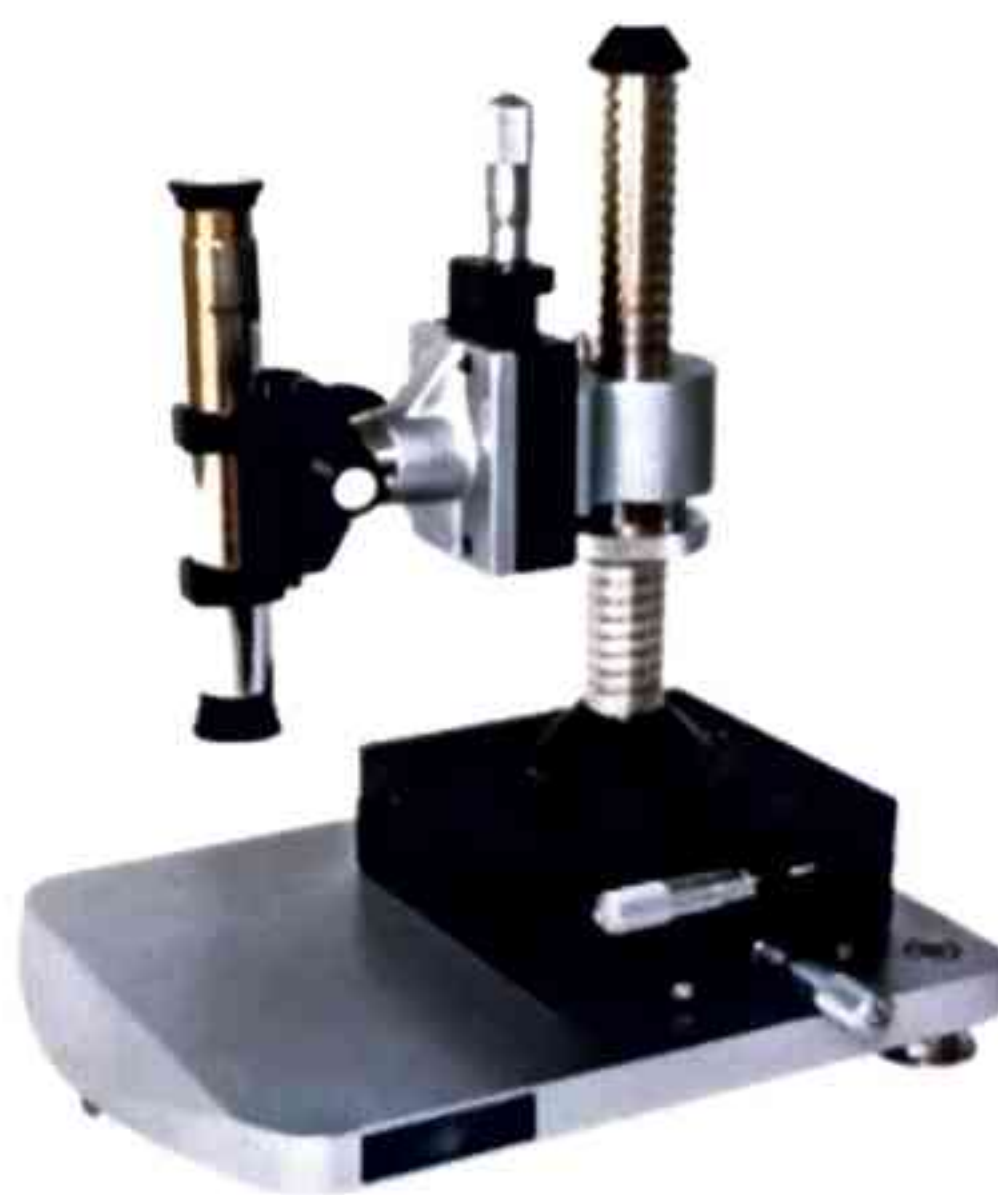**Where,**

γ (Gamma)= Surface tension of liquid

r = Radius of capillary tube

h = Height of liquid rise in the capillary

p = Density of liquid

g = Acceleration due to gravity

❖ Procedure:

i.   Take **appropriate size of capillary, clean and dry.**

ii.   Focus the travelling microscope to measure internal **diameter of the capillary tube.**

iii. **Take 50 ml of liquid in 100 ml of beaker.**

iv.   Fix the capillary in a stand and dip in it on the surface of the liquid in beaker.

v.   **When liquid rises** in the capillary, **measure the height** by travelling microscope by **focusing first at height meniscus,** remove the beaker and then focus at the tip of the capillary. Determine the density of liquid by pycnometer.

2. Drop formation method (stalagmometer)

❖ Principle

- When liquid comes **out of the capillary,** it first forms a drop at the tip of the **capillary tube** which gradually increase in size and **finally detaches from the tip.**

- The weight of drop equals to the total **surface tension** at the circumference of the tube.

- Hence,

$$\text{Weight of drop} = ST$$

$$m.g = 2\pi r\gamma$$

Where,

m = mass of drop

g = acceleration due to gravity

r = radius of the tip

γ = surface tension

$$v.\rho.g = 2\pi r\gamma$$

$$\gamma = \frac{v.\rho.g}{2\pi r}$$

- The **stalagmometer (Drop pipette)** is the apparatus used for determination of surface tension and one of the two methods are **used as given below.**

    i. Drop - Weight Method

    ii. Drop-number Method

i) <u>Drop - Weight Method</u>

- This method is carried out **by drop pipette or Stalagmometer** which consists of a glass tube with a **bulb approximately** at the middle of the tube. There are two markings on the pipette **marked as "A" and "B".**

- **There is a capillary bore** at the tip of the Stalagmometer.

- In a weighing **bottle about 20 drops** of liquid are received from **stalagmometer and weighed.**

- Thus weight of **one drop is found.**

- **Repeat the procedure for second liquid** (reference, usually water) and weight of one drop determined as before.

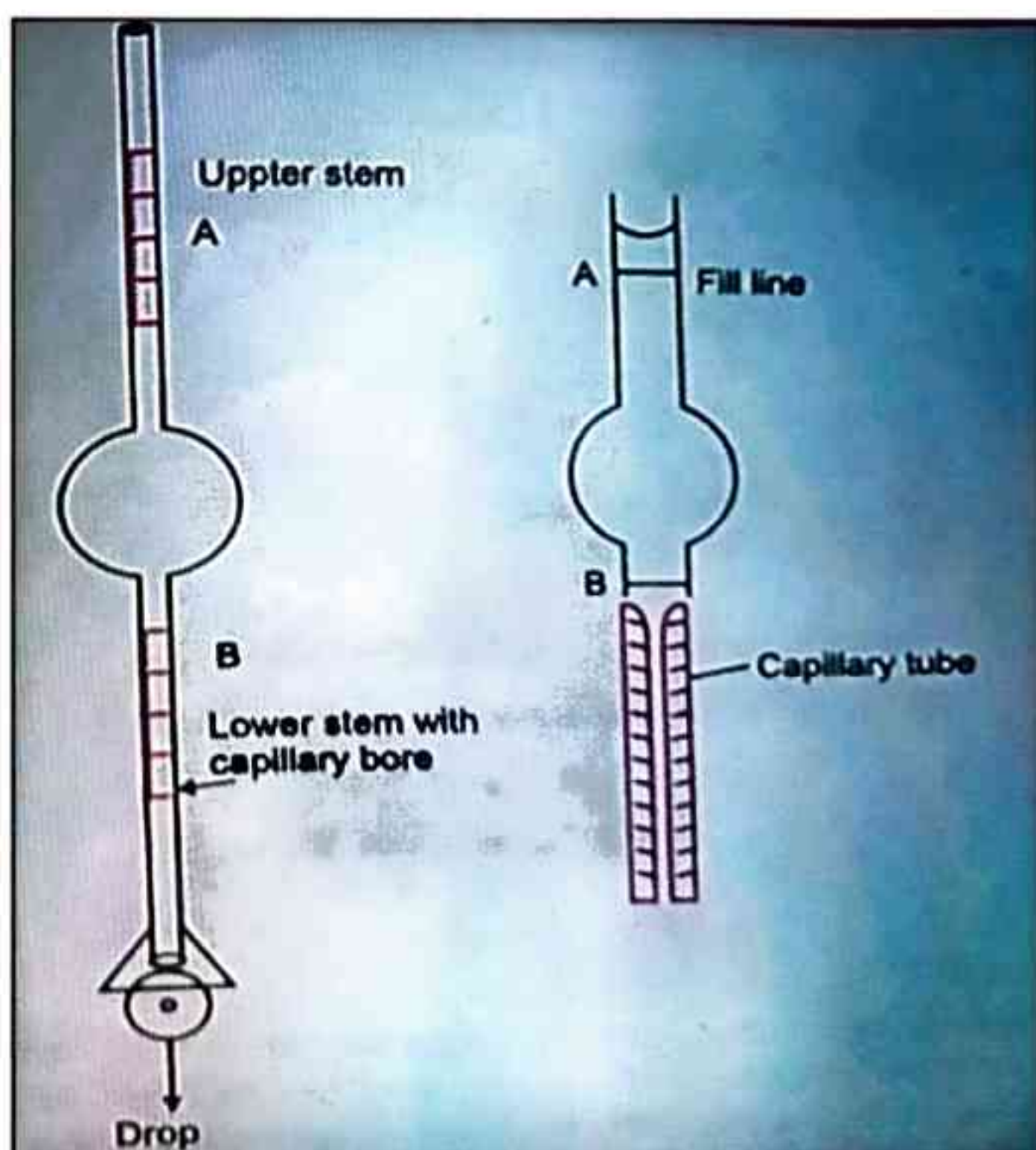- Using following equation one can **calculate the surface tension** of unknown liquid.

Upper stem
A
B
Lower stem with capillary bore
Drop

A Fill line
B
Capillary tube

Fig :- Stalagmometer

- This method is carried out by **drop pipette or stalagmometer** which consist of glass tube with a **bulb approximately** at the middle of the tube.
- **There are two markings** on this pipette **marked as "A" and "B".**
- There is a capillary bore **at the tip of the stalagmometer.**

❖ Procedure:

1) **Clean and dry Stalagmometer** and fix vertically on the stand.

2) **Suck given liquid up to the mark "A".**

3) Allow liquid to drop **slowly from the tip,**

4) **Collect about 20 drops in a clean tared vessel and weigh.**

5) Determine the weight of one drop by dividing **weight of liquid by** number of drops.

6) **Clean and dry Stalagmometer** and fill it with second reference liquid (say water) and determine the **weight of one drop** similarly as done **before from given liquid.**

For test liquid – $m_1 g = 2\pi r \gamma_1$ ————————————— (1)

For reference liquid $m_2 g = 2\pi r \gamma_2$ ————————————— (2)

Dividing equation (1) by equation (2)

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

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

Where

γ_1 = surface tension of test liquid

γ_2 = surface tension of reference (water) liquid

m_1 = weight of one drop of test liquid

m_2 = weight of one drop of reference liquid

ii. Drop-number Method

- This method is carried out by drop pipette or Stalagmometer by sucking the test liquid up is the mark 'A".

- Keep the Stalagmometer vertically and allow the liquid fall in the form of drop from mark 'A' to 'B', in a clean and dry beaker.

- Count the number of drops.

- Similarly count the number of drops of reference liquids (water) for the same volume.

- Suppose, n_1 and n_2 are the number of drops of test liquid and reference liquid respectively produce volume V from mark 'A' to 'B'.

- Then volume of one drop of test liquid = V/n_1 and the volume of one drop of reference liquid=V/n_2.

- We know that

- Mass of one drop = Volume x density

- Then, mass of one drop of test liquid $= \frac{v}{n1} \times \rho_1$ —————— (3)

- Similarly mass of one drop of reference liquid $= \frac{v}{n2} \times \rho_2$ —————— (4)

- Put the value of equation (3) in the equation (1), we get-

$$= \frac{v\rho_1 g}{n_1} = 2\pi r \gamma_1 \text{ ——————— (5)}$$

- Put the value of equation (4) in the equation (2), we get-

$$= \frac{v\rho_2 g}{n_2} = 2\pi r \gamma_2 \text{ ——————— (6)}$$

- Now divide equation (5) by equation (6) we get

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

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

ρ_1 = Density of test liquid

ρ_2 = Density of reference liquid

n_1 = Number of drops of test liquid

n_2 = Number of drops of reference liquid

γ_1 = Surface tension of test liquid_

γ_2 = Surface tension of reference liquid (water)

3. Maximum Bubble pressure Method

- In this method the maximum pressure required to break a bubble at the end of the capillary and at the moment of **breaking it is determined.**
- **Air pressure** is applied slowly through a tube dipping in experimental liquid. A bubble is formed and **slowly grows and then breaks.**
- **The pressure at which the air bubble breaks** is determined on manometer and surface tension calculated using following formula.

