Topic: Interfacial phenomena

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Prof. MASARRAT MUKADAM
ASSISTANT PROFESSOR
AIKTC SCHOOL OF PHARMACY, NEW PANVEL.

ANJUMAN-I-ISLAM'S
KALSEKAR TECHNICAL CAMPUS, NEW PANVEL
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TEACHING LEARING OUTCOMES

- To study and apply knowledge of Surface tension, Interfacial tension, Surface free energy Measurement of surface and interfacial tension-capillary rise method, drop number method, Drop weight method, Du Nuoy tensiometer method Spreading of liquids, Spreading coefficient, Surface active agents, Hydrophilic-Lipophilic balance, soluble monolayers
- To understand Adsorption at solid interfaces, Adsorption isotherms, Freundlich adsorption isotherm, Langmuir adsorption isotherm. Wetting, wetting agents and contact angle

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CONTENTS

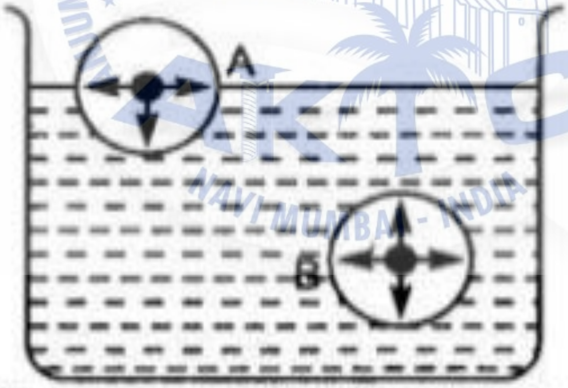
- Surface tension, Interfacial tension, Surface free energy.
- Measurement of surface and interfacial tension-capillary rise method, drop number method, Drop weight method, Du Nuoy tensiometer method.
- Spreading of liquids, Spreading coefficient, Surface active agents, Hydrophilic-Lipophilic balance, soluble monolayers.
- Adsorption at solid interfaces, Adsorption isotherms, Freundlich adsorption isotherm, Langmuir adsorption isotherm.
- Wetting, wetting agents and contact angle.

Chapter 5

Surface and interfacial phenomena

Surface Tension

- The boundary that forms between two phases say solid and liquid is called **interface.**
- **Surface tension** is defined as the force in dynes, acting on the surface of the liquid at right angles of the length of surface of 1 centimetre.
- The units of surface tension are **dyne/cm and N/m.**

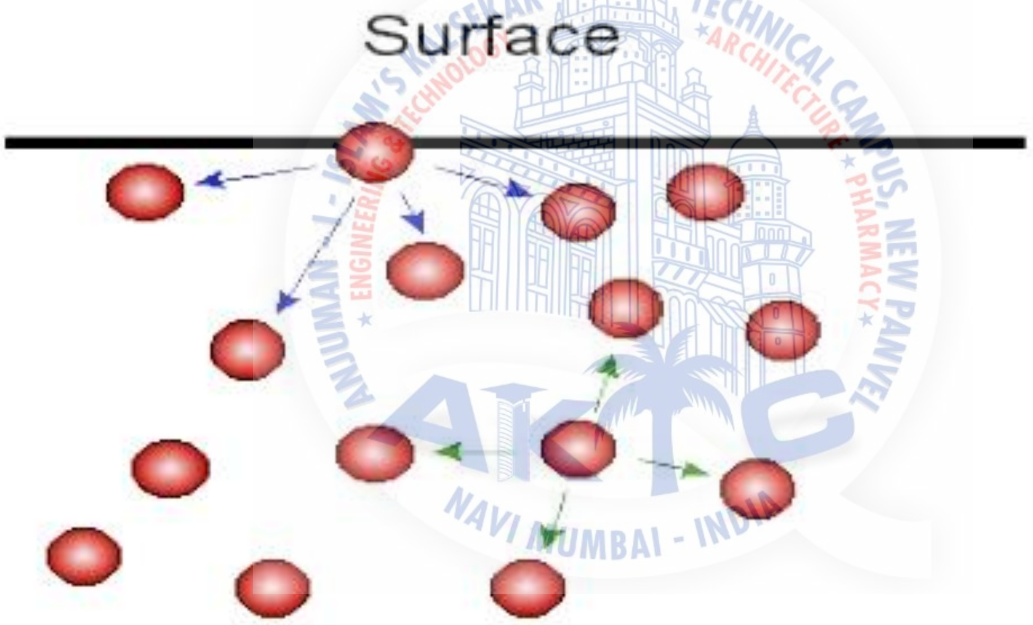


Phenomenon of surface tension

The phenomenon of surface tension is responsible for following processes.

