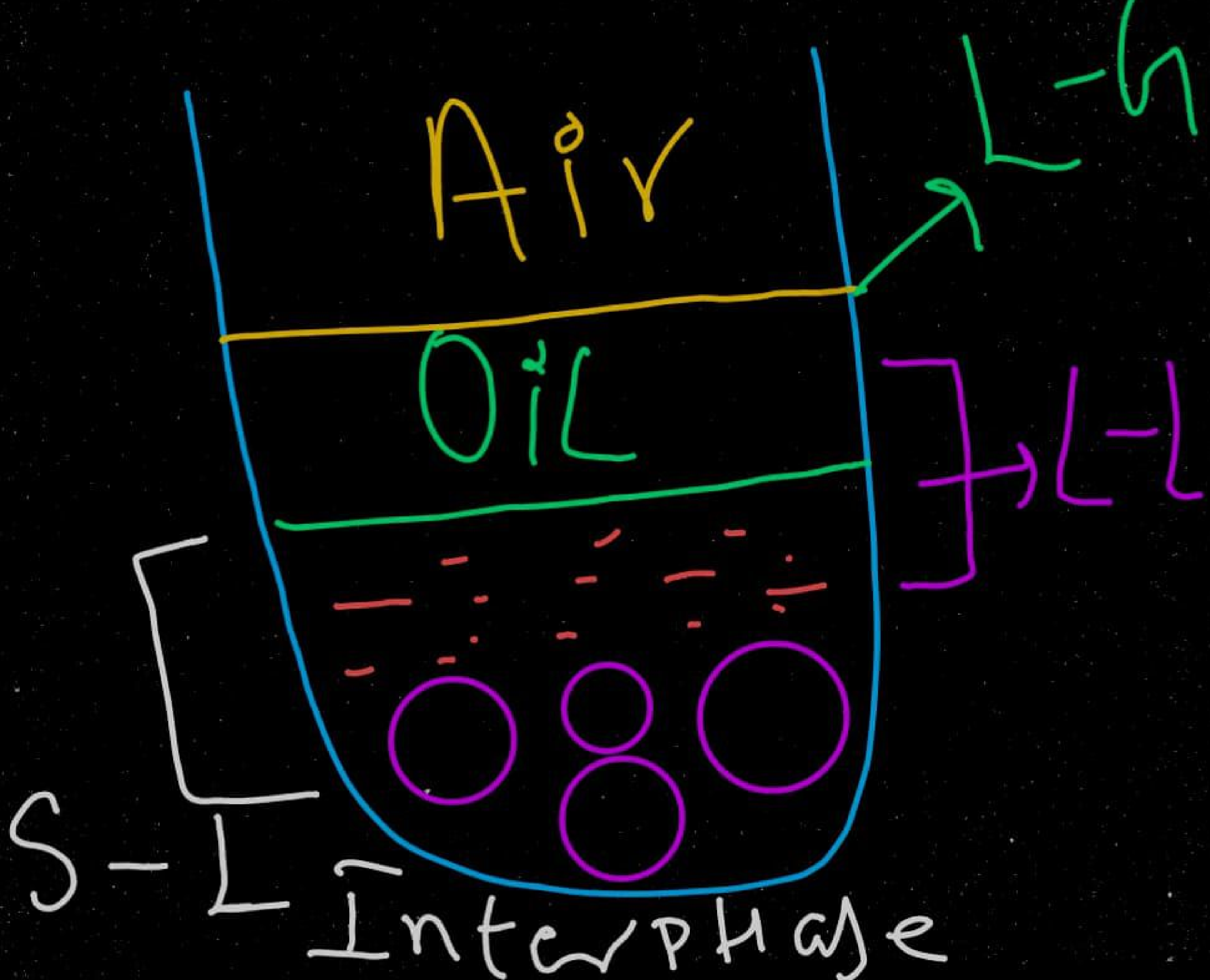
# UNIT – 3
# PHYSICAL PHARMACEUTICS

# SURFACE & INTERFACIAL PHENOMENA


Air
Oil
L-G
L-L
S-L
Interphase

# INTERFACES-

- Solid-solid: forms between 2 solids
- Liquid-liquid: forms between 2 liquids but liquids do not mix 
- Liquid-gas : forms between liquid and gas and is called as surface
- Solid-gas: forms between solid and gas and also called surface

- *Interface* is the boundary between two or more phases exist together

- It forms when 2 or more immiscible substance contact with each other

- Several types of interface can exist depending on whether the two adjacent phases are in solid, liquid or gaseous state.
- Important of Interfacial phenomena in pharmacy:
  - Adsorption of drugs onto solid adjuncts in dosage forms
  - Penetration of molecules through biological membranes
  - Emulsion formation and stability
  - The dispersion of insoluble particles in liquid media to form suspensions.

- To keep the equilibrium, an equal force must be applied to oppose the inward tension in the surface.

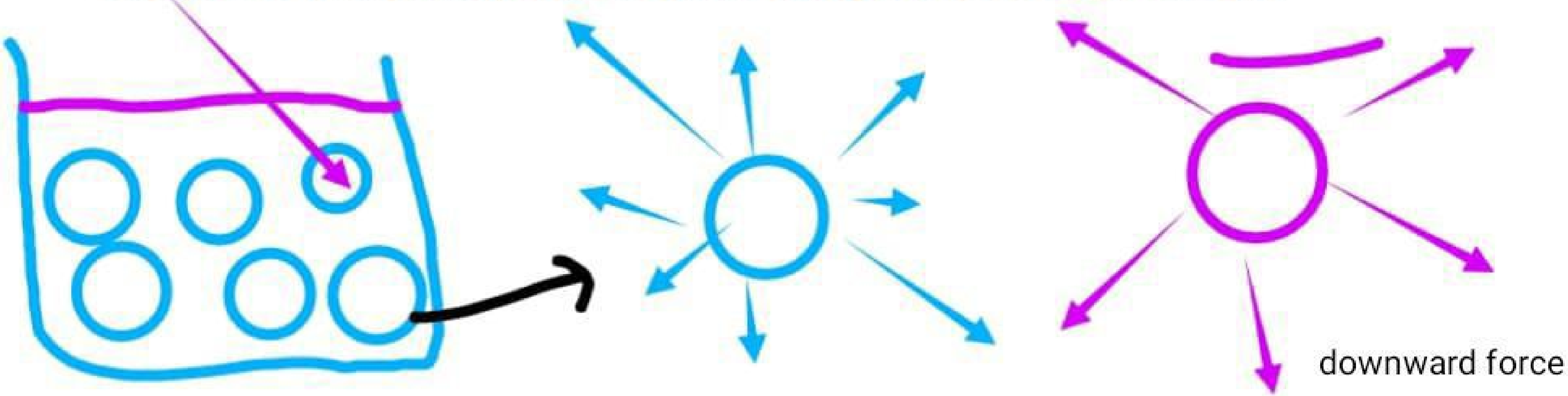
Thus *SURFACE TENSION* [$\gamma$] is the force per unit length that must be applied parallel to the surface so as to counterbalance the net inward pull and has the units of dyne/cm

*INTERFACIAL TENSION* is the force per unit length existing at the interface between two immiscible liquid phases and has the units of dyne/cm.



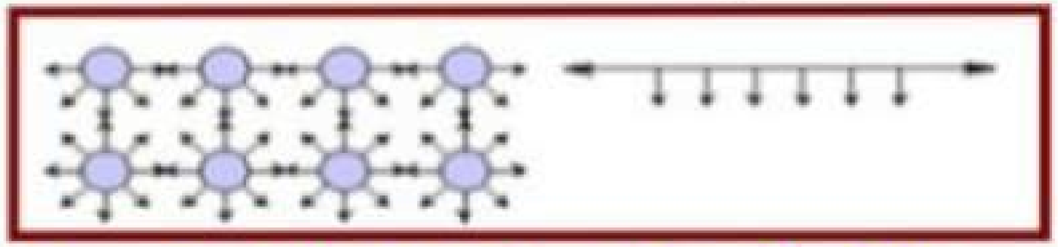
[DEPTH OF BIOLOGY]

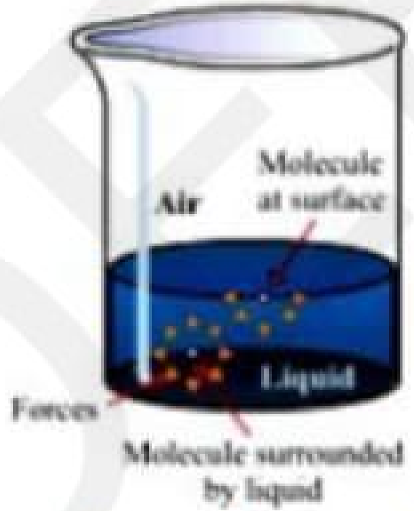
- if two liquid are completely miscible then no interficial tension exist between them