$$\rho = hdg + \frac{2\gamma}{r}$$

ρ = maximum pressure

γ = surface tension

r = radius of capillary

d = density of the liquid
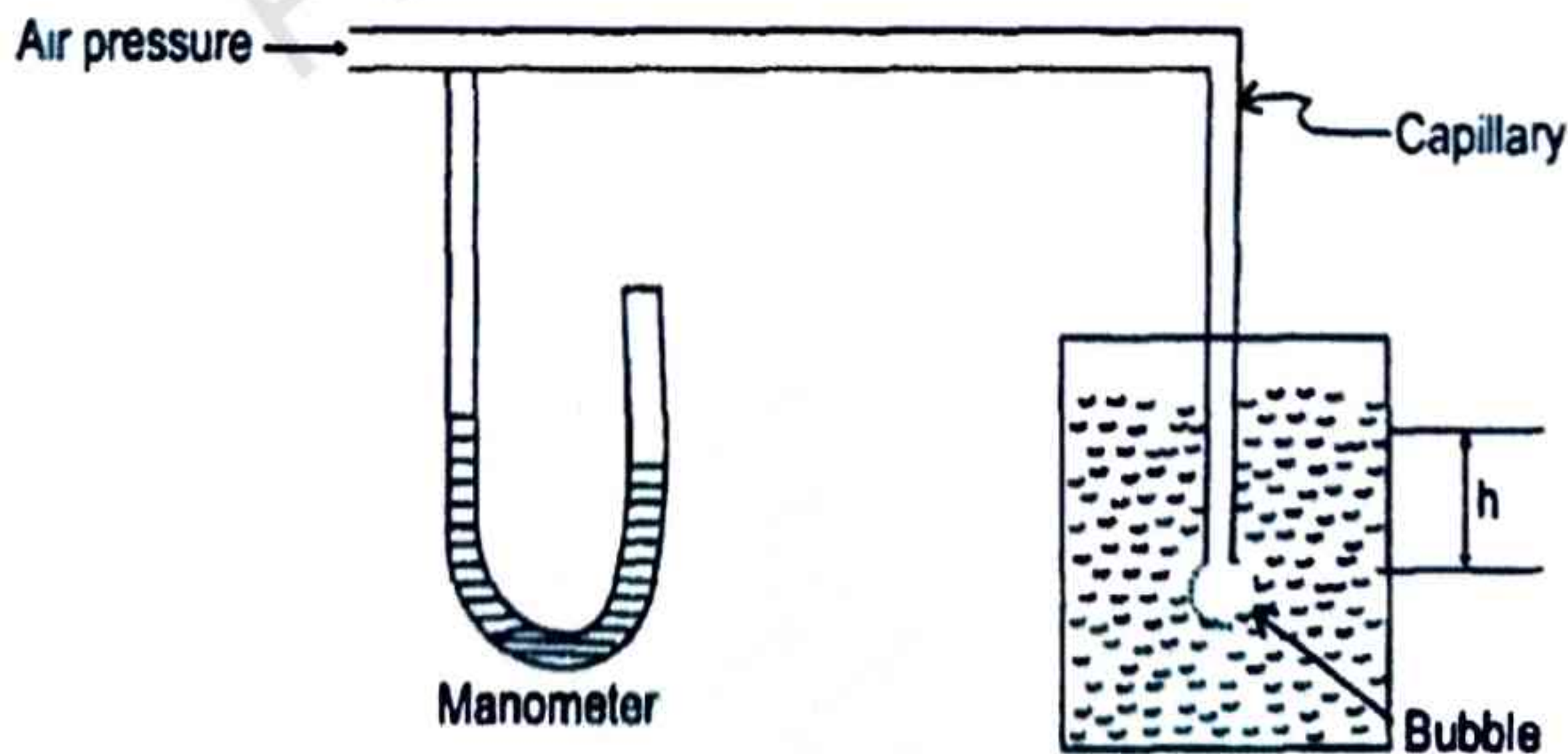
h = depth of liquid.

Fig :- Apparatus for Maximum bubble pressure method.

4. WILHELMY PLATE METHOD

- Wilhelmy plate method is used to measure equilibrium surface or interfacial tension at **air liquid or liquid-liquid interface.**

- A simple apparatus consists of a glass, mica or platinum plate attached **with the torsion micro-balance.**

- The plate is **oriented perpendicular** to the interface and the force exerted on the plate at interface between the two immiscible liquids or surface of the liquid is measured **using micro-balance.**

- When the vertically suspended plate touches the liquid surface or interface, then a force F, which **correlates with the surface tension** or interfacial tension y and with the contact angle θ, Thus, the force (F) exerted on the plate is equal to the surface tension multiplied by the **perimeter of the plate 2(l + d) and the contact angle** cos θ is the length of plate and d is the thickness of the plate.

- **The force exerted (F)** is the difference in the balance reading prior and after to detachment of plate, hence,

$$F\ (W_L - W)$$

- **The plate is cleaned and dried.**

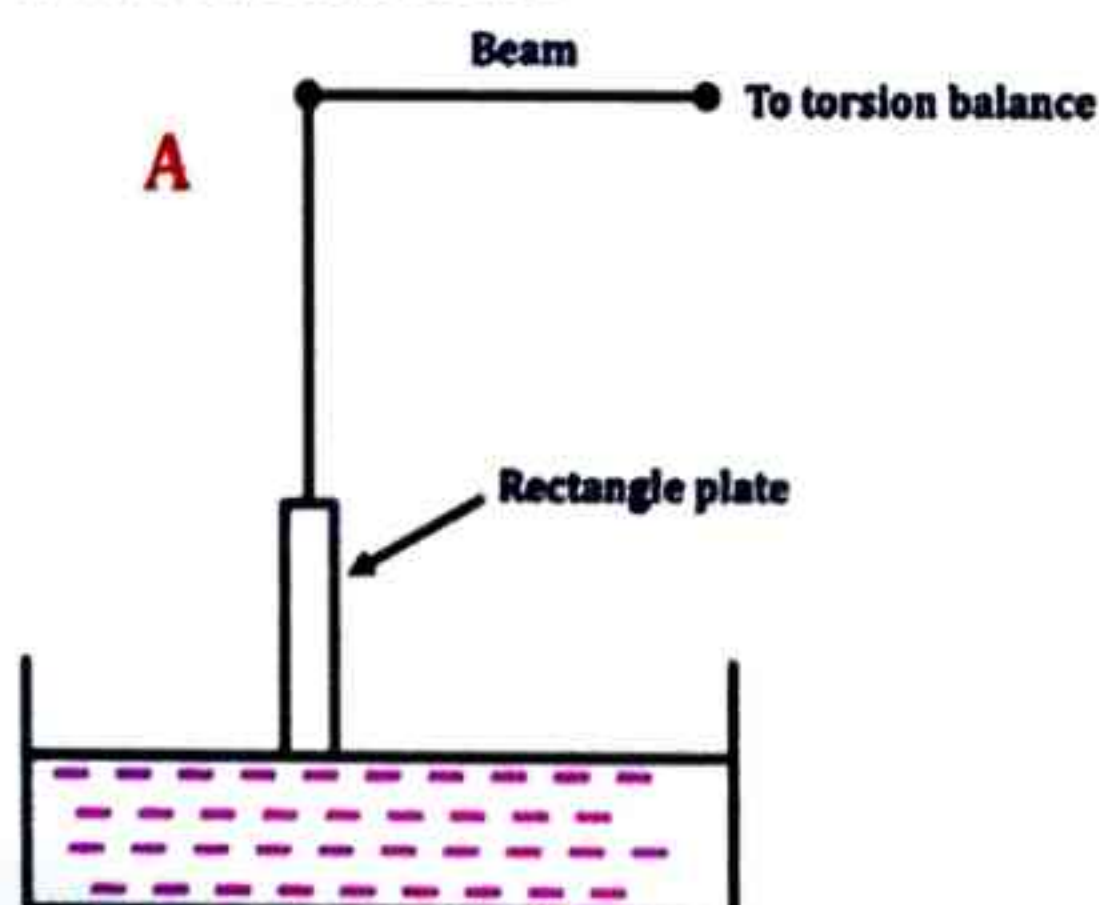- After the plate is completely dried, it is attached to a **balance with the thin metal wire**
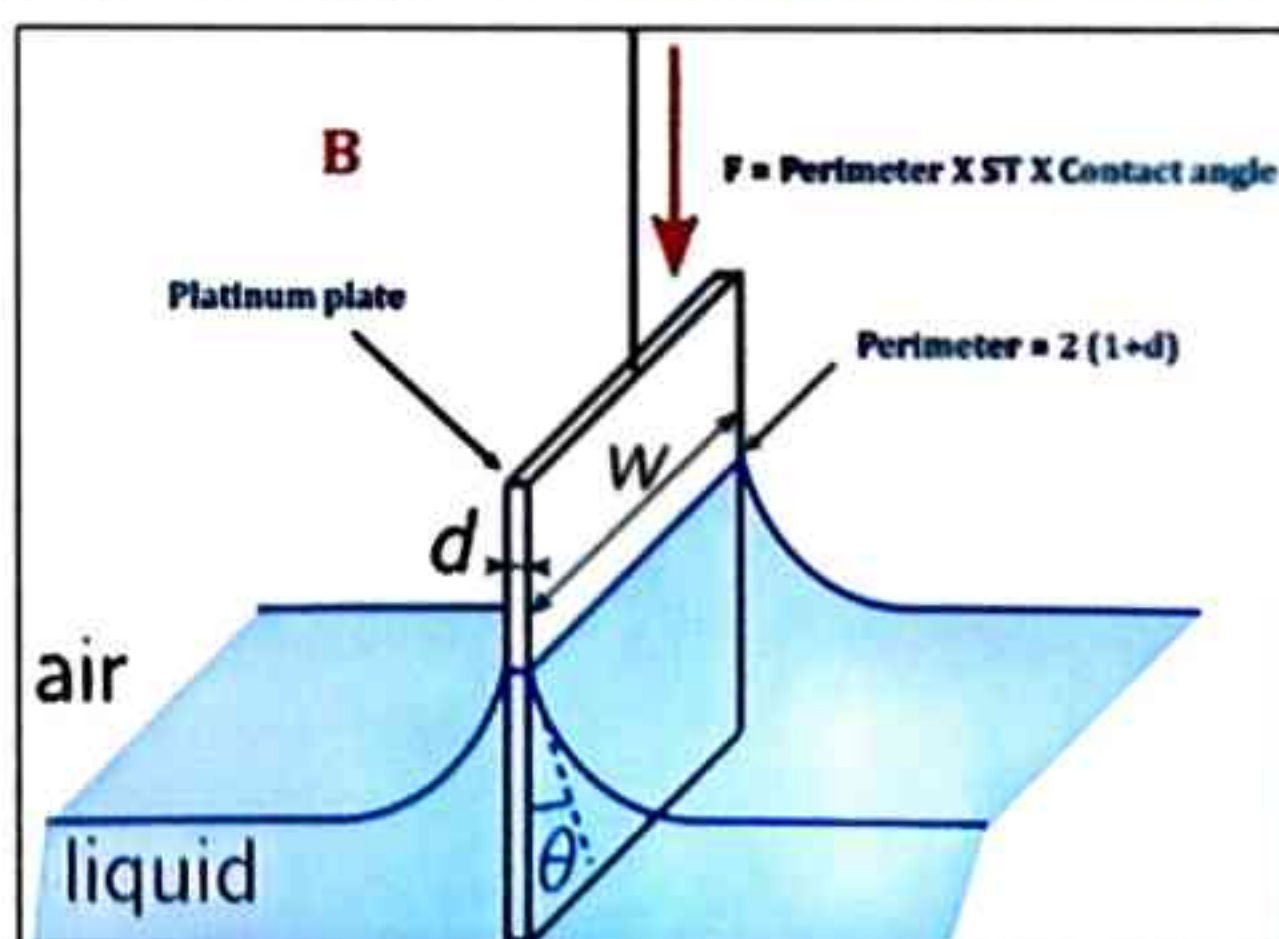

Fig :- Wilhelmy plate method

Fig :- Wilhelmy plate immersed in liquid

- **Take the liquid in a beaker** and the pale is immersed in the liquid now the liquid container or **beaker is gradually lowered**

- The reading of the **balance is noted immediately** just prior to the detachment of the plate and also the after **detachment of the plate in the air.**

- The **surface tension γ** is calculated using **Wilhelmy equation assuming** complete wetting of **plate (θ=0)**, where θ is the contact angle between the **liquid phase and the plate.**

- **Since (θ=0) hence, cos θ = 1.**

- **Thus, the exerted force**

$$F = 2\,(l+d)\,.\,\cos\theta\,.\,\gamma$$

$$(W_L - W) = 2\,(l+d)\,\gamma$$

$$\gamma = \frac{(W_L - W)}{2\,(l+d)}$$

✓ W_L= Reading of the balance prior to the detachment of the plate

✓ **W= Reading of the balance after to the detachment of the plate**

✓ **l= Width of plate**

✓ **d = Thickness of plate**

5. DuNouy ring method

- **The DuNouy tensiometer** is widely used for **measuring surface** and **interfacial tensions.**

- The principle of the instrument depends on the fact that the force necessary to detach a **platinum-iridium ring immersed at the surface** or **interface is proportional** to the **surface** or **interfacial tension.**

- One end of the **torsion wire is fixed** while the other attached to a knob having a pointer **which moves on a fixed scale.**