- Formation of spherical globules in emulsion.
- Formation of nearly spherical shape of falling water droplets.
- Formation of spherical shape of mercury particles on a flat surface.
- Rise of liquid in a capillary tube.
- Formation of hemispherical surface i.e lower meniscus, when water is filled in glass tube.

Surface tension of liquids



Interface

- *Interface* is the boundary between two or more phases exist together
- The properties of the molecules forming the interface are different from those in the bulk that these molecules are forming an *interfacial phase.*
- 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.

LIQUID INTERFACES

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.

- *For the molecules at the surface (at the liquid/air interface)*
  - Only attractive cohesive forces with other liquid molecules which are situated below and adjacent to them.
  - They can develop adhesive forces of attraction with the molecules of the other phase in the interface
  - The net effect is that the molecules at the surface of the liquid experience an inward force towards the bulk of the liquid and pull the molecules and contract the surface with a force F .

- To keep the equilibrium, an equal force must be applied to oppose the inward tension in the surface.
- Thus *SURFACE TENSION* [γ] 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.
- Invariably, interfacial tensions are less than surface tensions because an adhesive forces, between the two liquid phases forming the interface are greater than when a liquid and a gas phase exist together.
- If two liquids are completely miscible, no interfacial tension exists between them.
- Greater surface tension reflects higher intermolecular force of attraction, thus, increase in hydrogen bonds or molecular weight cause increase in ST

Surface free energy

- Surface free energy is defined as the work required to increase the area of the liquid by 1 sq cm.
- ABCD is a rectangular wire as shown in figure.
- The side of AD=L and is movable.
- A drop of soap solution is placed on the frame, so that it forms film within the frame.
- When force is applied downwards, the film gets stretched as the movable bar AD goes down until the film breaks.

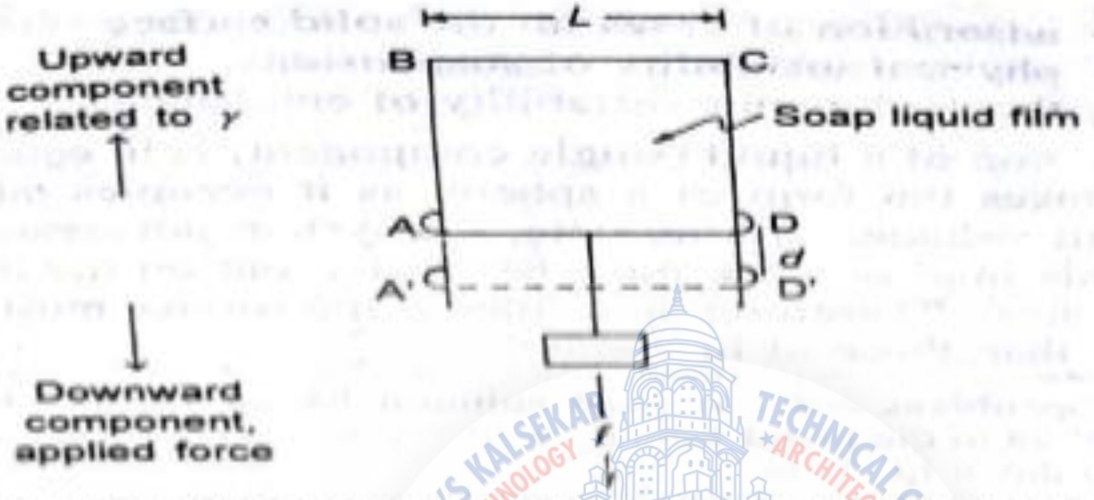


Figure 5-5. Wire frame apparatus. AD is a movable arm.

If force 'f' 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

$$\text{Work done } (W) = \text{force} \times \text{distance moved}$$

$$W = f \times d \qquad (12)$$

The above force acts against the surface tension (upward component), γ, of the liquid, since surface tension tries to contract the liquid. There are two surfaces of each length 'L' on either side of the wire. The force acting on the surface is:

$$f = \gamma \times 2L \qquad (13)$$

Substituting equation (13) in equation (12) gives

$$W = \gamma \times 2L \times d \qquad (14)$$

Since, $2L \times d$ is equal to increase in surface area 'ΔA' produced by extending the soap film, equation (14) changes to:

$$W = \gamma \times \Delta A \qquad (15)$$

$$\text{or} \quad \Delta G = \gamma \times \Delta A$$

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

$$\boxed{W = \gamma \, \Delta A}$$

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

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.