## Surface and Interfacial Tensions

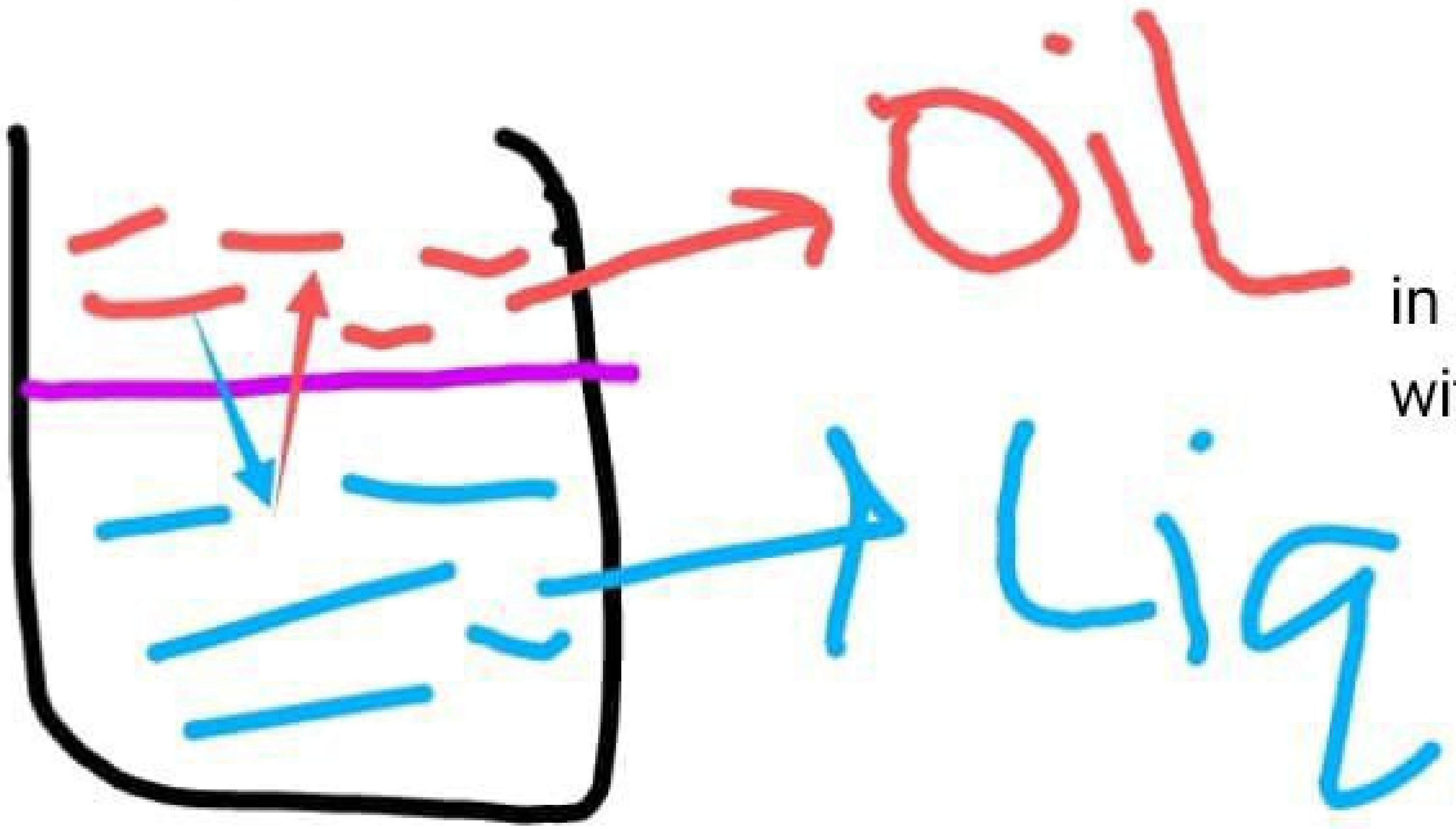
- In the liquid state, the cohesive forces between adjacent molecules are well developed.






- *For the molecules in the bulk of a liquid*

They are surrounded in all directions by other molecules for which they have an equal attraction.




in liq. molecules are attract with cohesive force

[DEPTH OF BIOLOGY]

# SURFACE FREE ENERGY

To increase surface area.😍

The work W required to create a unit area of surface is known as ***SURFACE FREE ENERGY/UNIT AREA*** (ergs/cm $^2$)



*erg = dyne . cm*

Its equivalent to the surface tension γ

Thus the greater the area A of interfacial contact between the phases, the greater the free energy.

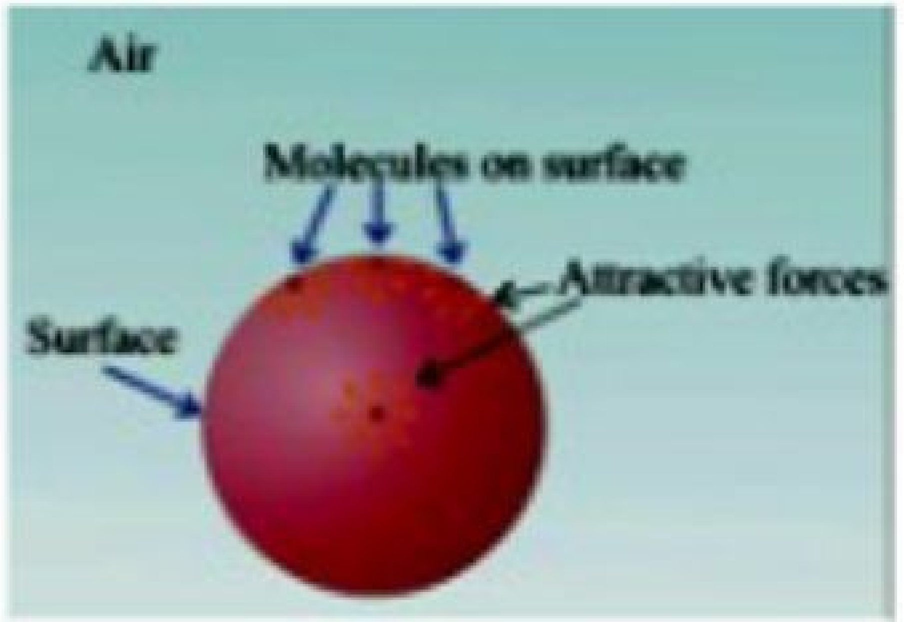
surface tension

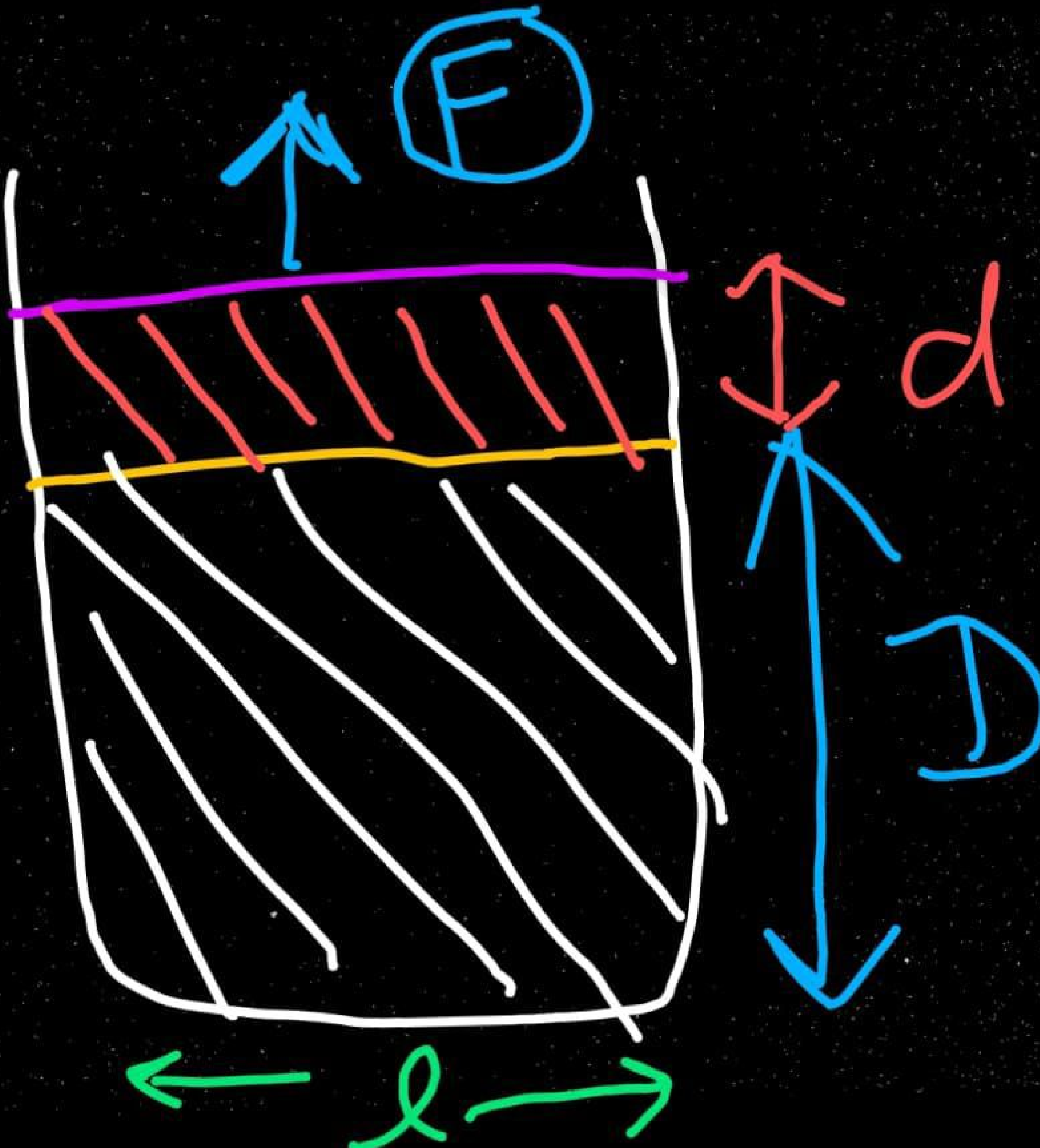
$$W = \gamma \Delta A$$

l × change in delta d

For equilibrium, the surface free energy of a system must be at a minimum.

Thus Liquid droplets tend to assume a spherical shape since a sphere has the smallest surface area per unit volume.