- The **force required** to detach the ring in this manner is provided by a torsion wire and is recorded in **dynes on a calibrated dial.**
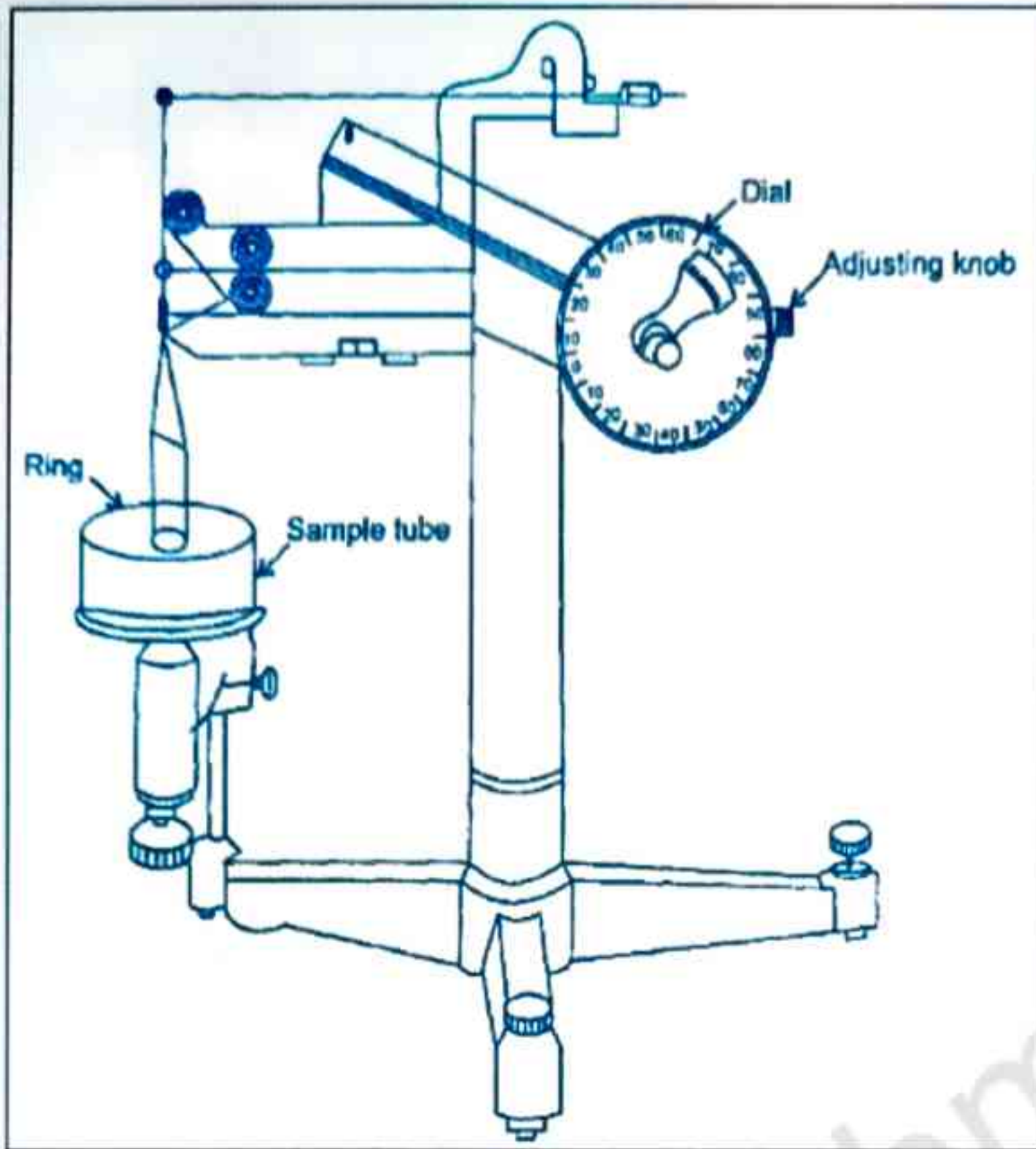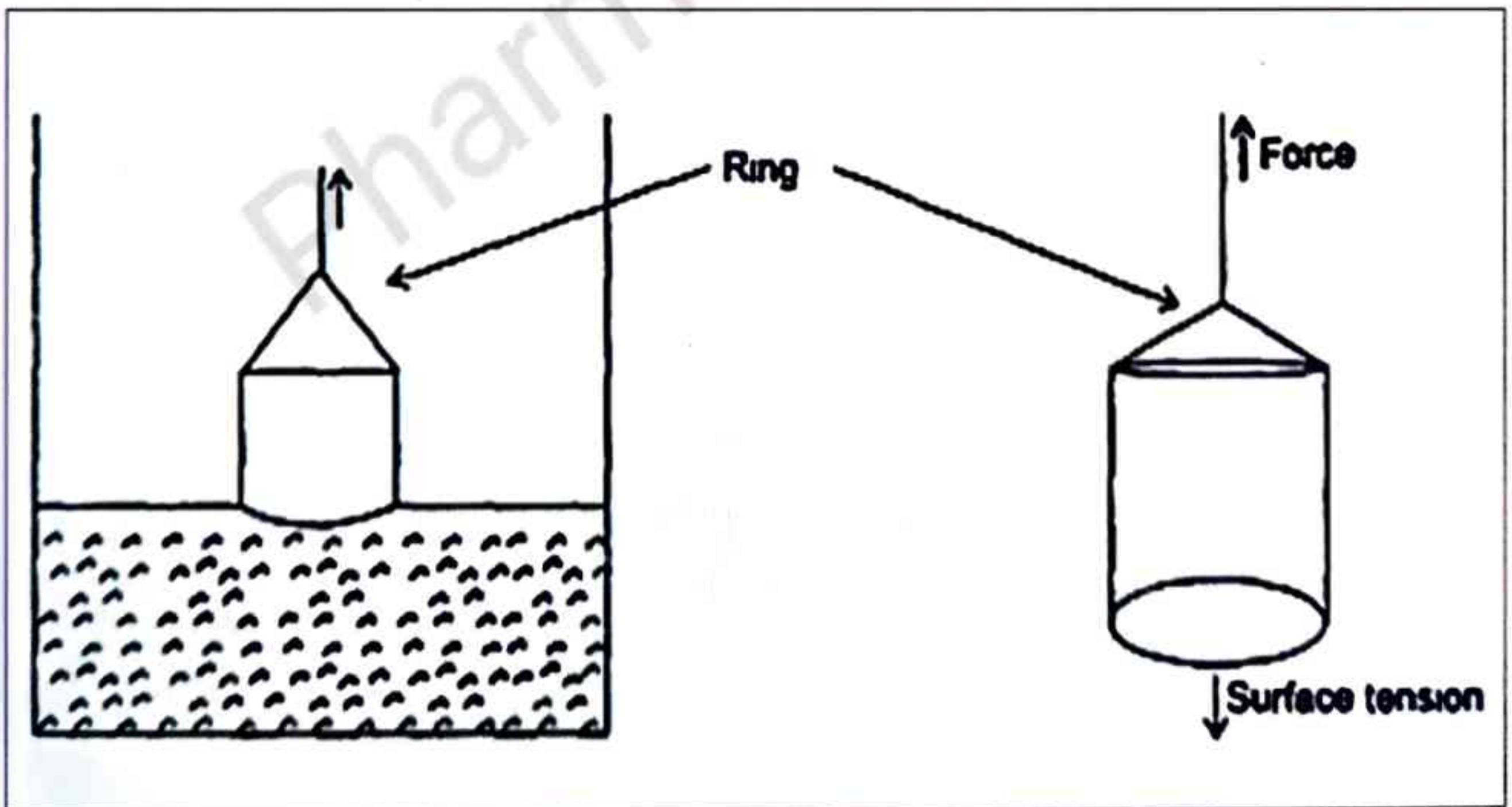

Fig :- DuNouy tensiometer

Fig :- DuNouy ring tensiometer

The **representation of the tensiometer** ring pulling a column of **water above the surface.**

The surface tension can be computed from following formula

$$\gamma = \frac{\text{dial reading (dynes)}}{2 \times \text{ring ciecumference}} \times \text{Correction factor B}$$

- The **correction factor** is essential because certain variables must be **consider to avoid errors** like radius of ring, **radius of wire used** to form the ring and volume of the liquid **raised out of the surface.**

❖ Procedure

- The **step-wise procedure** to conduct the experiment to determine the surface tension of a given liquid can be done as follows:

1. **Clean the ring thoroughly before use.**
2. Attach the ring to the lever arm.
3. **Fill liquid sample** in a vessel such as an evaporating dish, Petri dish, or beaker with a diameter of at least 4.5 cm to minimum depth of 1.0 cm.
4. Record the exact temperature.
5. Place the vessel on the sample table.
6. Raise the sample table assembly until the ring immersed approximately **5 mm** in the liquid.
7. Lower the sample table assembly until the ring is just **below the surface of the liquid.**
8. Continue lowering the sample table assembly slowly until the ring is just **within the surface of the liquid.** At this juncture, the reading on the dial is still zero
9. Gradually increase the **torsion of the wire while** slowly lowering the table. Continue this until the liquid film breaks and the ring breaks free.
10. The dial reading at the breaking point to the liquid film is the force of the pull exerted on the **ring, or the apparent surface tension.**

11. **This apparent surface tension** must be **adjusted by using a correction factor** that accounts for the **circumference of the ring**, the size of wire used in the ring, and the **density of the liquid**. This can be obtained **from the charts given literature.**

❑ SPREADING COEFFICIENT

- The **concept of work of cohesion** and **work of adhesion** help to understand the spreading of one liquid on another and predict whether it would spread **spontaneously or not.**

- **There exists a mathematical relationship**, which can be used to forecast the **outcome of the situation called** as spreading **coefficient, denoted by** S.

- There are two possibilities, first, the liquid can spread over the surface of sublayer liquid or second, the added liquid **determining net loss in free energy**

- If a **force is applied on this liquid tube** to separate into two parts, then the work done is called the **work of cohesion.**

- If a force is applied to cause the liquids to separate, we have done three **things and the work done** is called **the work of adhesion (W$_a$)**

- The **spreading of liquid** is controlled by surface tensions of pure immiscible liquids and interfacial **tension between them.**

- **When a drop of liquid (oleic acid)** is placed on the surface of water, it will spread as a film if force of adhesion is greater than cohesive forces. This phenomena is **important in absorption** of medicament from dosage form **E.g:- from cream or lotion.**

- For the **stabilization of emulsion spreading** coefficient phenomena is useful.

Now consider the hypothetical cylinder (cross-section area, 1 cm²) of the sublayer **liquid S overlaid** with a similar section of the **spreading liquid L.**
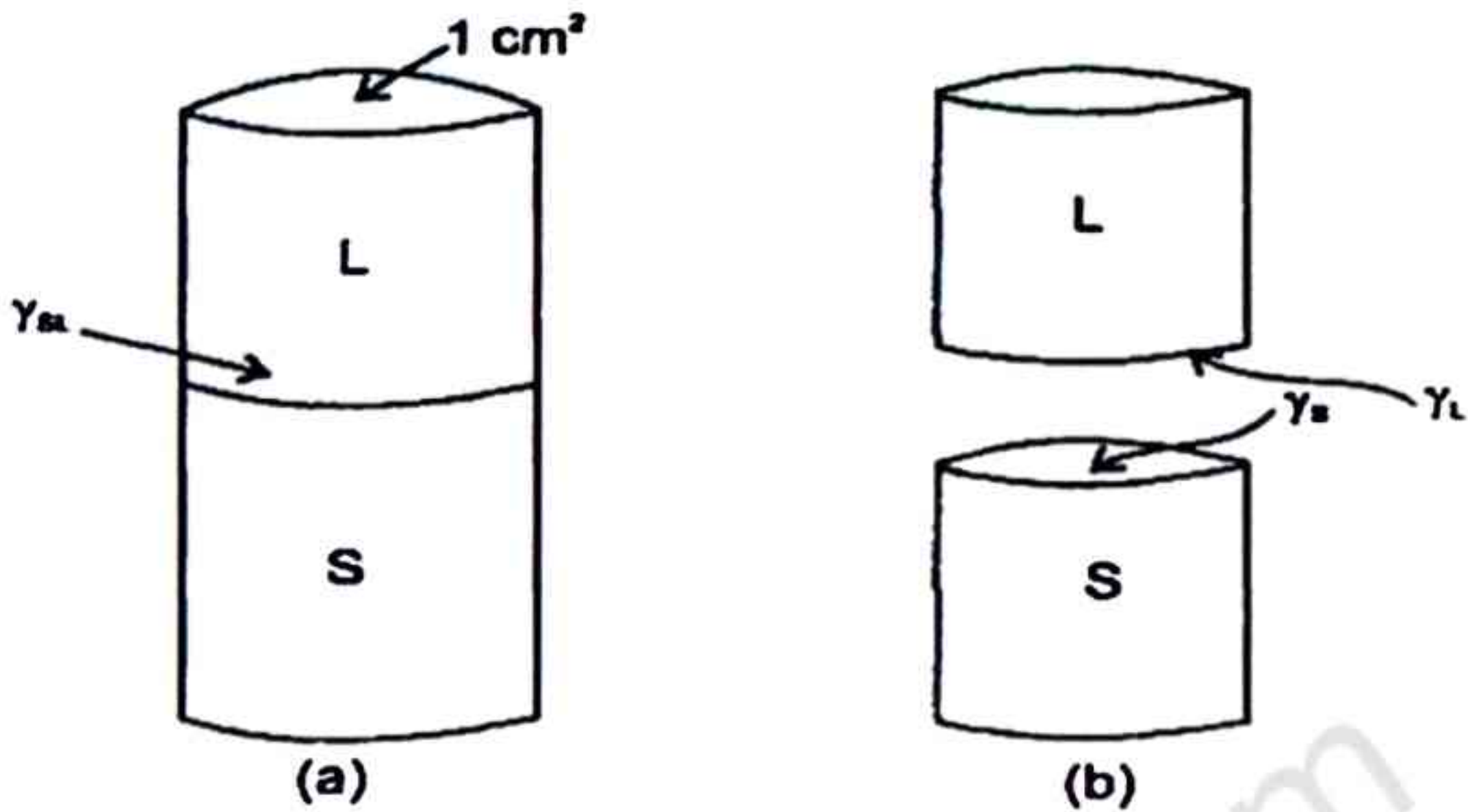

Fig :- Representation of the work of adhesion involved in separating a substrate and an overlying liquid

$$\text{The work of adhesion} = W_a = \gamma_L + \gamma_s - \gamma_{Ls} \quad\text{——— (1)}$$

Where,

- γ_L and γ_s are newly created surface tension and γ_{Ls} interfacial tension that has been **destroyed in the process.**

- The work of cohesion, required to separate the molecules of the spreading liquid so that it can flow over the **sublayer. Here is no interfacial tension.**

- Now consider a hypothetical cylinder is divided two **new surfaces are created.**