Dertermination of surface and interfacial tension

- Different methods used for the determination of surface and interfacial tension are

1. Capillary rise
2. Tensiometer
3. Bubble pressure
4. Drop weight (drop count)

Measurement of Surface and Inter-facial Tensions

Methods for measuring surface and interfacial tension

1- Capillary rise method

2- Ring (Du Nouy) tensiometer

3- Drop weight method (Stalagmometer)

The choice of the method for measuring surface and interfacial tension depend on:

- Whether surface or interfacial tension is to be determined.
- The accuracy desired
- The size of sample.

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 mole-cules 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.*

- 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:*

$$\boxed{a = \gamma \cos \theta}$$

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

$$\boxed{a = 2 \pi r \gamma \cos \theta}$$

Where

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

Cont. angle water and glass

Cont. angle Mercury and glass

The downward force of gravity (mass x acceleration) is given by

$$\boxed{\pi r^2 h (p - p^o) g + w}$$

Where:

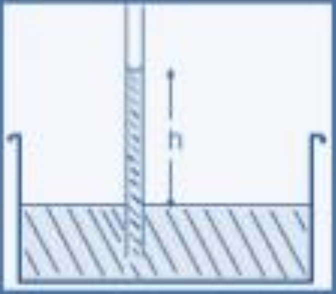
πr^2 = the cross-sectional area

h = the height of the liquid column to the lowest point of the meniscus

$(p - p\,o)$ = the difference in the density of the liquid p and its vapor po

g = the acceleration of gravity

w = the weight of the upper part of the meniscus.



At Maximum height, the opposing forces are in equilibrium

$$\boxed{2 \pi r \gamma \cos \Theta = \pi r^2 h (p - p\,o) g + w}$$

$p\,o$, Θ and w can usually be disregarded
Hence the surface tension can be calculated.

$$\boxed{2 \pi r \gamma = \pi r^2 h p g}$$

$$\boxed{\gamma = 1/2\, r h p g}$$

Capillary rise method

- When a capillary tube is placed in the liquid contained a beaker, the liquid rises up in the tube to a certain distance. This is because the adhesive forces between the liquid molecules and glass are stronger than the cohesive forces between the liquid molecules.
- 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.

- The phenomenon of capillary rise is observed in several instances in nature.

1. Underground water rising on to the surface.
2. Oil rising through wick in a lamp.
3. To certain extent, water rising from the soil to the branches above the ground in the plants.