F
d
D
l

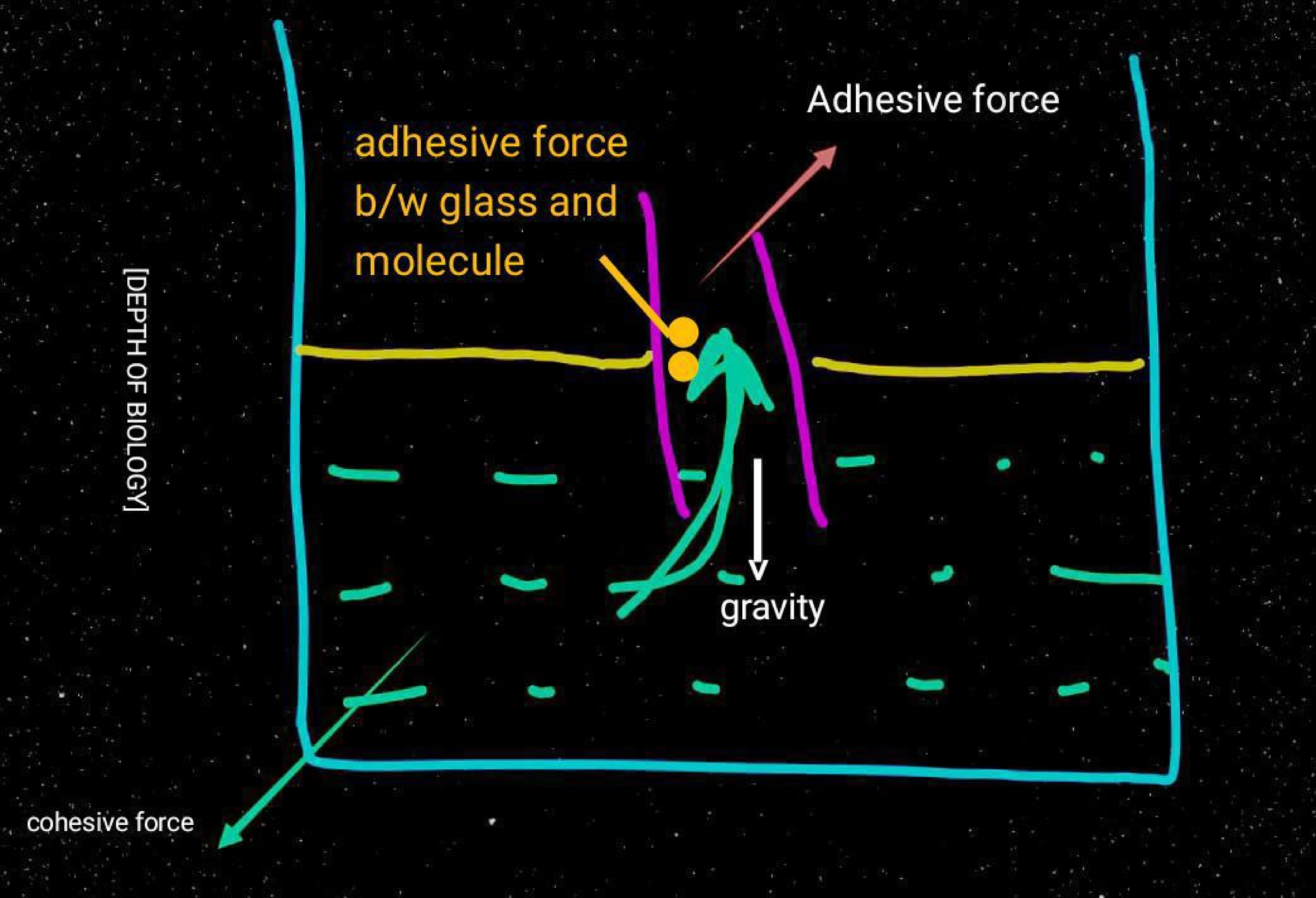
# METHODS FOR MEASURING SURFACE AND INTERFACIAL TENSION

## Capillary Rise Method

### The Principle

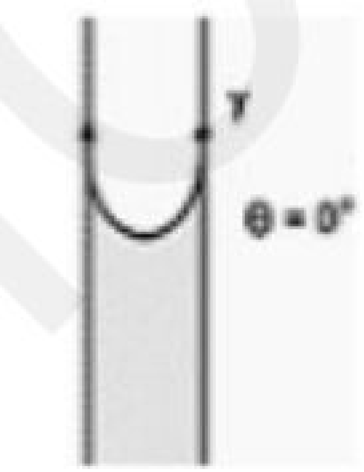
- When a capillary tube is placed in a liquid, it rises up the tube a certain distance. By measuring this rise, it is possible to determine the surface tension of the liquid. It is not possible, to obtain interfacial tensions using the capillary rise method.
- Cohesive force is the force existing between like molecules in the surface of a liquid
- Adhesive force is the force existing between unlike molecules, such as that between a liquid and the wall of a glass capillary tube

✓ *When the force of Adhesion is greater than the cohesion, the liquid is said to* ***wet the capillary wall, spreading over it****, and rising in the tube.*


Adhesive force
adhesive force
b/w glass and
molecule
[DEPTH OF BIOLOGY]
gravity
cohesive force

- If a capillary tube of inside radius = r immersed in a liquid that wet its surface, the liquid continues to rise in the tube due to the surface tension, until the upward movement is just balanced by the downward force of gravity due to the weight of the liquid 
- *The upward component of the force* resulting from the surface tension of the liquid at any point on the circumference is given *by:*

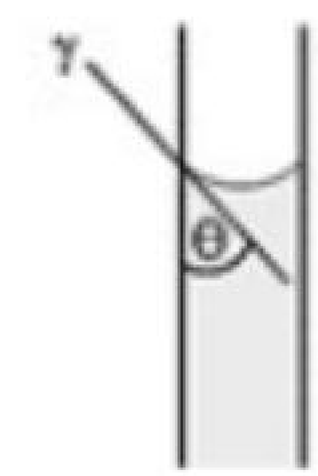
$$a = \gamma \cos \theta$$



Cont. angle water and glass

*Thus the total upward force around the inside circumference of the tube is*

$$a = 2 \pi r \gamma \cos \theta \quad (1)$$

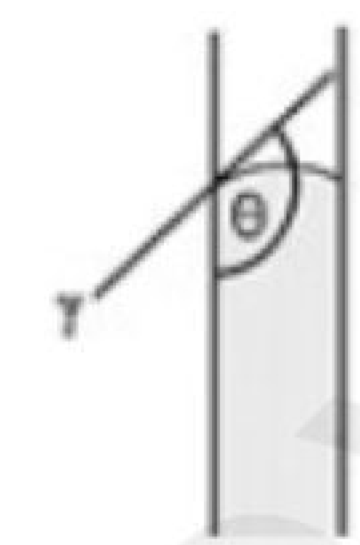



*Where*

$\theta$ *= the contact angle between the surface of the liquid and the capillary wall*

$2 \pi r$ = the inside circumference of the capillary.

*For water the angle $\theta$ is insignificant, i.e. the liquid wets the capillary wall so that $\cos \theta$ = unity*



Cont. angle Mercury and glass

Downward force => $f = mgh + w$ (2)

/ potential energy with gravity

\ weight of liq.

$d = m/v$

$d = m/\pi r 2$

$M = rho \times \pi r^2$ (3)



Put equation (3) in (2)

↓

$f = rho\ \pi r^2 gh + w$

upward = downward

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

(gamma)

$$\gamma = \frac{1}{2}\left[\rho g h r + w\right]$$

(gamma) $\gamma$ → Surface Tension

$\rho$ → density

$g$ → Gravitation

$h$ → Height of raising fluid

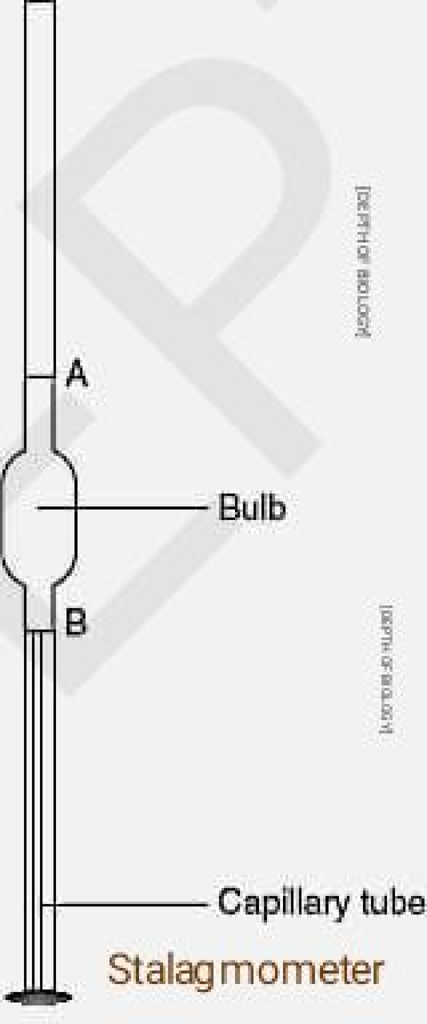
$r$ → radius

$w$ → weight

# DROP COUNT METHOD

- Used to measure surface tension of liquid

1. Take known liquid whose surface tension is known
2. Fill staglometer with that liquid till point A & close it from bottom with the help of finger
3. Release slowly dropwise from capillary untill it reaches point B 
4. Do same with other liquid ( with unknown surface tension)




Stalagmometer

- $w = 2\pi r \gamma$ [$2\pi r$ is circumference of capillary]
- 1st case when we take water

gamma = surface tension

- $W1 = 2\pi r \gamma n1$
- $\gamma 1 = w1 / 2\pi r.n1$ 
- 2nd case when we take unknown ST liquid

$W2 = 2\pi r \gamma 2 \, n2$

$\gamma 2 = w2 / 2\pi r.n2$

now we know that

$W = mg$ & $\rho = m/v$

So , $w = \rho vg$ 

- Putting these value in main equation;
- $\gamma_1 = V\rho_1 g / 2\pi r n_1$
- $\gamma_2 = V\rho_2 g / 2\pi r n_2$



- on comparing,

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

(rho)