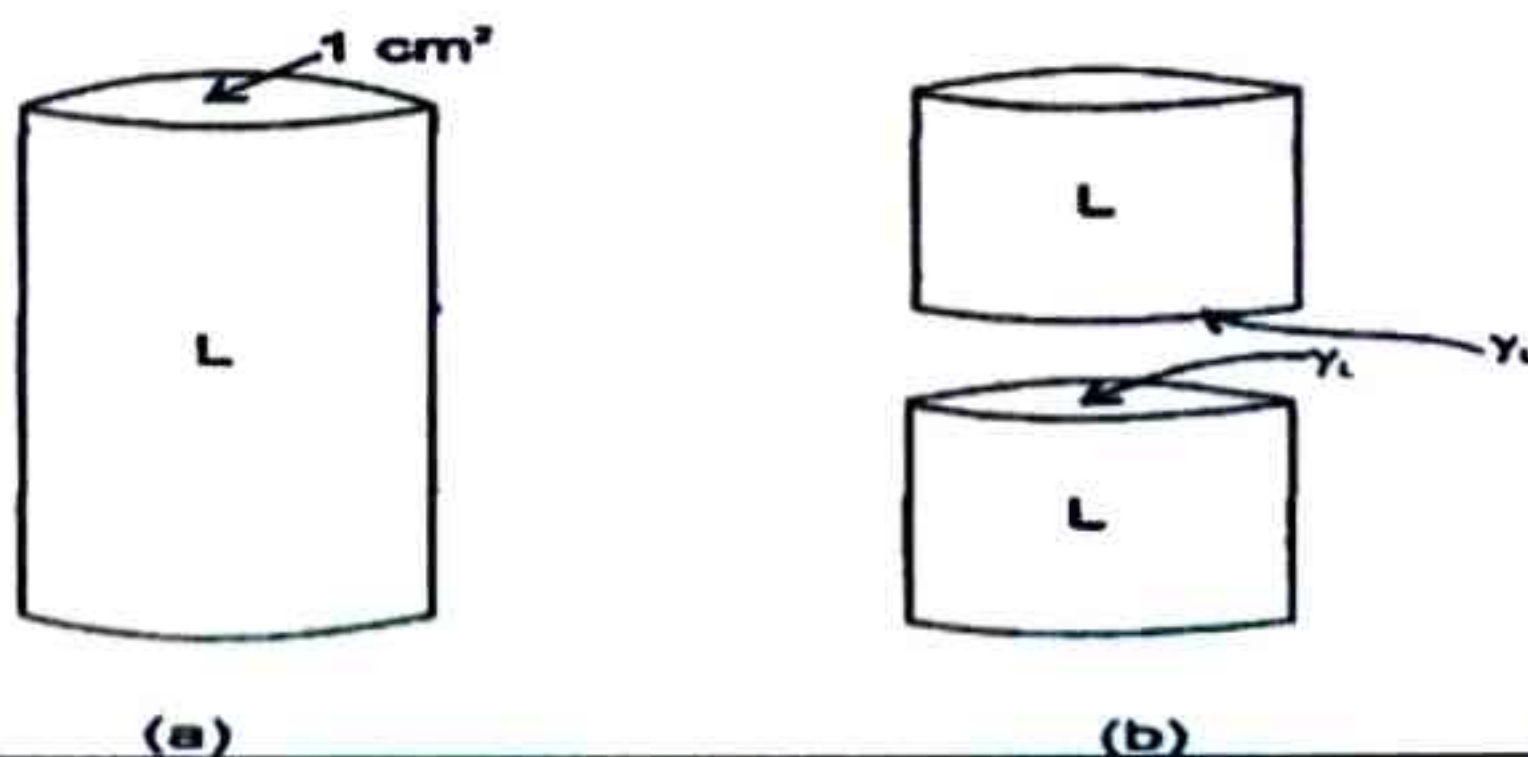$$\text{The work of cohesion} = W_c = 2\gamma_L \quad\text{——— (2)}$$

Fig :- Representation of the work of cohesion involved in separating like molecules in a liquid.

- The work of adhesion is greater than **the work of cohesion.**

- The spreading coefficient, S, is obtained from Eqs. 1 & 2

$$S = W_a - W_c$$

$$= (\gamma_L + \gamma_s - \gamma_{Ls}) - 2\gamma_L \quad \text{———— (3)}$$

$$S = \gamma_s - (\gamma_L + \gamma_{Ls}) \quad \text{———— (4)}$$

- If, S is **positive**, it indicates spreading and if negative indicates no spreading.

- For the organic liquids spread on water, initial spreading coefficient may be positive or negative, but the final **spreading coefficient always negative.**
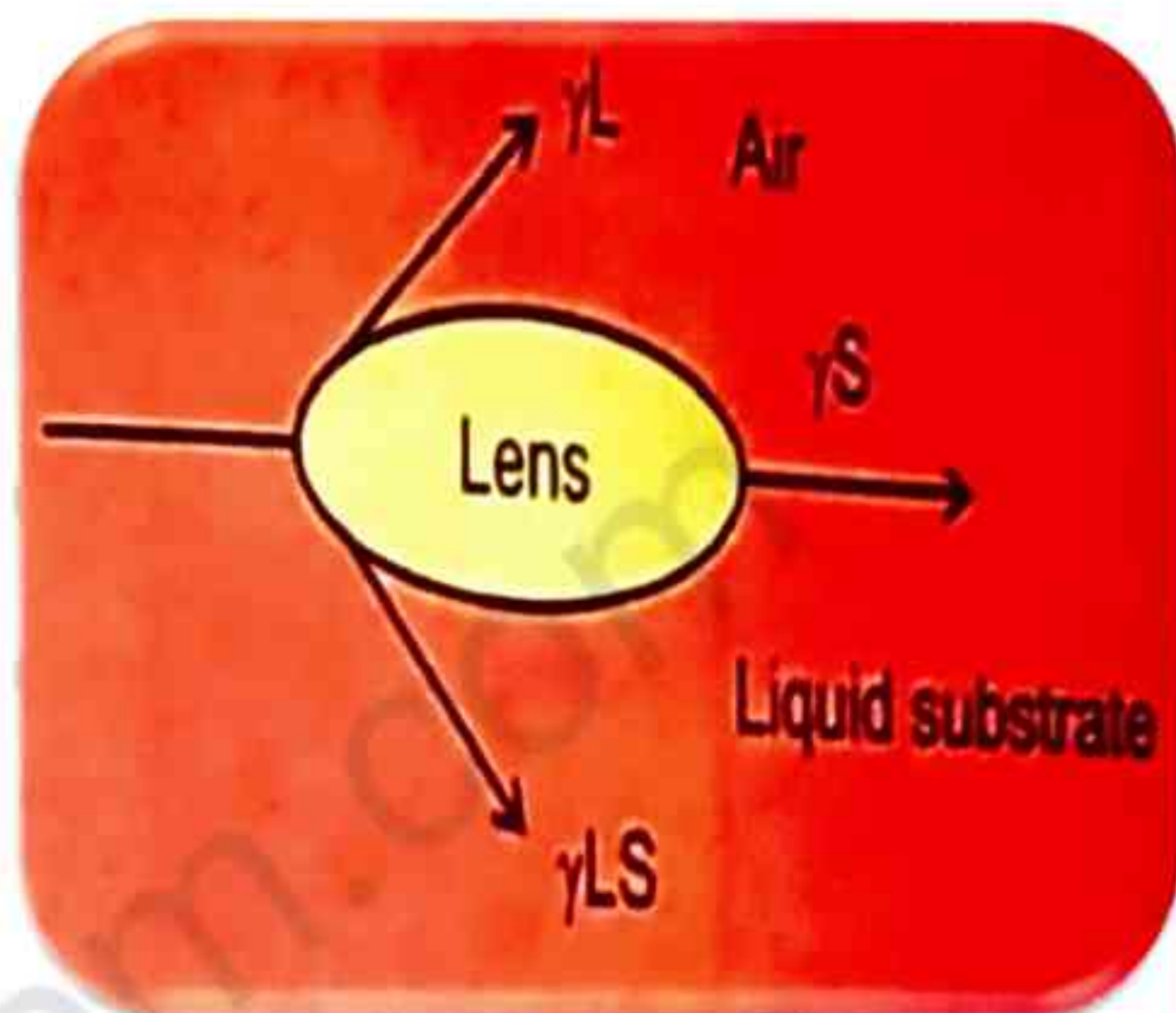
❖ **Initial spreading coefficient S at 20°**

SUBSTANCE	S (DYNES/CM)
Ethyl alcohol	50.4
Propionic acid	45.8
Ethyl ether	45.5
Chloroform	13
Benzene	8.9
Hexane	3.4

❖ **Application of spreading coefficient in Pharmacy:**

a) **Absorption of medicament** from dermatological dosage form.

   Ex :- Lotion, Cream

b) **Stabilization of emulsion**

c) **Coating of the tablets**

❑ ADSORPTION AT LIQUID INTERFACES

- The phenomenon of **adsorption is the adhesion** of atom, ions, or molecules from a gas, or liquid, a dissolved solid to the **surface or interface**

  i. Gas/liquid interface

  ii. Liquid/liquid interface

❖ **The adsorption at the interface is of two types:**

i) Positive adsorption

- **This is the adsorption** when certain solute **molecules and ions** when added to a liquid are partitioned in favor of **surface or the interface.**

- The resulted in the increase in the **concentration of such molecules** and ion at the **than in the bulk of the liquid** and lowers the surface free tension

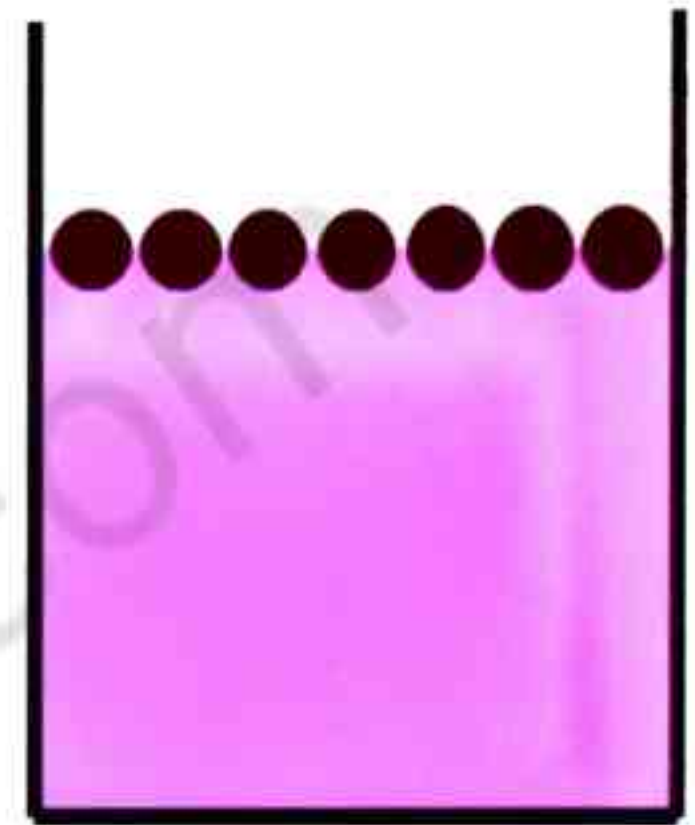- This surface **interface and interfacial** tension.

Fig :- Positive adsorbtion

ii) Negative adsorption

- This is the adsorption when **certain molecules** like inorganic electrolytes are partitioned in **favor of bulk of the liquid.**

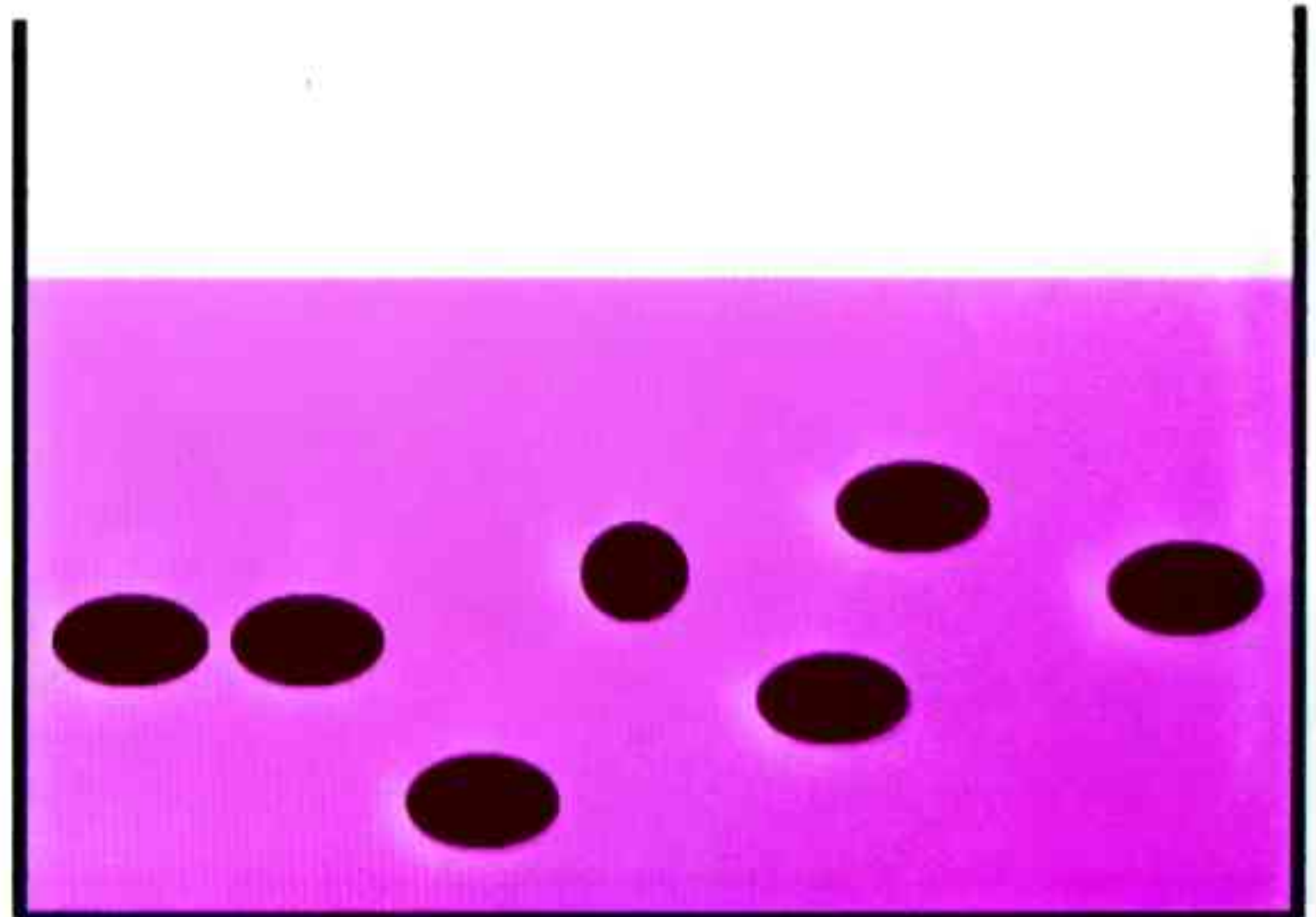- This resulted in the in the surface free energy and surface tension.

Fig :- Negative adsorbtion

❏ SURFACE ACTIVE AGENTS

- Molecules and ions that are adsorbed at the interface are **termed surface active agents or surfactants.**

- Surfactants or amphiphiles have a certain affinity for both polar and non polar solvents.

- Amphiphile may be **hydrophilic (water - loving); lipophilic (oil- loving)** or well balanced between these two extremes. **Ex: straight - chain alcohols, amines and acids.**

- ❖ **Types of surfactants**
   i. **Anionic Surfactant**
   ii. **Cationic Surfactant**
   iii.**Non-ionic surfactants**
   iv. **Amphoteric Surfactants**
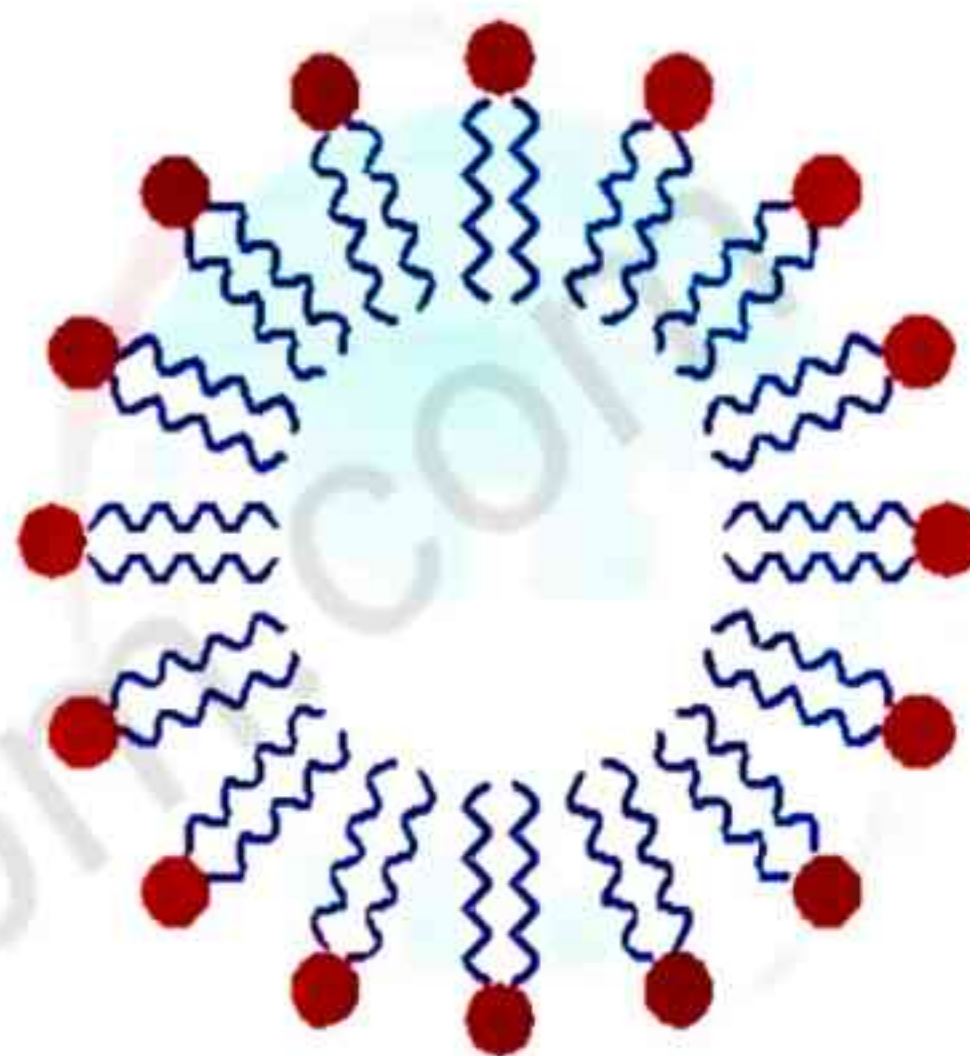
i) Anionic Surfactants

- Mostly anionic surfactants are those containing carboxylate, sulfonate and **sulfate ions.**

- **Carboxylate ions** are known as soaps and generally are prepared by the saponification of natural acid **glycerides in alkaline solution.**

ii) Non-ionic Surfactants

- Nonionic Surfactants do **not ionize in aqueous solution**, because their hydrophilic group is of a **non-dissociable type**, such as alcohol, phenol, ether, ester, or amide.

- **A large proportion of these nonionic surfactants** are made of hydrophilic portion (by the presence of a polyethylene glycol chain) and lipophilic **portion (alkyl or alkylbenzene)**

iii) Cationic Surfactants

- It includes long chain cations such as amine salts and quaternary ammonium salts. Mostly used as antimicrobial preservatives.

iv) Amphoteric Surfactants

- Those surfactants containing carboxylate or phosphate groups as the anion, and amino or quaternary ammonium groups as the cation.

- Zwitterionic (amphoteric) surfactants have both cationic and anionic centers attached to the same molecule.

- The anionic part can be variable and include sulfonates while cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations.

- Zwitterionic surfactants are often sensitive to pH and will behave as anionic or cationic based on pH.

Type of Surfactants
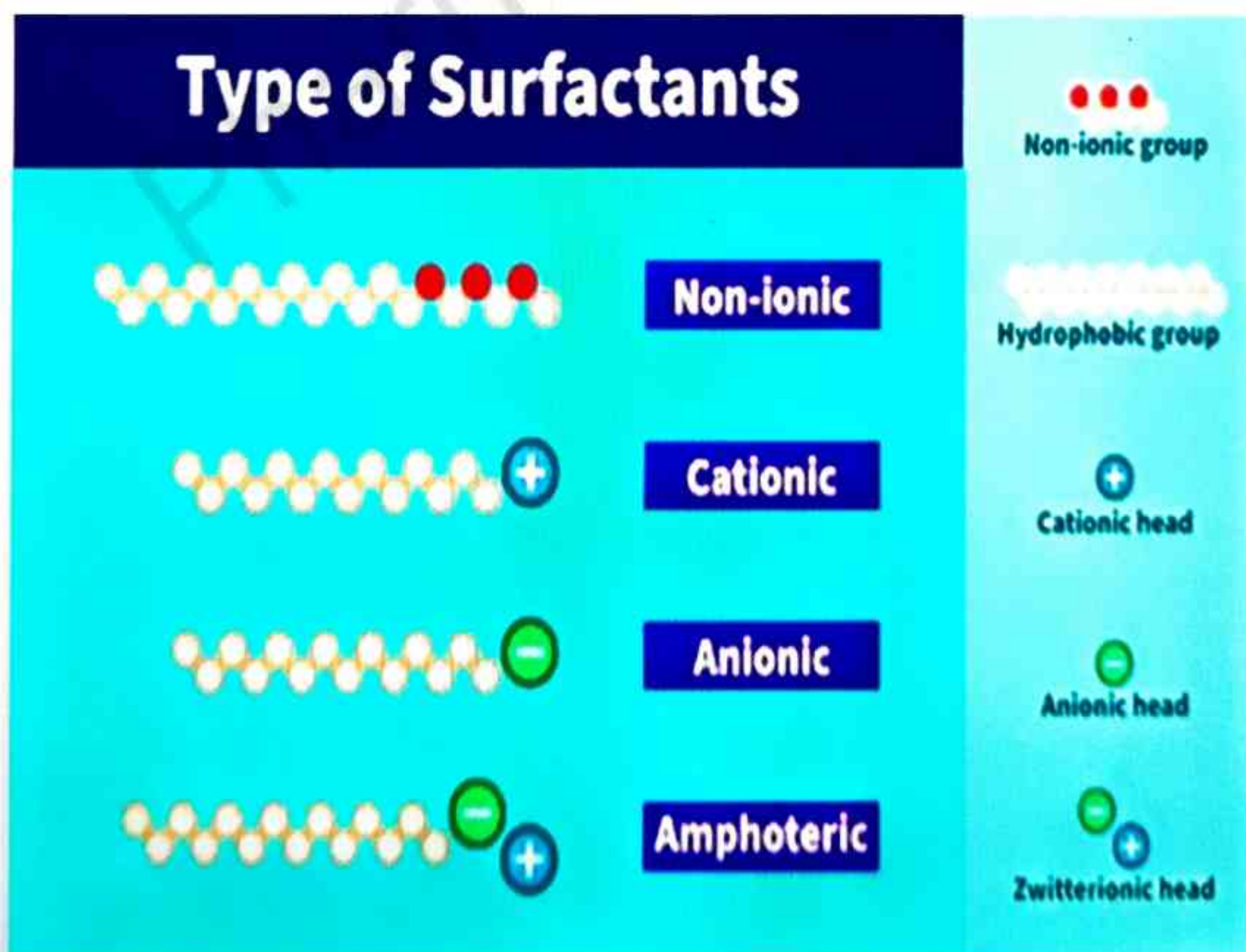
- **When a surfactant is dissolved** in water at low concentration, a fraction of **it will be adsorbed at the air-water** interface, and **remainder will reside** in the bulk in the **form of monomers**.

- **As the concentration is increased 50** or more monomers come together to form colloidal **aggregates termed micelles**.

- The concentration at which aggregation occurs is **called critical micelle concentration or CMC.**

- Surfactants are added in **pharmaceutical preparations** for various purposes such as **solubilizing agents**, wetting agents, foaming agents, suspending or **emulsifying agents etc.**
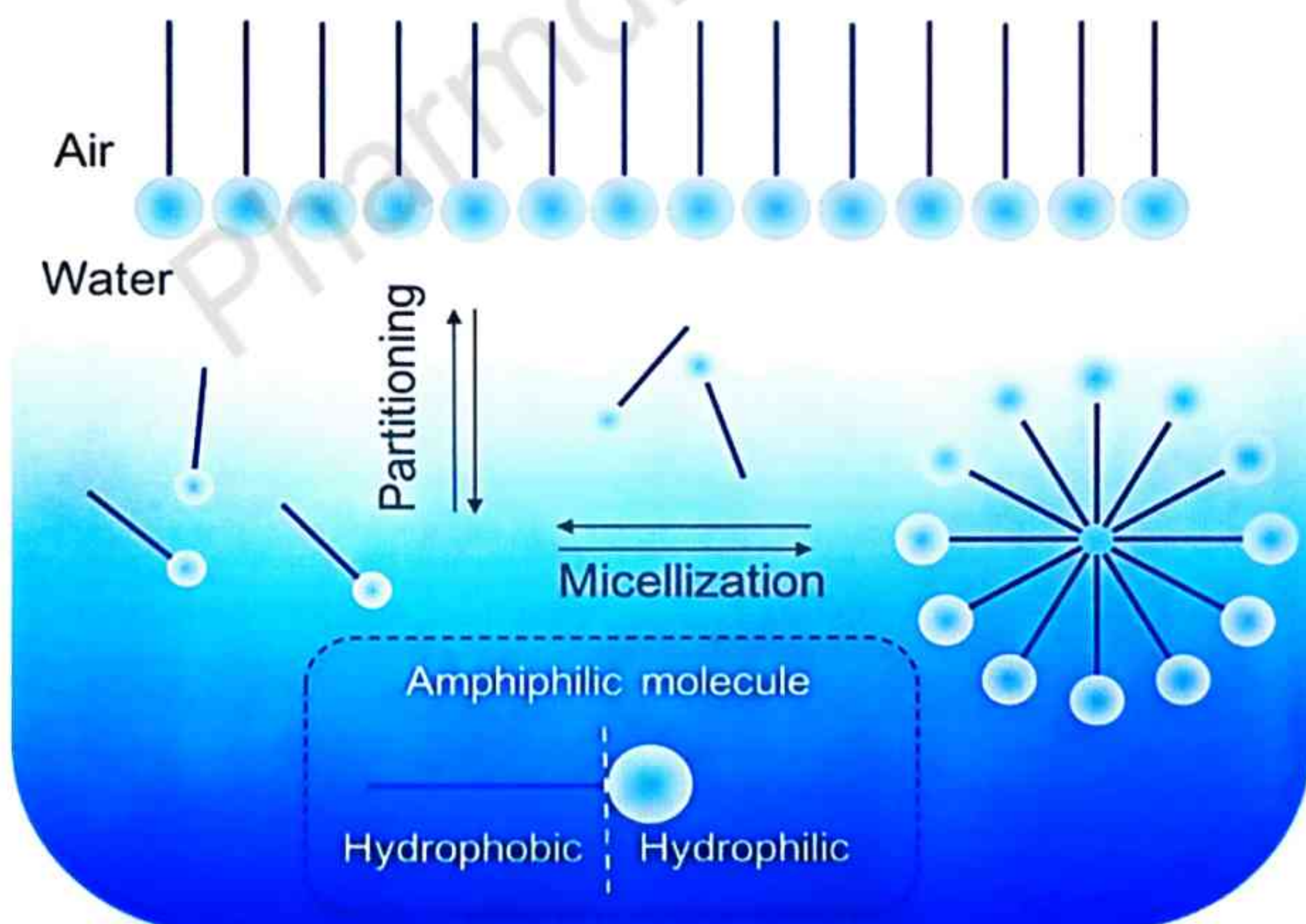