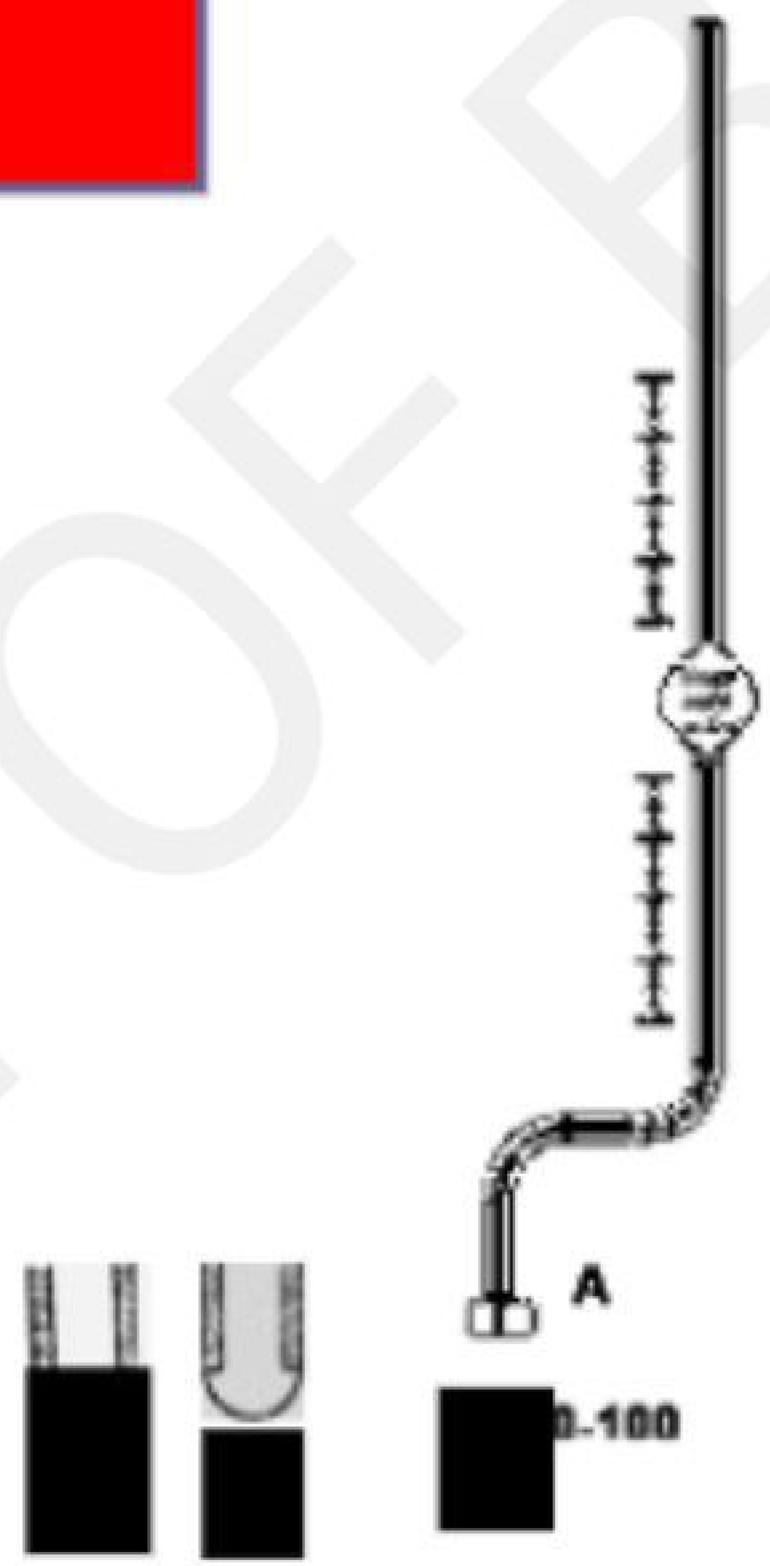
we have to find out gamma 2

# Drop Weight method

If the volume or weight of a drop as it is detached from a tip of known radius is determined, *the surface and interfacial tension* can be calculated from

$$= \gamma \frac{\Phi\ mg}{\pi\ r} = \frac{\Phi\ V\ \rho g}{2\ \pi\ r\ 2}$$

Where m = the mass of the drop
V = the volume of the drop
p = the density of the liquid
r = the radius of the tip
*g*the acceleration due to gravity =
Φ = a correction factor




- *The correction factor is required as not all the drop leaves the tip on detachment*
- *The tip must be wetted by the liquid so as the drop doesn't climb the outside of the tube.*

drop → weight

$\omega_1$ (weight of drop with known surface Tension)

$W_2$ = (Weight of drop with unknown surface Tension)



$\omega_1 = 2\pi r \gamma_1$

$\omega_2 = 2\pi r \gamma_2$

$\gamma_1 = \frac{\omega_1}{2\pi r}$

$\gamma_2 = \frac{\omega_2}{2\pi r}$

(radius same bcz capillary same)

$$\frac{\gamma_1}{\gamma_2} = \frac{\frac{\omega_1}{2\pi r}}{\frac{\omega_2}{2\pi r}}$$

$$\boxed{\frac{\gamma_1}{\gamma_2} = \frac{\omega_1}{\omega_2}}$$

# WILHELMY PLATE METHOD

- Put rectangular plate in liquid whose ST has to be find out
- Now ST is applied on plate which pulls it downwards [DEPTH OF BIOLOGY]

•Now we pull the plate outward with some force so the ST opposes it

[DEPTH OF BIOLOGY]

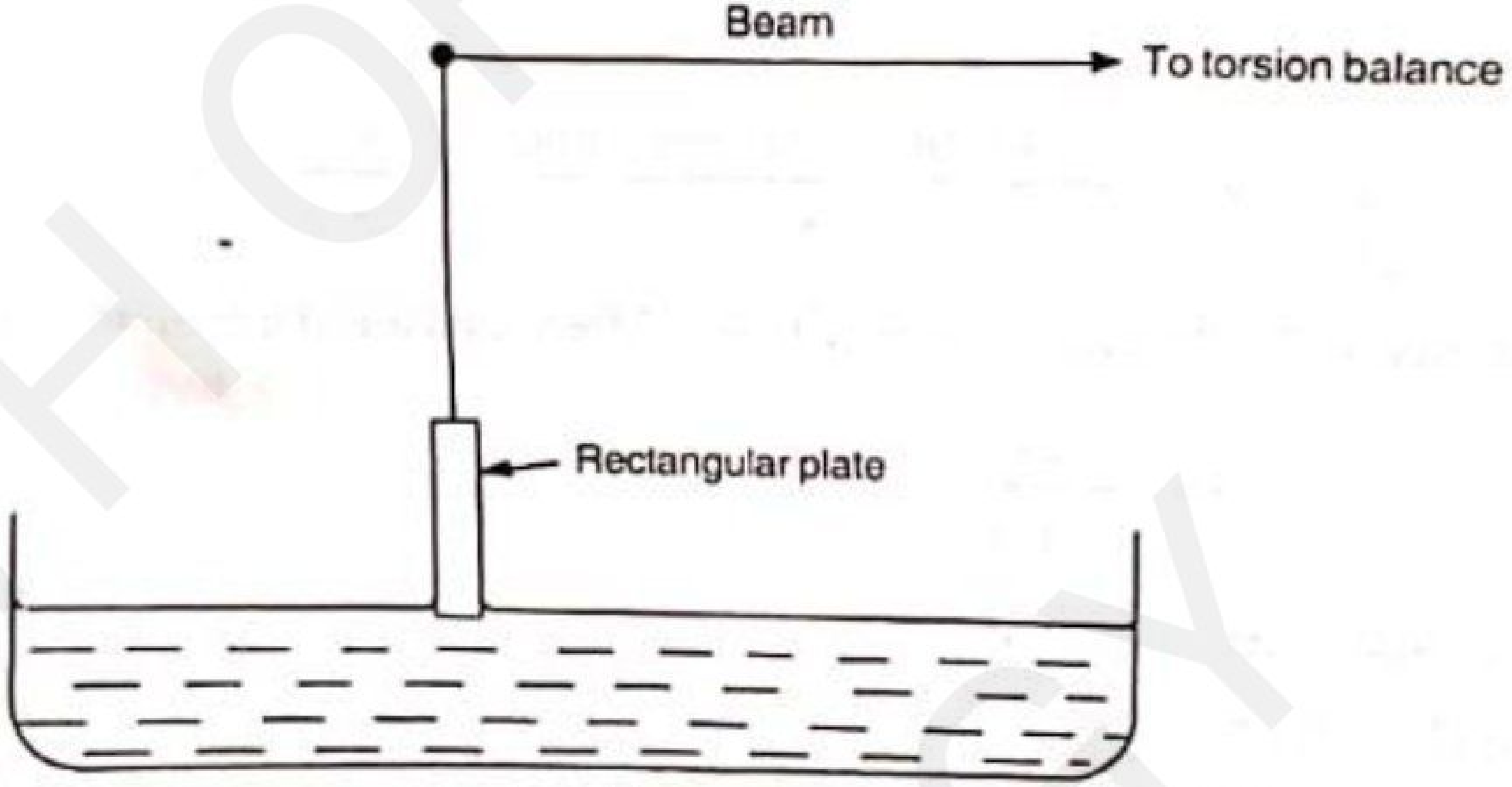



Fig. 3.7. Wilhelmy plate method.

- The force with which we pulled out plate from liquid is same as surface tension of liquid



- $\boldsymbol{\gamma = F / L} \cos\theta$

gamma = surface tension

F = force applied

L = length of rectangular plate

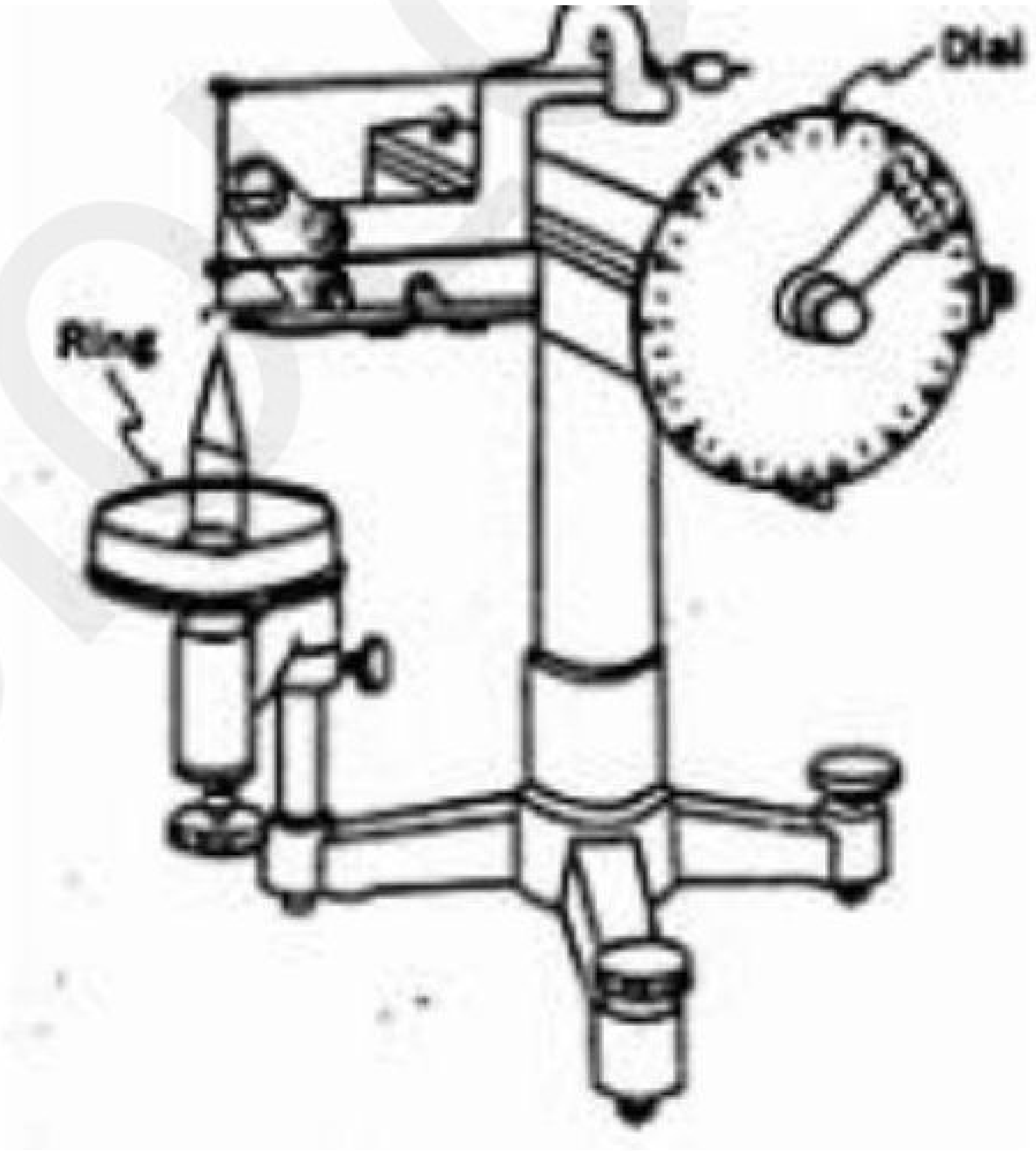
⊘ = angle of contact



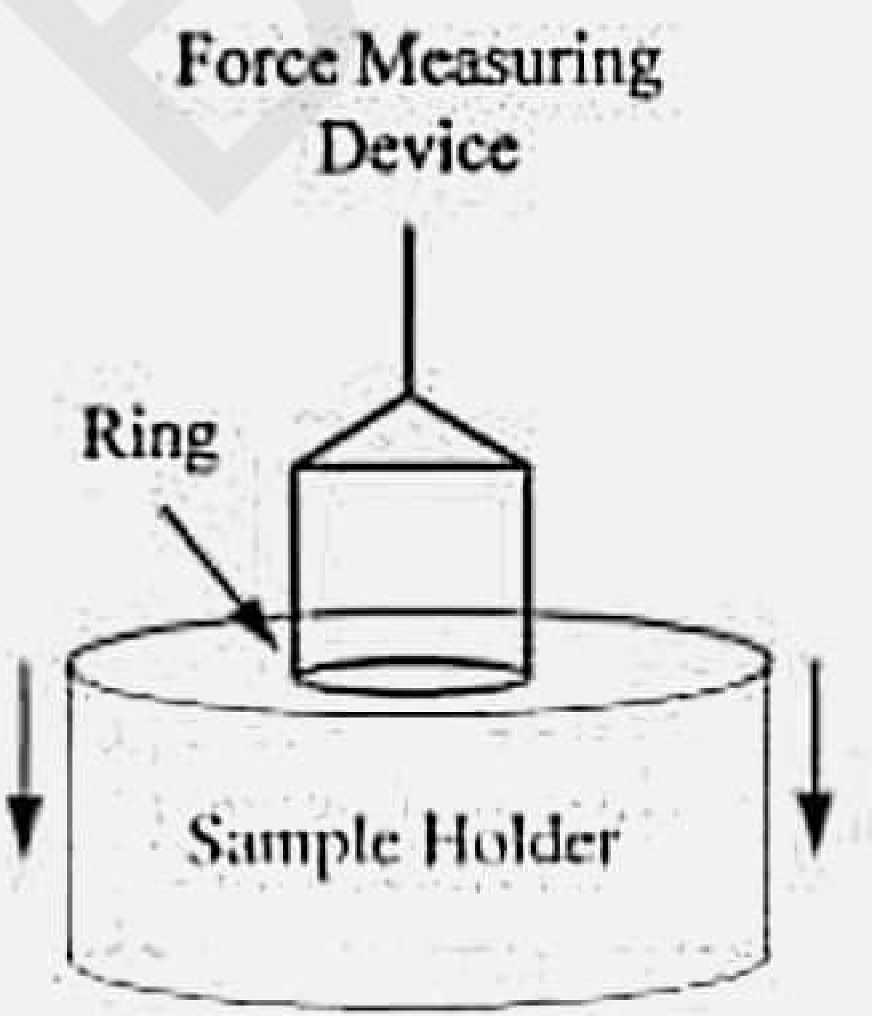
for H2O cos ⊘ = 1

# RING DETACHMENT METHOD

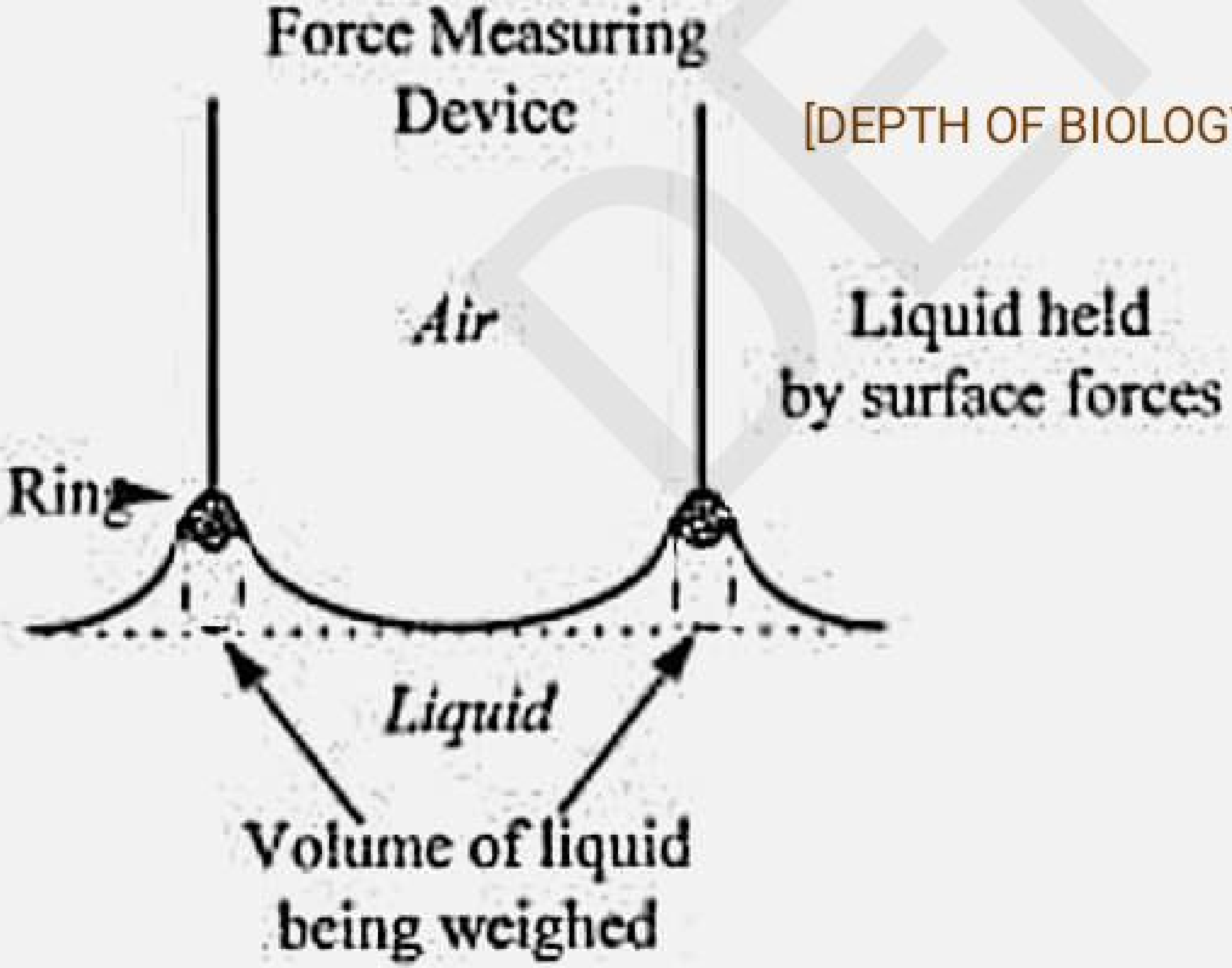
- Ring (Du Nouy) Tensiometer
- For measuring surface and interfacial tensions. [DEPTH OF BIOLOGY]
- The principle of the instrument depends on the fact that : the force necessary to detach a platinum-iridium ring immersed at the surface or interface is proportional to the surface or interfacial tension.
- The force of detachment is recorded in dyneson a calibrated dial
- The surface tension is given by: $\gamma = F / 2\pi(R1 + R2)$




[DEPTH OF BIOLOGY]