Fig :- Critical micelle concentration

❏ HLB SCALE

- **Griffin (1949) found** a useful method for calculating balanced mixture of emulsifying agents to form a **stable emulsion.**
- Generally, each emulsifying agent has a **hydrophilic portion** and a **lipophilic portion.**

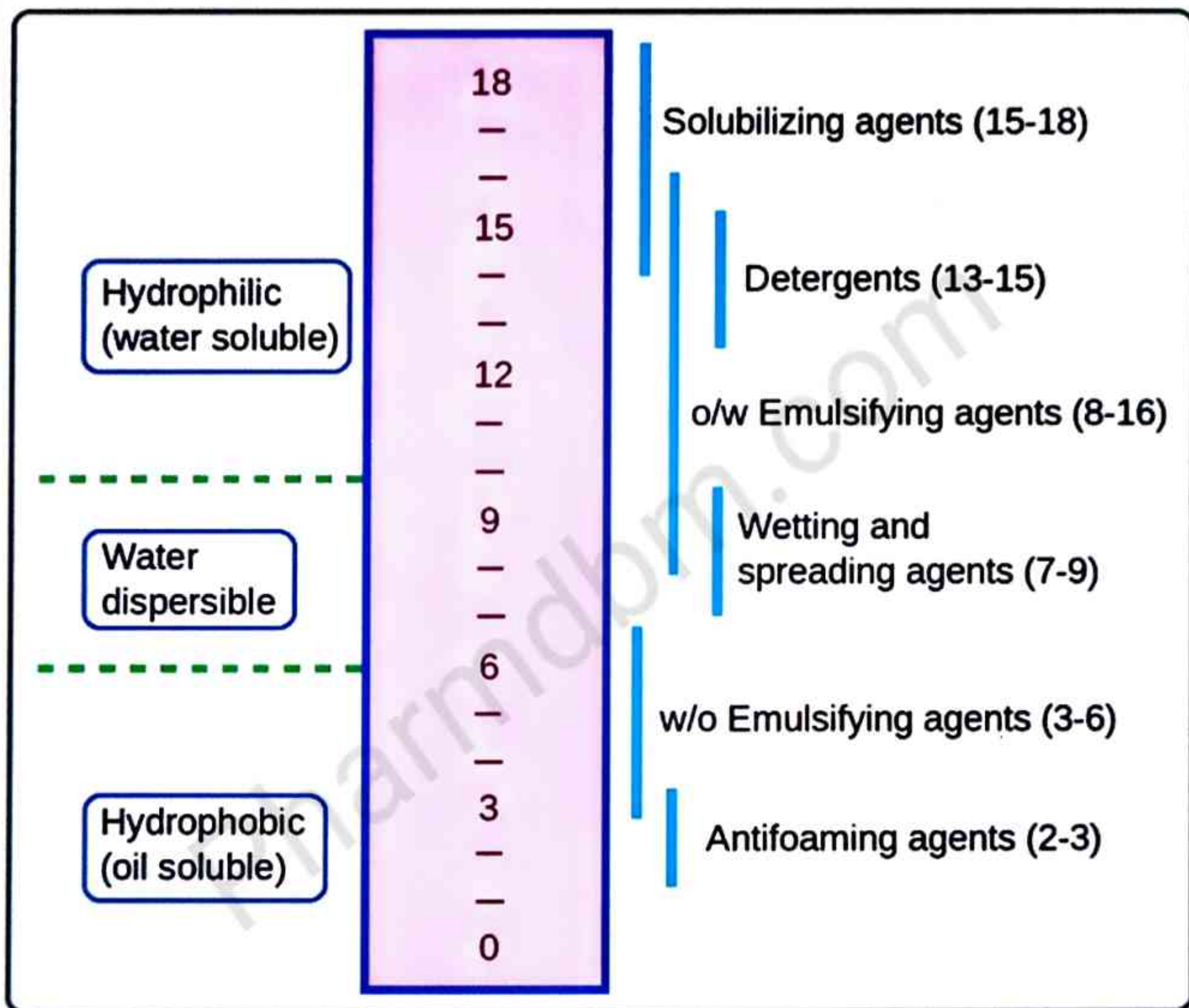**Fig :- A scale showing surfactant function on the basis of the HLB values.**

- Each portion might be more or less predominant resulting in providing **different types of emulsions.**
- A method has been devised to categorize emulsifying agents on the basis of their hydrophile - **lipophile balance or 'HLB'** Each emulsifying agent has in polarity.
- A scale is framed called HLB scale, **having values from 1 to 20.**

❖ Synthetic emulsifiers

TYPE	NAME OF EMULSIFIERS	HLB
ANIONIC	Glyceryl monostearate	11
	Triethanolamine oleate	12
	Sodium oleate	18
	Potassium oleate	20
	Sodium lauryl sulphate	40
CATIONIC	Benzalkonium chloride	25-30
	N-cetyl N –ethyl morpholinium Etho-sulphate	
NONIONIC	Sodium monooleate (span 80)	4.3
	Sodium monolaurate (span 20)	8.6
	Polyoxymethylene monostearate (tween 60)	11.1
	Polyoxymethylene sorbitan monooleate (tween 80)	15.0
	Polyoxymethylene sorbitan monolaurate	16.7

❖ Required HLB value of oils & wax

MATERIAL	FOR W/O	FOR O/W
Bees wax	4	12
Cetyl alcohol	-	15
Liquid paraffin	5	12
Soft paraffin	5	12
Wool fat	8	10

❖ Activity and HLB value of surfactants

| ACTIVITY	HLB
Antifoaming	1 to 3
Emulsifier (w/o)	3 to 6
Wetting agents	7 to 9
Emulsifiers (o/w)	8 to 18
Solubilizers	15 to 20
Detergents	13 to 15

❑ SOLUBILIZATION

- This technique was introduced **by Mc Bain in 1937**.

- It is the **dissolution of poorly soluble solute** molecules in water in presence of **surfactants and forms thermodynamically** stable solution.

- The process of dissolution in presence of surfactants have been described as the **formation of micelles (colloidal aggregate of surfactant)**, which enhances the solubility of poorly soluble solute, when surfactant of proper HLB is added in **low concentration to liquid**, it tends to **orient at air-liquid interface**.

❖ **Formation of micelles**

   a) **Surfactant in low concentration**

   b) **Surfactant in high concentration**

   c) **Surfactant in the concentration of CMC**
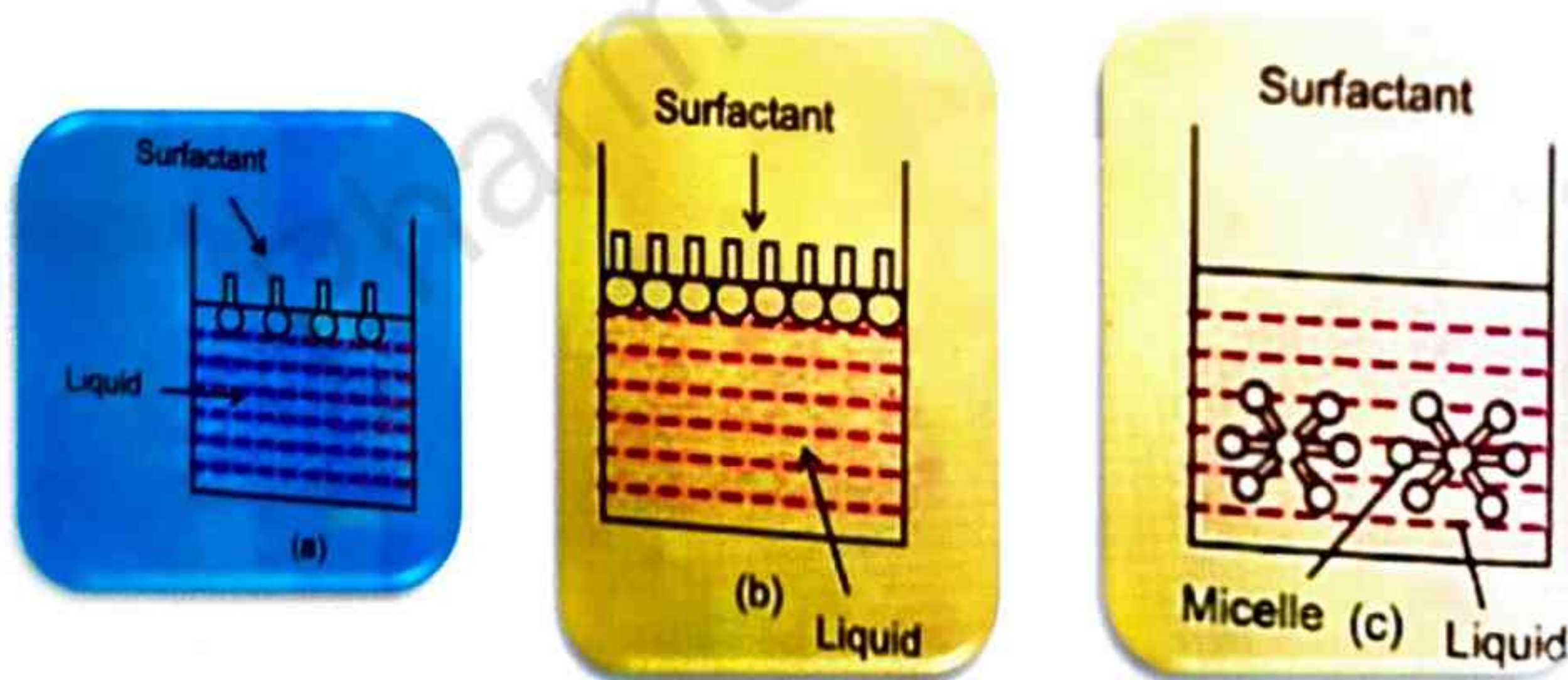
- If surfactant is continued to be added in higher concentrations, air-liquid interface is fully occupied, **Figure (b)**.

- At still higher concentrations, the surfactant molecules of ions are forced to go into the bulk of the liquid, **when the particular concentration** of **surfactant molecule is maintained** in the system, aggregates of surfactants are formed **called micelles, figure (c)**.

- The concentration of surfactant at which micelles formation takes place is called **critical micelle concentration (cmc).**

- **Micelles may be of various shapes** like:- **spherical, sausage, rod** or **lamellar.**

- Micelle formation increases the solubility of a **solute by virtue** of its dissolving in or being **absorbed onto the micelle.**

- **This function of surfactant** starts only at **cmc and increases** with the concentration of the micelles.

- As such cresol has **only 2% v/v solubility** in water but with soap solution we can dissolve up to 50% v/v cresol in **water (Lysol solution).**
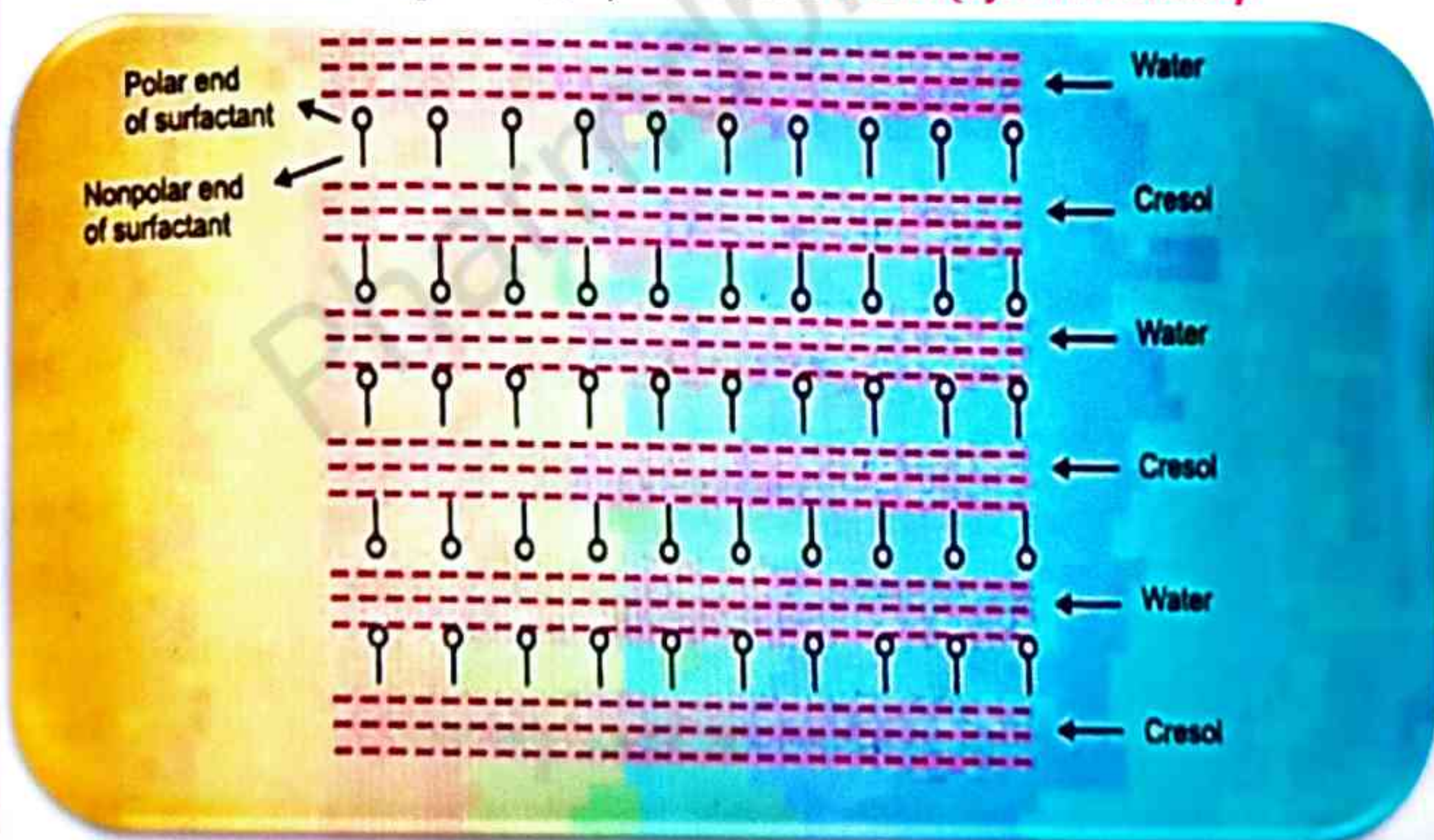

Fig :- Lamellar micelles solubilize the cresol in water

- The technique is useful to solubilize many water insoluble **vitamins like A, D and K** and to prepare solutions of **Chloroxylenol and Hexachlorophene.**

❑ DETERGENCY

- Detergency is a **complex process involving** the removal of foreign matter from surfaces.