Force Measuring
Device
Ring
Sample Holder



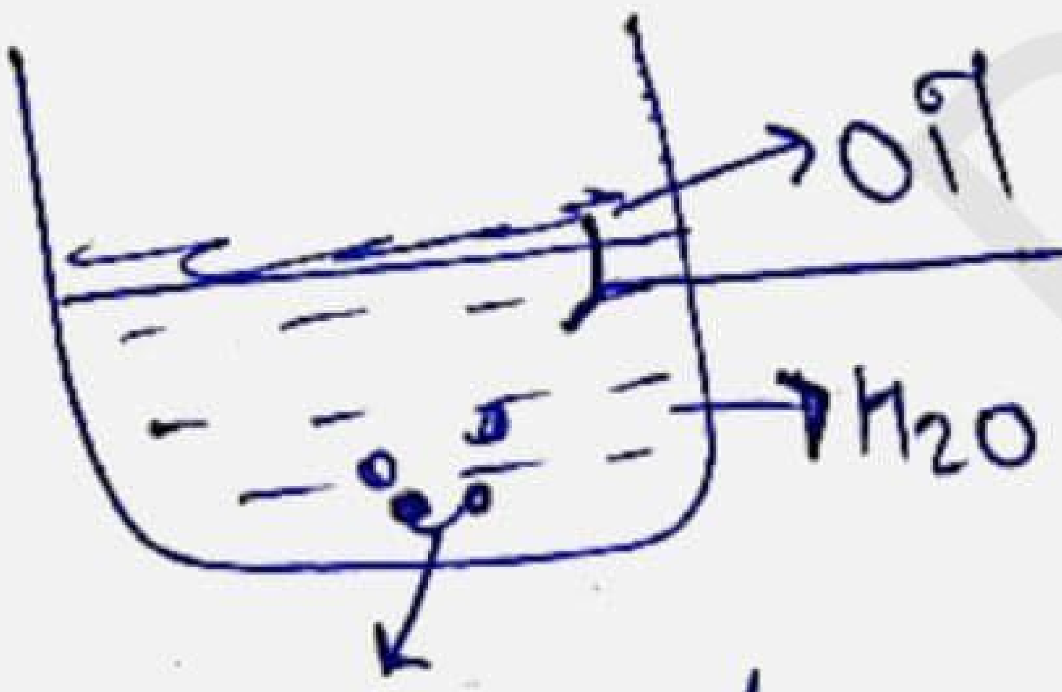

Force Measuring
Device
Air
Liquid held
by surface forces
Ring
Liquid
Volume of liquid
being weighed

- Where:
- F = the detachment force
- R1 and R 2= the inner and outer radii of the ring.
- $\gamma = F / 2\pi (R1 + R2)$

ring outer and
inner surface radius

[$\gamma_S > (\gamma_L + \gamma_{LS})$
spreading occur].

## Spreading Cofficient




→ B/w 2 molecule diff· (oil & $H_2O$).
Adheshive force.

Cohesive force



[cohesive force ↓
Adhesive force ↑] → that's why oil can't mix.

$[S = W_A - W_C] \rightarrow (1)$

S → Spreading Cofficient



$W_C = \gamma_L \cdot \Delta A + \gamma_L \cdot \Delta A$ (If area is 1 $cm^2$).

$[W_C = \gamma_L + \gamma_L \quad W_C = 2\gamma_L]$ → (2)

$W_A \Rightarrow$ Adhesive oil & $H_2O$

$W_A = \gamma_L \cdot \Delta A + \gamma_S \cdot \Delta A - \gamma_{LS} \cdot \Delta A$ (If $\Delta A = 1 cm^2$)

$W_A = \gamma_L + \gamma_S - \gamma_{LS}$ → (3)

o o drop → $\gamma_S$ (Let)
$\gamma_L$ (Surface tension)

$[S = W_A - W_C]$

Put value of eq. 2 & 3 into (1)

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

- common liya hai*

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

# ADSORPTION AT LIQUID INTERFACE

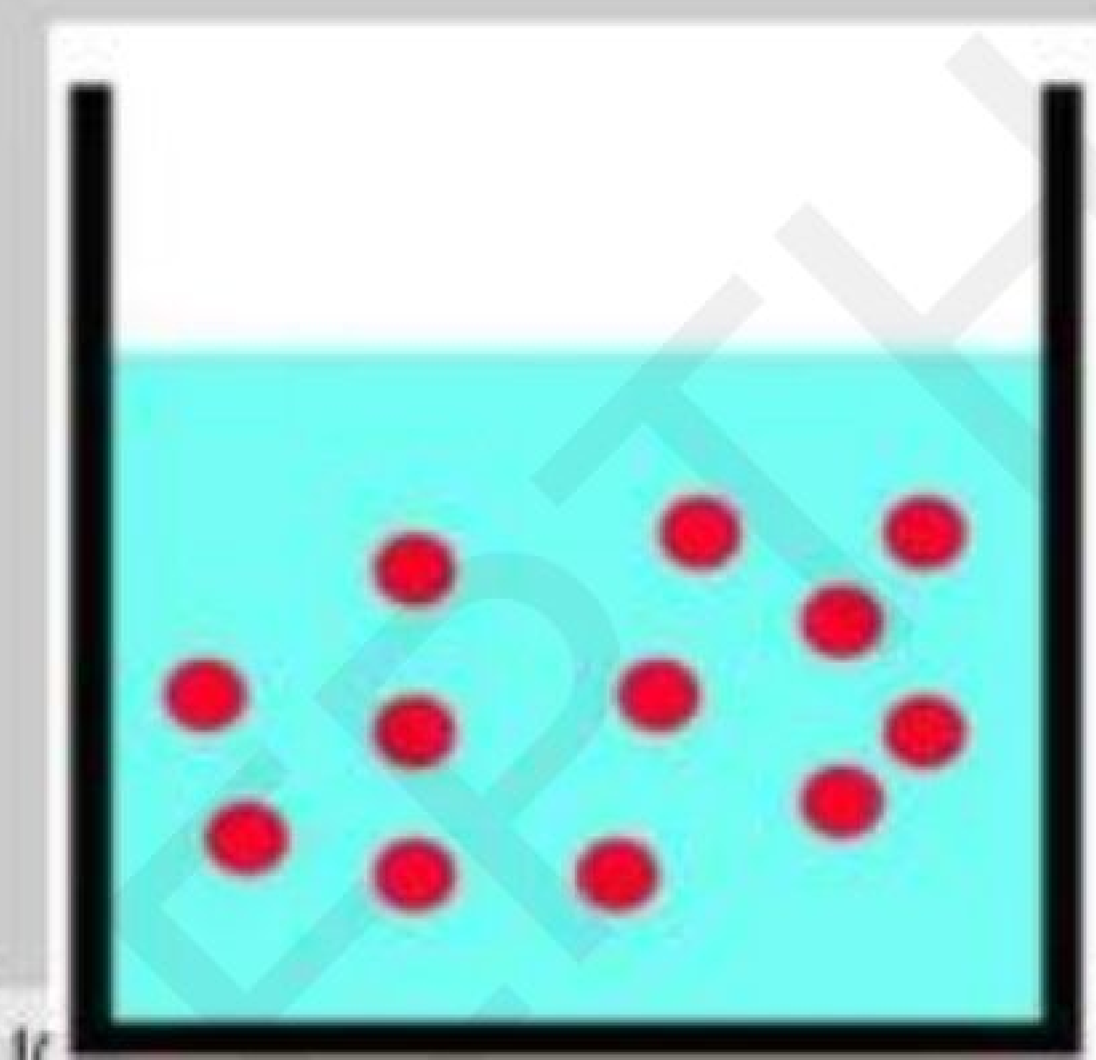
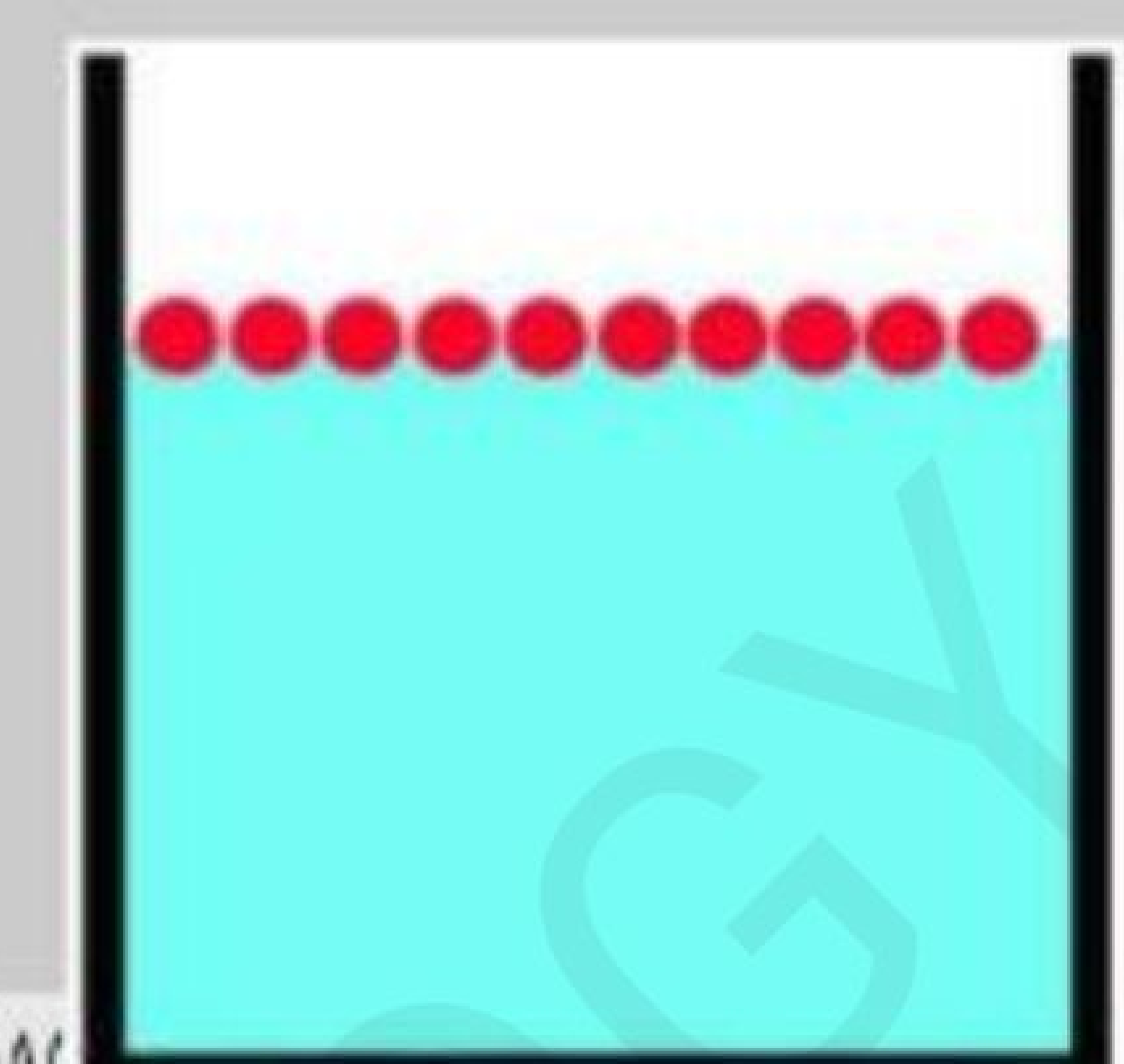
- Adsorption is defined as deposition of one molecule on surface of another
- There are 2 types of adsorption

cohesive ( same molecule force)

adhesive force applied on 2 diff. molecule

adhesive force is more as compared to cohesive force



| NEGATIVE ADSORPTION | POSITIVE ADSORPTION |
|---|---|
| Molecules partitioned in favour of bulk | Molecules partitioned in favour of surface/interface |
| Increase in the surface tension | Decrease in the surface tension |
|  |  |
| Eg: Glu… de | Eg: Tw… |

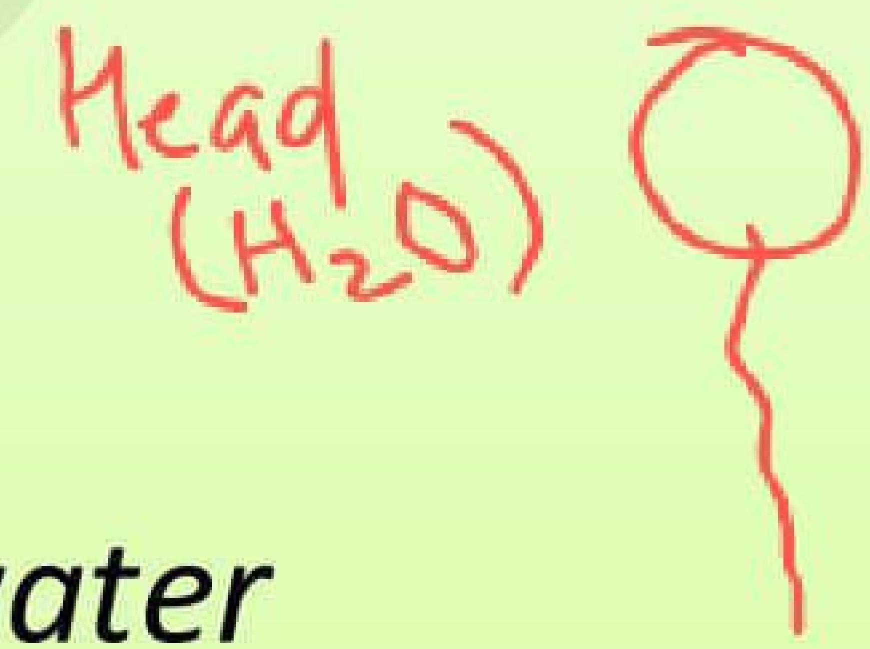
# SURFACTANTS



- Solute molecules or ions that are adsorbed at surface/ interface & reduce interfacial tension are termed as **surfactants**

- Surfactant molecules are **ampiphiles** .they contain a polar head & a non polar tail. 

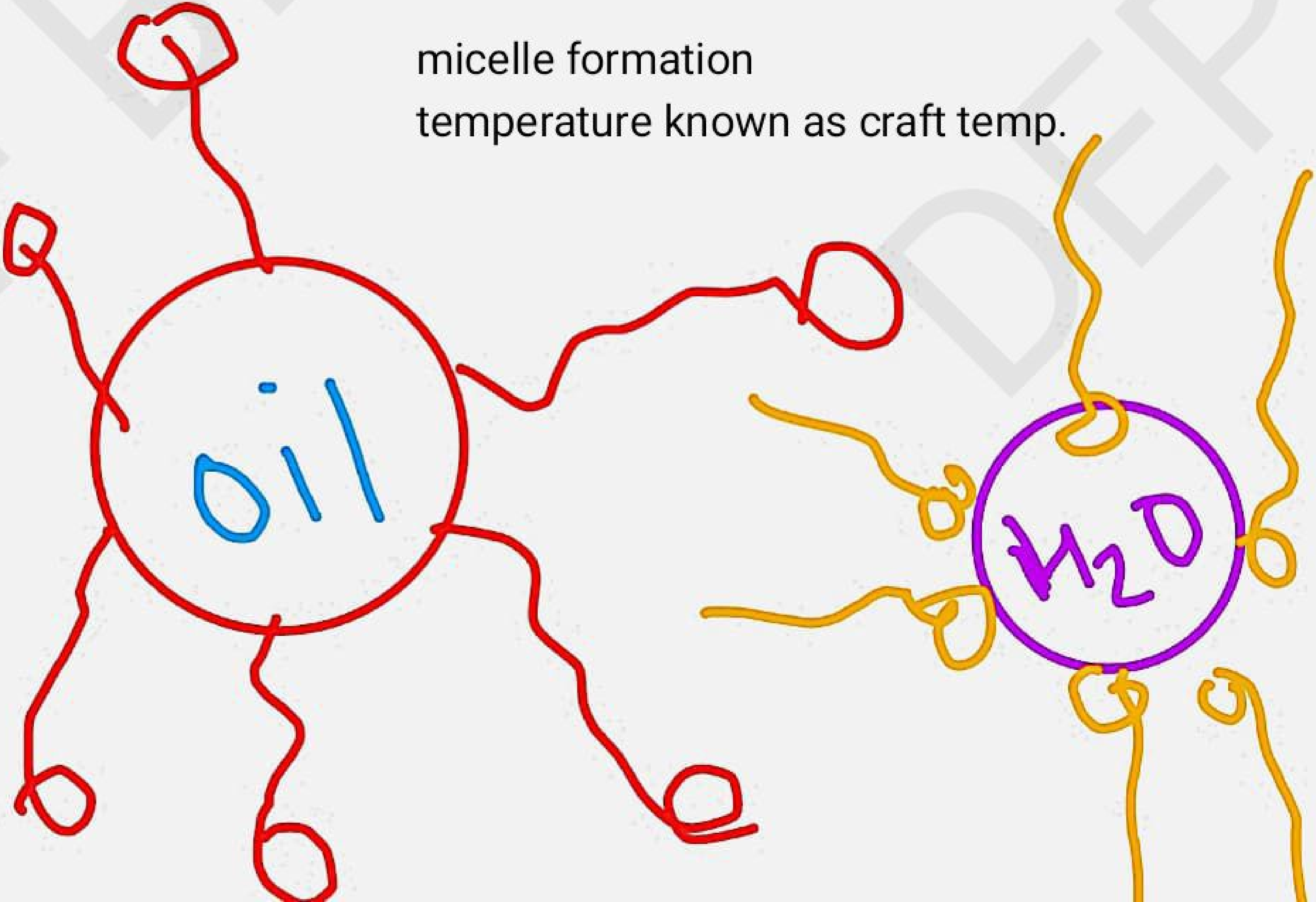
- Surfactant may be **hydrophilic** if it is predominantly polar in nature and **lipophilic** if it is predominantly non polar



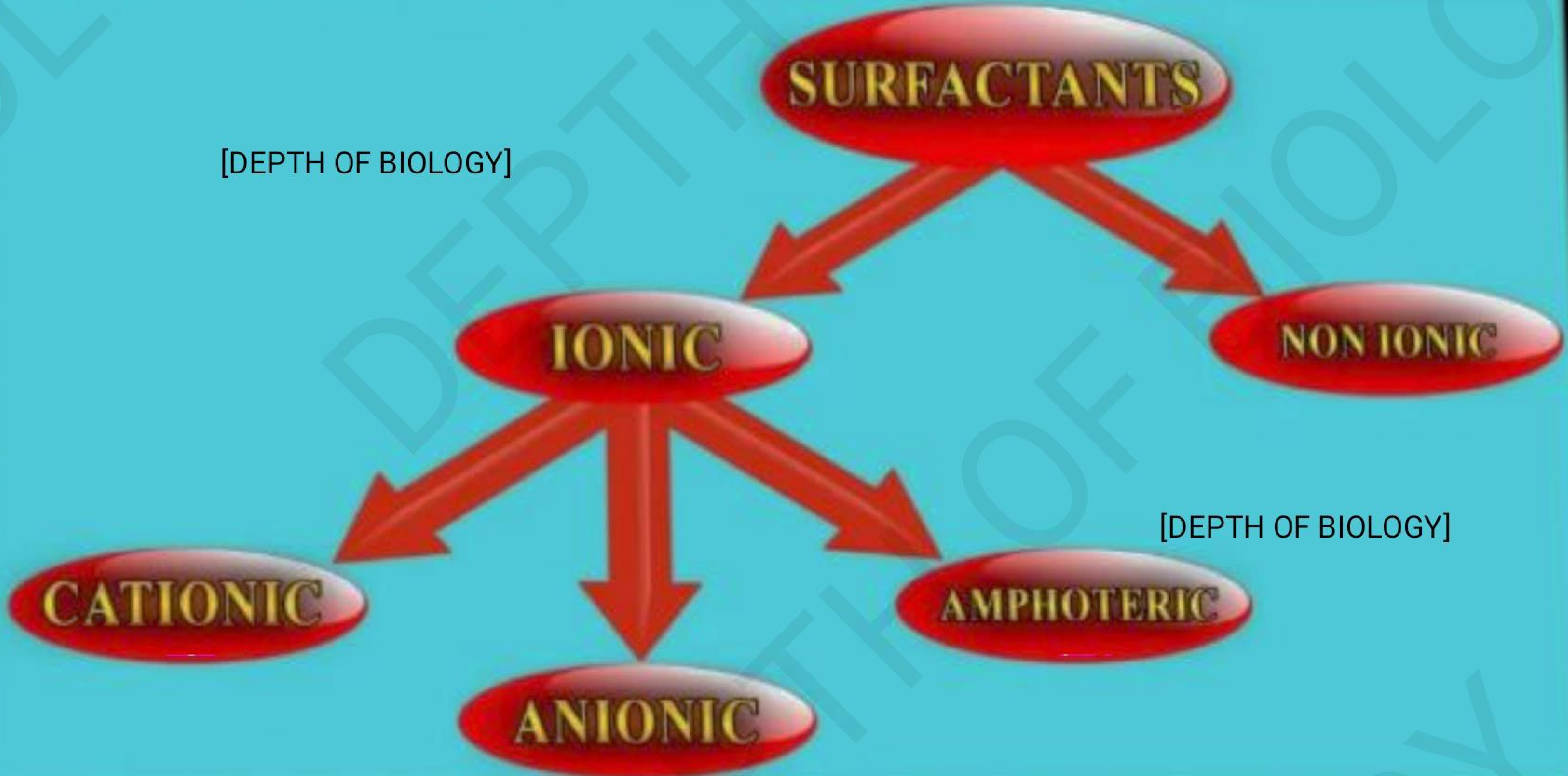

- *When a surfactant is added to water*
- *-hydrophilic head will be oriented towards water*
- *- Lipophilic end will be oriented away from water*

micelle formation

temperature known as craft temp.