- **Surfactants are used for the** removal of dirt **through the detergency effect.**

- Initial wetting of the dirt and of the surface to be cleaned is carried out by deflocculation and **suspension or emulsification** or solubilization of the dirt particles.

- It also involves foaming of the **agent for entertainment** and washing **away of the particles.**

- A wetting agent that when **dissolved in water**, lowers the advancing contact angle, aids in displacing an air phase at the surface and replacing it with a liquid phase.

❖ **Wetting agents are useful in :-**

i. Displacement of air from sulfur, charcoal and other powders for dispersing these **drugs in liquid vehicles**

The Tongue - Mucous Membrane

ii. Displacement of air from the matrix of cotton pads and bandages so that medicinal solutions may be **absorbed** for application to various **body areas.**

iii. Displacement of dirt and debris **using detergents** in the washing of wounds.

iv. The application of medicinal lotions and sprays to the surface of the skin **and mucous membrane**
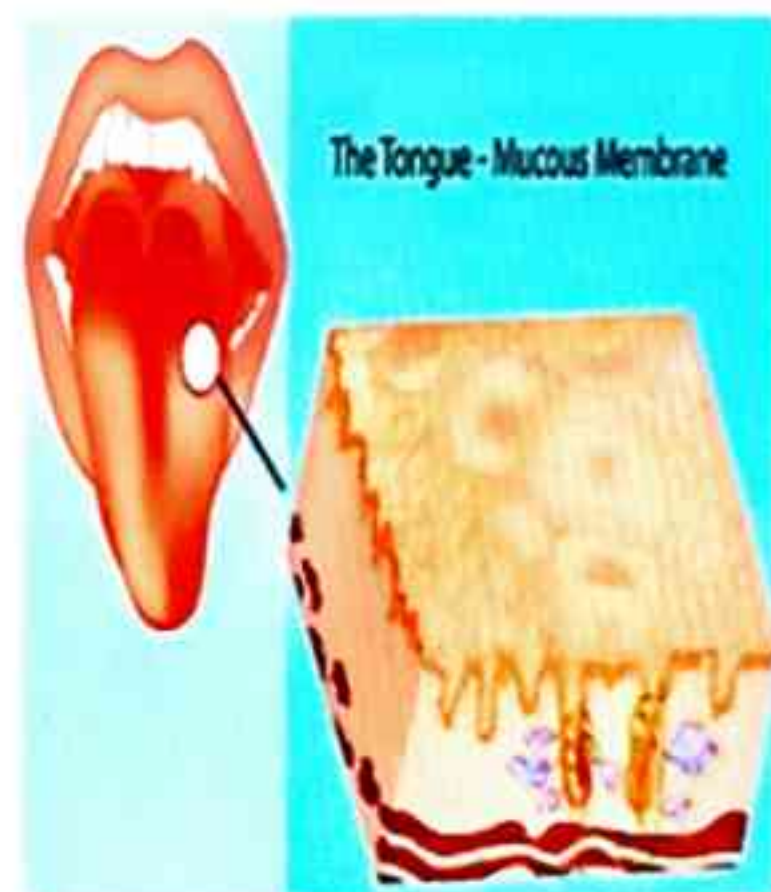
❑ ADSORPTION AT SOLID INTERFACE

- The substance in **adsorbed state is called adsorbate.**
- When **adsorption occurs at the interface between** liquid and solid, the solid is usually called the adsorbent for **gas-liquid interfaces** sometimes the **liquid is called adsorbent.**

➤ **The adsorption process is generally classified as**

   i.   **Physisorption** ii. **Chemisorption**

❖ Solid-Gas Adsorption

- Solids adsorb gases to certain extent, but the phenomenon is not prominent unless adsorbent possess large surface area.
- The adsorption of gas on to a **solid surface is of mainly of two types.**

i) Physisorption

- Physisorption is **the** physical bonding of gas molecules **to the surface of a solid or liquid that the gas comes into contact with at low temperatures.**
- This occurs due **to Van der Waals forces.**
- The weak, long-range bonding is not surface specific and takes place between all **gas molecules on any surface.**

➤ **Characteristics of physisorption**

   i.   It is a general phenomenon and occurs in **any solid/fluid systems.**
   ii. **Minimum change** in electronic state of adsorbate and adsorbent is observed.

ii) Chemisorption

- Chemisorption is an **adsorption process** that involves a chemical reaction and that implies the formation of a covalent bond between the molecule and one or **more atoms on the surface.**

➤ Characteristics of Chemisorption:

i. The phenomenon is characterized **by chemical specificity.**

ii. Change in electronic state may be detectable by suitable physical means (Eg:- UV, IR, microwave spectroscopy, conductivity etc.)

➤ Factors Affecting Adsorption

i) Surface area of adsorbent

- Being surface phenomena extent of adsorption depends on available **surface area of adsorbent.**

- Finely divided materials since has large surface area, more adsorption is **observed on their surfaces.**

ii) Nature of adsorbate

- The amount of adsorbate adsorbed on solids depends on its nature, easily liquefiable gases **adsorbed to greater extent.**

iii) Temperature

- As seen under the characteristics of physical adsorption, it decreases with increase in temperature, while chemical adsorption increases with **increase in temperature.**

iv) Pressure

- **Applying LeChatelier's principle,** dynamic equilibrium exists between adsorbed gas molecules and molecules in contact with adsorbate.

- In fact, it is observed that increase in **pressure increases adsorption.**

❖ ADSORPTION ISOTHERMS

Adsorption isotherm is the **relation between the quantity** of adsorbate adsorbed and the partial pressure in the gas phase (or composition of bulk phase, in adsorptions from liquids) under equilibrium conditions at **constant temperature.**

❖ Types of Isotherms:

Types of Isotherms:
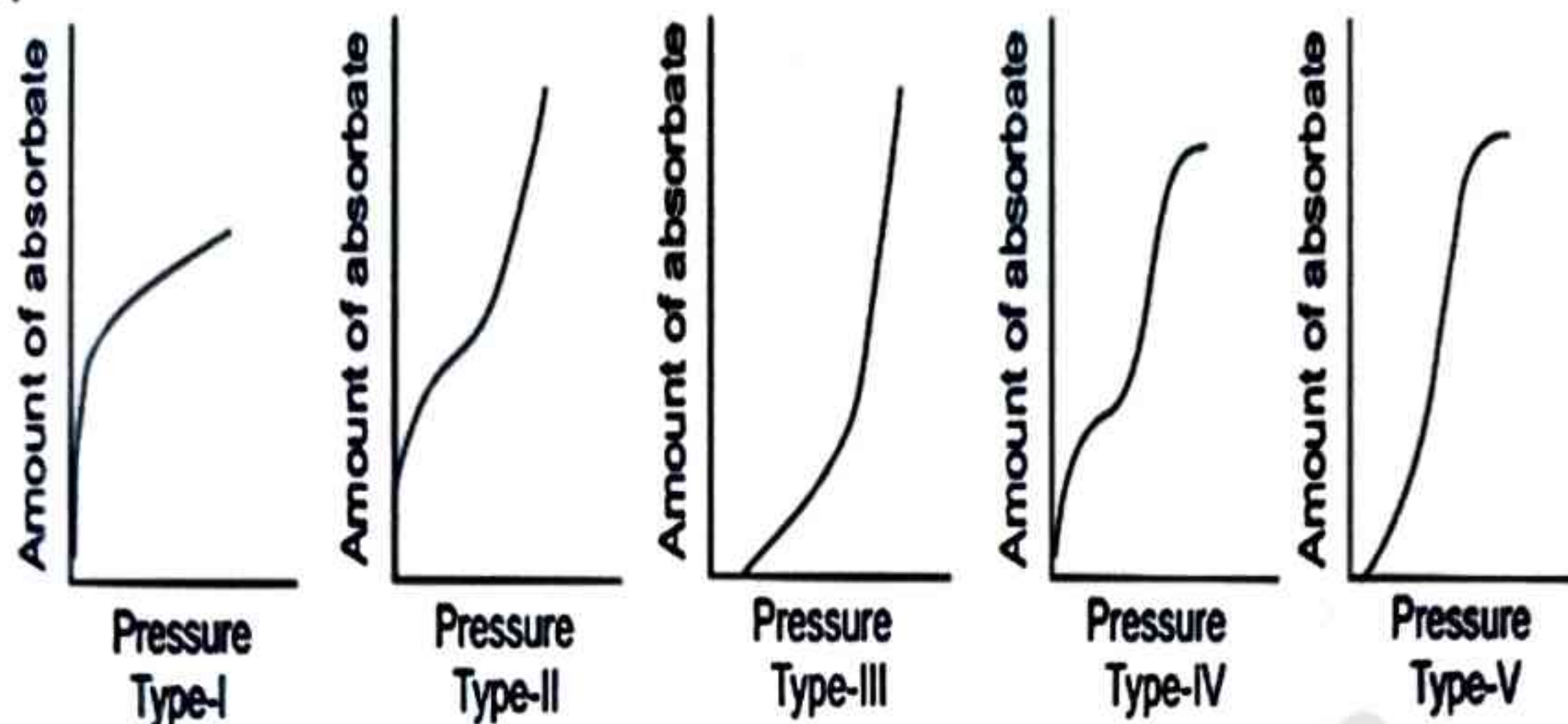
> ## Type-I

- **Langmuir and Freundlich isotherms** are of Type-I where adsorption takes place on non-porous solids.

- It represents behaviour of **nitrogen or oxygen on charcoal**.

- Total surface area can be **determined from this isotherm** by multiplying the total number of **molecules in the volume of gas** adsorbed by the **cross-sectional area of the molecule**.

> ## Type-II (BET EQUATION)

- In this type of isotherm gases are physically adsorbed on a non-porous solid forming **monolayer followed by multilayer formation**.

- The first inflection in the curve represents formation of monolayer and subsequent increase in pressure **shows multilayer adsorption**.

- This isotherm is explained by **BET (Branauer, Emmett and Teller) equation**.

$$\left[\frac{P}{y}(P_0 - P)\right] = \left[\frac{1}{y_m b}\right] + \left[\frac{(b-1)}{y_m b}\right] \times \left[\frac{P}{P_0}\right]$$

- ✓ **P is pressure of the adsorbate**
- ✓ **y is mass of vapour per gram of adsorbent**
- ✓ **P_0 is vapor pressure at saturation of adsorbent by adsorbate**
- ✓ **y_m is amount of vapour adsorbed per unit mass of adsorbent**
- ✓ **b is constant**

➤ Type-III

- This **isotherm is rarely observed for example**, bromine and iodine on silica gel, where heat of adsorption in the first layer is less than the latent heat of **condensation in the next layers.**
- The constant b of the **BET equation is less than two.**

➤ Type-IV

- **This isotherm is typical of adsorption** onto porous solids where if the first point is extrapolated to **zero pressure repres**ents the amount of gas required in forming **monolayer on solid surface.**
- **Condensation within the capil**laries is responsible for the further adsorption.
- The example of this type is **adsorption of benzene** on ferric oxide and **silica gel.**

➤ Type-V

- It is like type-III adsorption as **capillary condensation** is observed on the porous solids for example, adsorption of water vapor on **charcoal at 100°C.**