# SURFACTANTS CLASSIFICATION



# *Anionic Surfactants*

It ionises in aqueous solutions to yield a large anion and a small cation

This anions are responsible for its action



They are mostly carboxylates

- Potassium **stearate soap**
- **di(2-ethyl hexyl)** sodium **sulpho succinate**
- Sodium **cetyl succinate**
- Sodium **lauryl sulphate**

unpleasent in taste
so not suitable for internal use

# Cationic Surfactants

It ionises in aqueous solutions to yield a large cation and a small anion



This cations are responsible for its action

They are Amines and Quaternary Ammonium salts

Mainly used as anti microbial agents and preservatives

- **Cetrimide (Cetyl trimethyl ammonium bromide)**

# *Amphoteric Surfactants*

they have both group
cationic and anionic in same molecule

Contain Carboxylate/Phosphate groups as anion
Ammonium/Quaternary ammonium groups as cations

They include Polypeptides, Proteins, Cephalins, Lecithins, etc.



- **N- dodecyl alanine**

Also known as zwitter ionic molecule

# Non-Ionic Surfactants

Widely used in pharmaceutical industries

Do not ionises in aqueous solutions

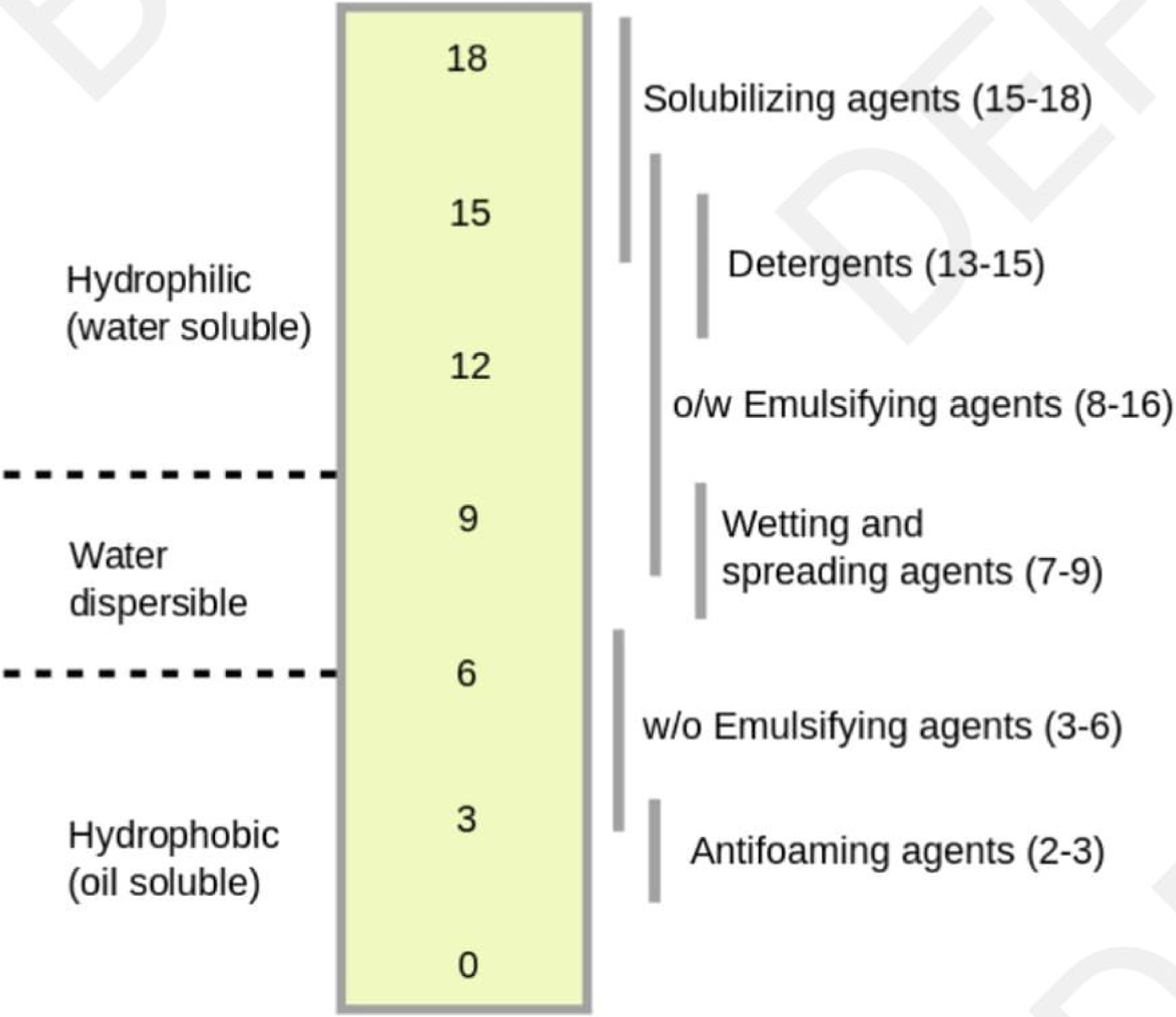


- **Polyoxy-ethylene sorbitan fatty acid esters**

**Tweens, Spans,etc**

# Hydrophilic Lipophilic Balance

- A scale showing classification of surfactant function on the basis of HLB values of surfactants.
- The higher the HLB of a surfactant the more hydrophilic it is.
- Example: *Spans* with low HLB are lipophilic. Tweens with high HLB are hydrophilic.


18
15
12
9
6
3
0
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)

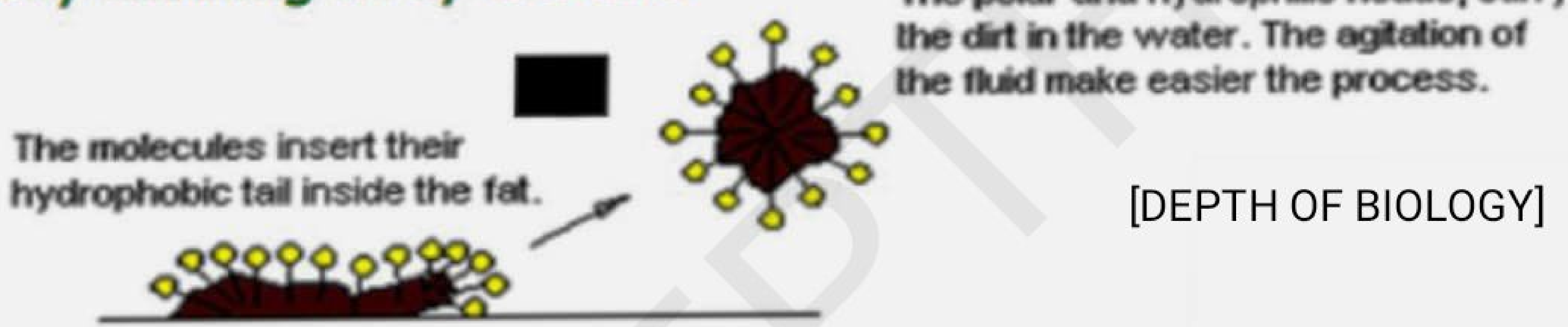
# SOLUBILIZATION

- Process in which the solubility of organic compound is increases in it`s aqueous medium with the help of surfactants 
- Used is many industries for the mixing of 2 immiscible liquid & help in making of drugs

# DETERGENCY

- Process in which dirt is removed from surface with the help of surface detergent 
- This are basically made up with surfactants
- It reduces the adhesive force so dirt particles are easily removed from surface

- Detergents are surfactants used for removal of dirt.
- Detergency involves:
  - Initial wetting of the dirt and the surface to be cleaned.
  - Deflocculation and suspension, emulsification or solubilisation of the dirt particles
  - Finally washing away the dirt.



How surfactants remove the dirt

# ADSORPTION AT SOLID INTERFACE

- When on surface of solid any substance is deposited , it is called **ADSORPTION AT SOLID INTERFACE.**
- Adsorbate is the substance which is deposited
- Adsorbent is the surface where this process takes place 



- On the basis of attraction forces between adsorbate & adsorbent , adsorption is divided into 2 types

| *Properties* | *Physical adsorption* | *Chemical absorption* |
|---|---|---|
| Adsorption forces | Weak van der Waals forces Heat of adsorption <50 kJ/mol | Involves transfer or sharing of electrons between adsorbent and adsorbed molecules. Heat of adsorption is about 60–420 kJ/mol |
| Specificity | Nonspecific, will occur to some degree in any system | Specific, that is, occurs only when reaction is possible between adsorbent and adsorbate |
| Reversibility | Reversible, that is, adsorbate can be removed easily from surface in an unchanged form | Irreversible, that is, adsorbate is removed with difficulty in a changed form. For example, oxygen adsorbed by carbon is removed as carbon dioxide |
| Number of adsorbed layers | Monomolecular layer formed at low pressure, followed by an additional layer as pressure increases (multilayer) | Restricted to formation of monolayer |
| Rate of adsorption | Rapid at all temperature | Proceeds at a finite rate,which increases rapidly with rise in temperature |