Type-I

i. **Freundlich isotherms**

ii. **Langmuir**

Freundlich adsorption isotherm

Langmuir adsorption isotherm
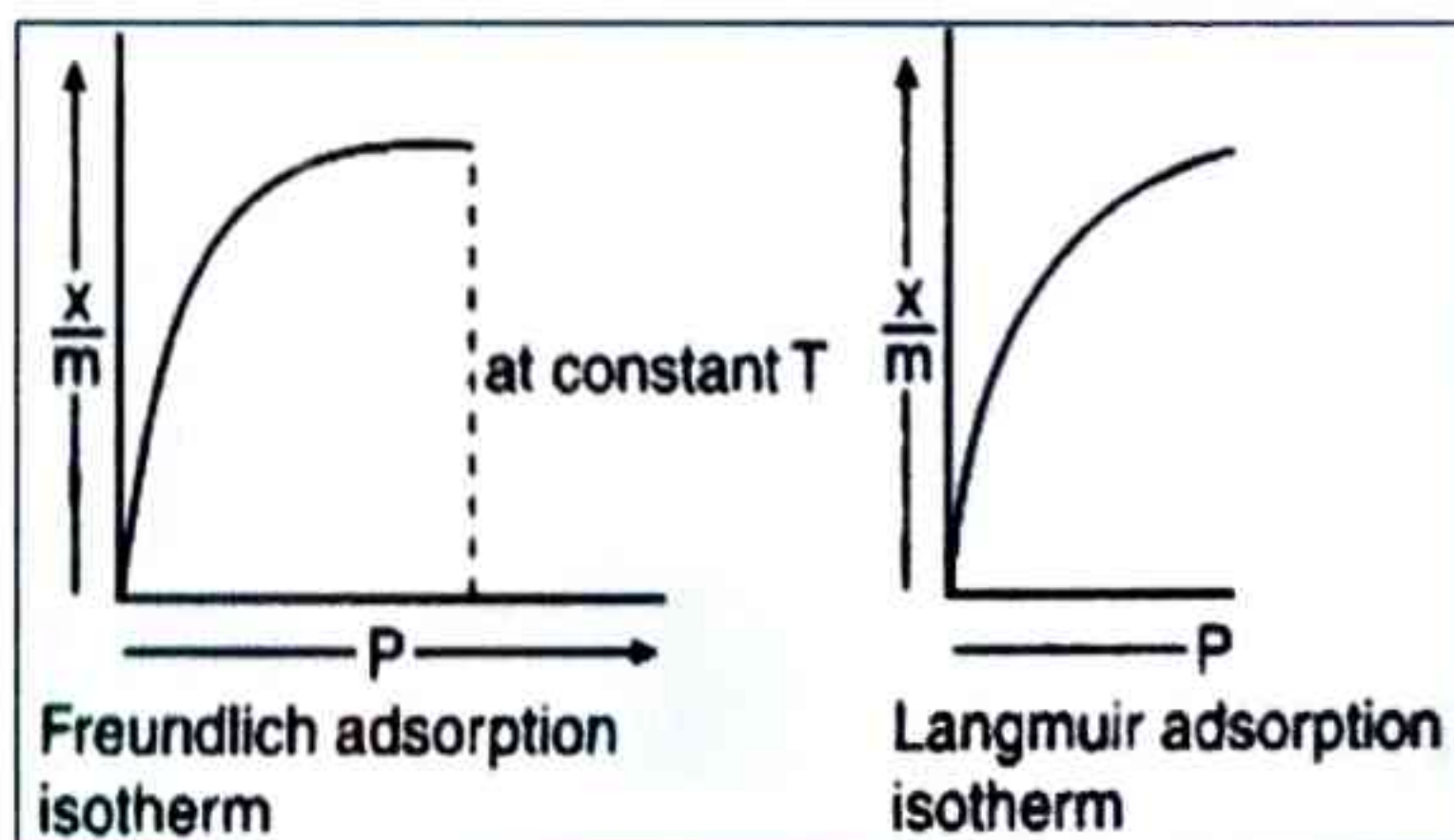
❖ Freundlich's Adsorption Isotherm:

The scientist **Freundlich's studied adsorption** of gas on solid and from the experimental data; he gave empirical equation called equation of **Freudlich's adsorption isotherm**,

$$y = \frac{w}{m} = kP^{1/b}$$

Where,

- ✓ y = Amount
- ✓ (w) = Adsorbate adsorbed by m gram of adsorbent at equilibrium
- ✓ P = Pressure and are determined from the experiment at constant temperature.
- ✓ The constants k and b depends on nature of adsorbate and adsorbent as well as on temperature.
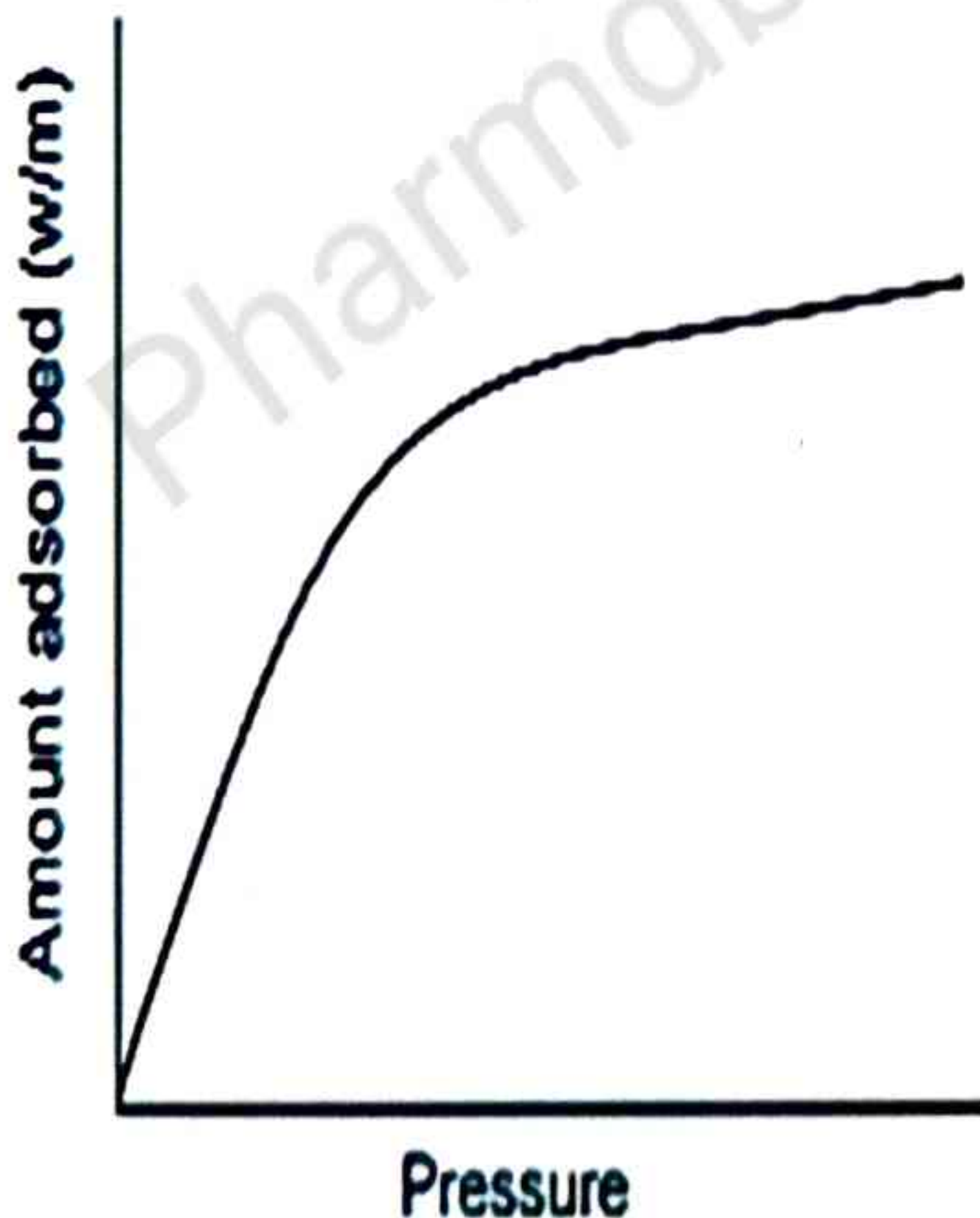

Fig :- Freundlich adsorption isotherm

❖ Langmuir Adsorption Isotherm:

- In 1916, scientist **Irving Langmuir (1916)** published a new isotherm for gases adsorbed on solids, which retained his name.

- It is an empirical isotherm **derived from assumptions.**

➢ **There are certain assumptions on which Langmuir proposed his theory, they are**

  i. **Fixed number of vacant** or adsorption sites are available on the surface of solid.

  ii. All the vacant sites are of equal size and **shape on the surface of adsorbent.**

  iii. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is **released during this process.**

  iv. Adsorption is **monolayer or unilayer.**

  v. Dynamic equilibrium exists between **adsorbed gaseous molecule** and the free **gaseous molecules.**

- **Langmuir had developed** an equation based on the theory that the molecules or atoms of gas are adsorbed on active **sites of the solid to form a layer one molecule thick.**

- If fraction of **active centers occupied** on surface of adsorbent by gas molecules at **pressure P is expressed as** θ then the fraction of sites **unoccupied is $1 - \theta$.**

- The rate of adsorption

  ✓ (R_1) = proportional to **unoccupied spots and the**

  ✓ P = pressure

  ✓ (R_2) = The rate of evaporation of molecule bound on surface is proportional to the fraction of surface occupied, θ.

- ✓ $R_1 \propto$ fraction of sites unoccupied × Pressure
- ✓ $R_1 = k_1 (1 - \theta) P$ ——————————————— (1)
- ✓ $R_2 \propto$ Fraction of sites occupied
- ✓ $R_2 = k_2 \theta$ ————————————— (2)

At equilibrium,

$$R_1 = R_2$$

$$k_1(1 - \theta) P = k_2 \theta \text{——————————————(3)}$$

After rearranging equation

$$\theta = \frac{k_1 P}{k_2 + k_1 P}$$

$$\theta = \frac{\left(\dfrac{K_1}{K_2}\right) P}{1 + \left(\dfrac{K_1}{K_2}\right) P} \text{———————————————— (4)}$$

Replacing θ by y/y_m and k_1/k_2 by b.

Where,

y = is mass of gas adsorbed per gram of adsorbent at

P = pressure at constant temperature

y_m = mass of gas that adsorbed on 1 gram of adsorbent to form complete monolayer.

On substituting the values for θ and k_1/k_2 the following equation is obtained

$$\frac{y}{ym} = \frac{bp}{1 + bp} \text{————————————————— (5)}$$

$$y = \frac{y_m bp}{1 + bp} \text{—————————————————— (6)}$$

- The **equation (6) is known** as **Langmuir adsorption isotherm equation** and it can also be **written in the following form.**
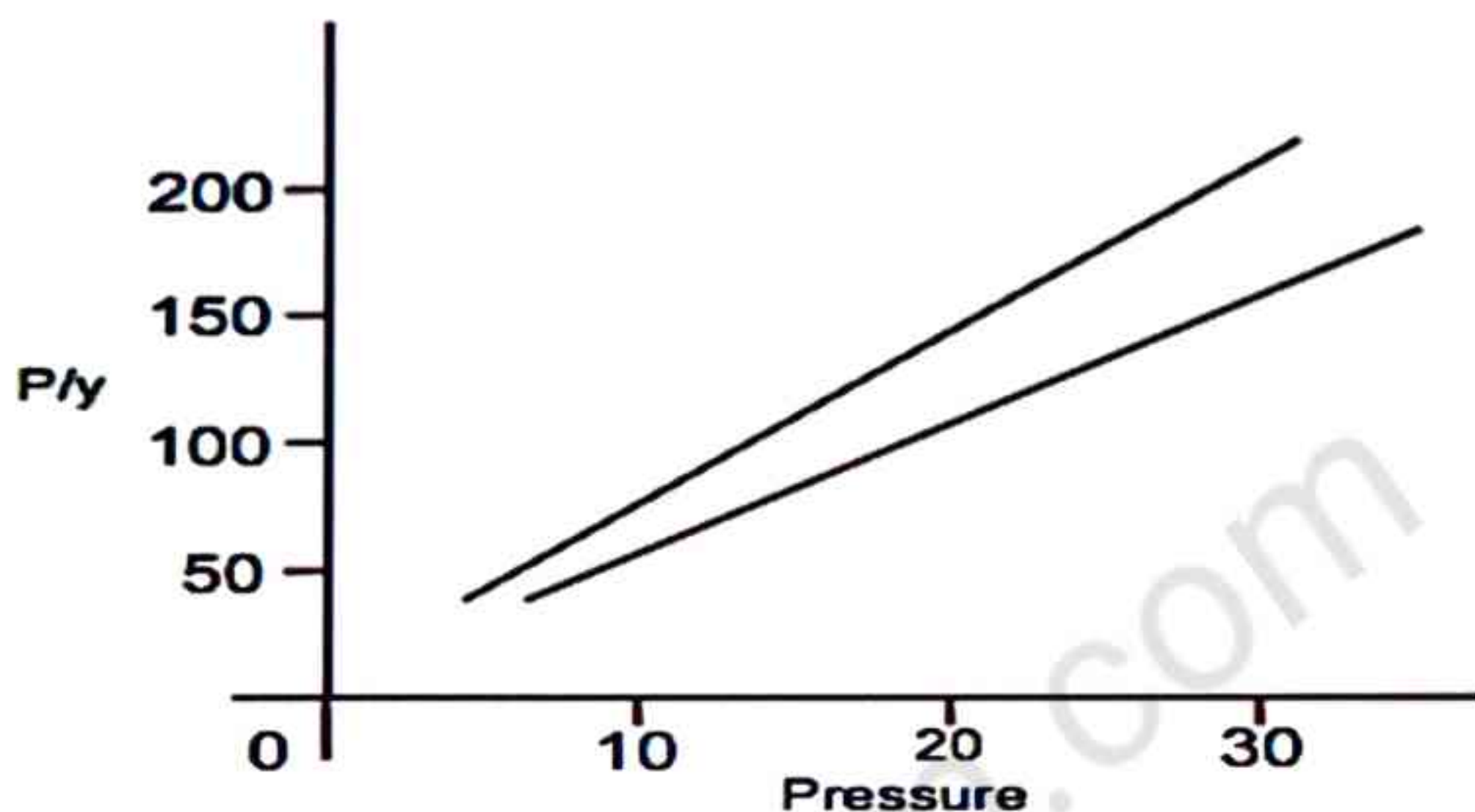
$$\frac{P}{y} = \frac{1}{y_m b} + \frac{P}{y_m} \hspace{2cm} (7)$$

Fig :-Langmuir adsorption isotherm

- **By plotting a graph of P/y against P.**
- **We get a straight line with slope equal to y_m and intercept as b.**

❖ Applications of adsorption

i. **Adsorption of poisonous** gases at the **surface of mask.** It is used by the coal miners. **Adsorption of traces of air to remove from the devices.**

ii. Adsorption of moisture in the medicine by silica gel pellets in order to **store in a controlled humidity.**

iii. Adsorption of coloring agent by **charcoal to get a clear solution.**

iv. **Adsorption of catalysts** on reactants in order to **increase the rate of reaction**