Capillary rise method

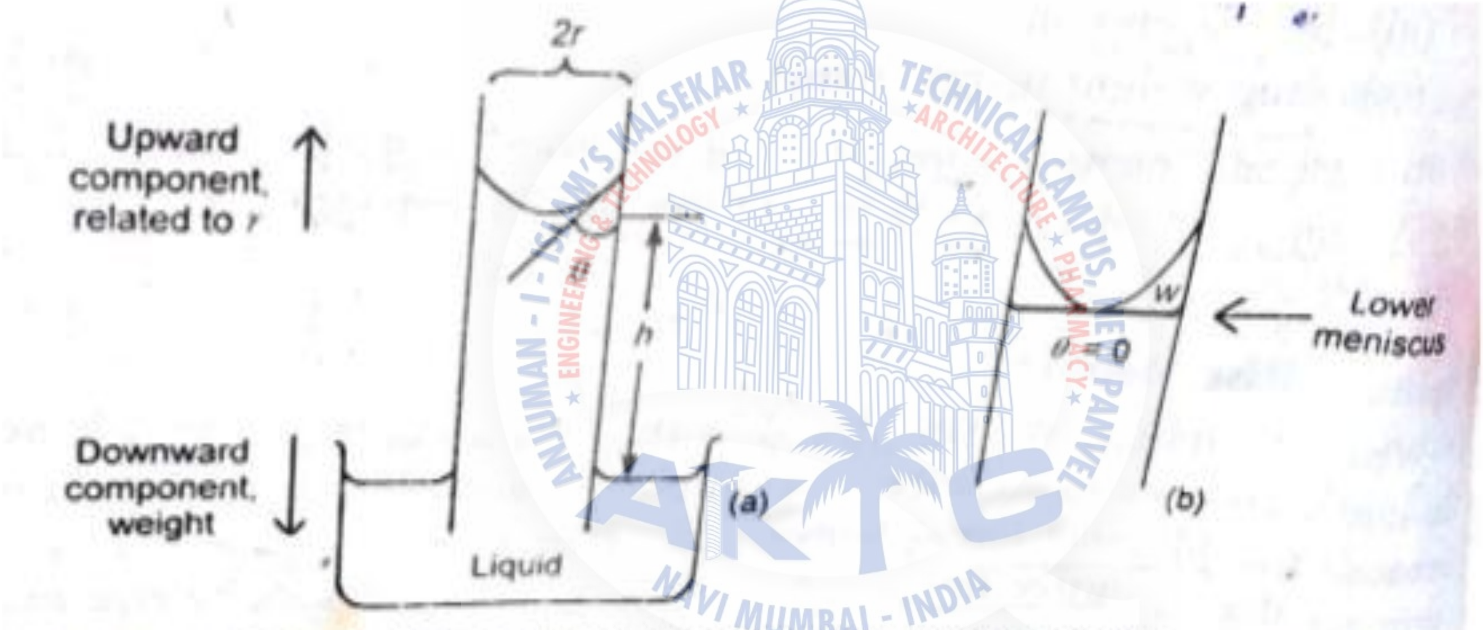


Figure 5-3. (a) Measuring surface tension by means of the capillary rise method. (b) Enlarged view of the meniscus, 'w' is neglected.

The derivation for the determination of surface tension by capillary rise is as follows.

Upward component

Upward component, $\alpha=\gamma.\text{Cos}\theta$

γ= surface tension of the liquid,

Θ= contact angle between the surface of the liquid and capillary wall.

- The total upward force around the inside circumference ($2\pi r$) of the tube is

Upward component, $\alpha=\gamma.\ 2\pi r\ .\text{Cos}\theta$

- For liquids used in pharmacy, **$\text{Cos}\theta=1$**, so upward component,

Upward component, $\alpha=\gamma.\ 2\pi r$

Downward component

- The counteracting force is gravity and depends on the weight of the liquid in the capillary rise.

Downward component, b= mass x acceleration

But density= $\frac{mass}{volume}$

So, mass= density x volume

Downward component, b= density x volume x acceleration

But volume= cross sectional area x height= $\pi r^2 h$

Downward component, b= $\pi r^2 h$ x p x g

- At the equilibrium, these opposing forces are equal,

Upward component = Downward component

$$a=b$$

$$\gamma .\ 2\pi r = \pi r^2 h \times p \times g$$

$$\gamma = \frac{1}{2} rphg$$

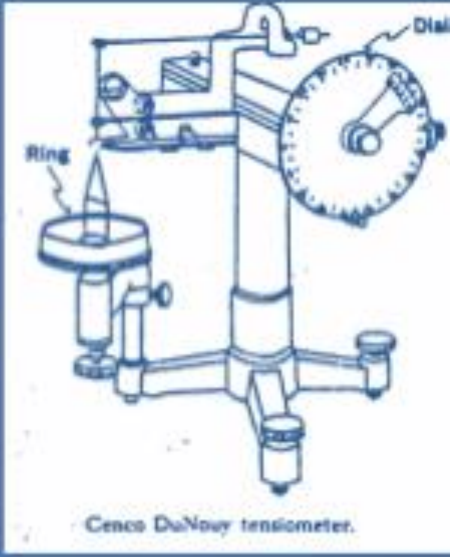
Ring (Du Nouy) Tensiometer

- For measuring surface and interfacial tensions.

The principle

- 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 dynes on a calibrated dial
- The surface tension is given by:

$$\gamma = F / 2\pi (R_1 + R_2)$$



Cenco DuNouy tensiometer.

Where:

F = the detachment force

R_1 and R_2 = the inner and outer radii of the ring.

Drop Weight and drop volume 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

$$\boxed{\gamma = \frac{\Phi m g}{2 \pi r} = \frac{\Phi V p g}{2 \pi r}}$$

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.***

Tensiometer (DuNouy Ring method)

- DuNouy tensiometer is widely used to measure surface and interfacial tensions.
- This method is convenient for rapid determination, especially when the quantity of liquid available is small.
- It works on the principle of force required to detach the platinium-iridium ring immersed at the interface or surface. The force is equal to the surface and interfacial tension.

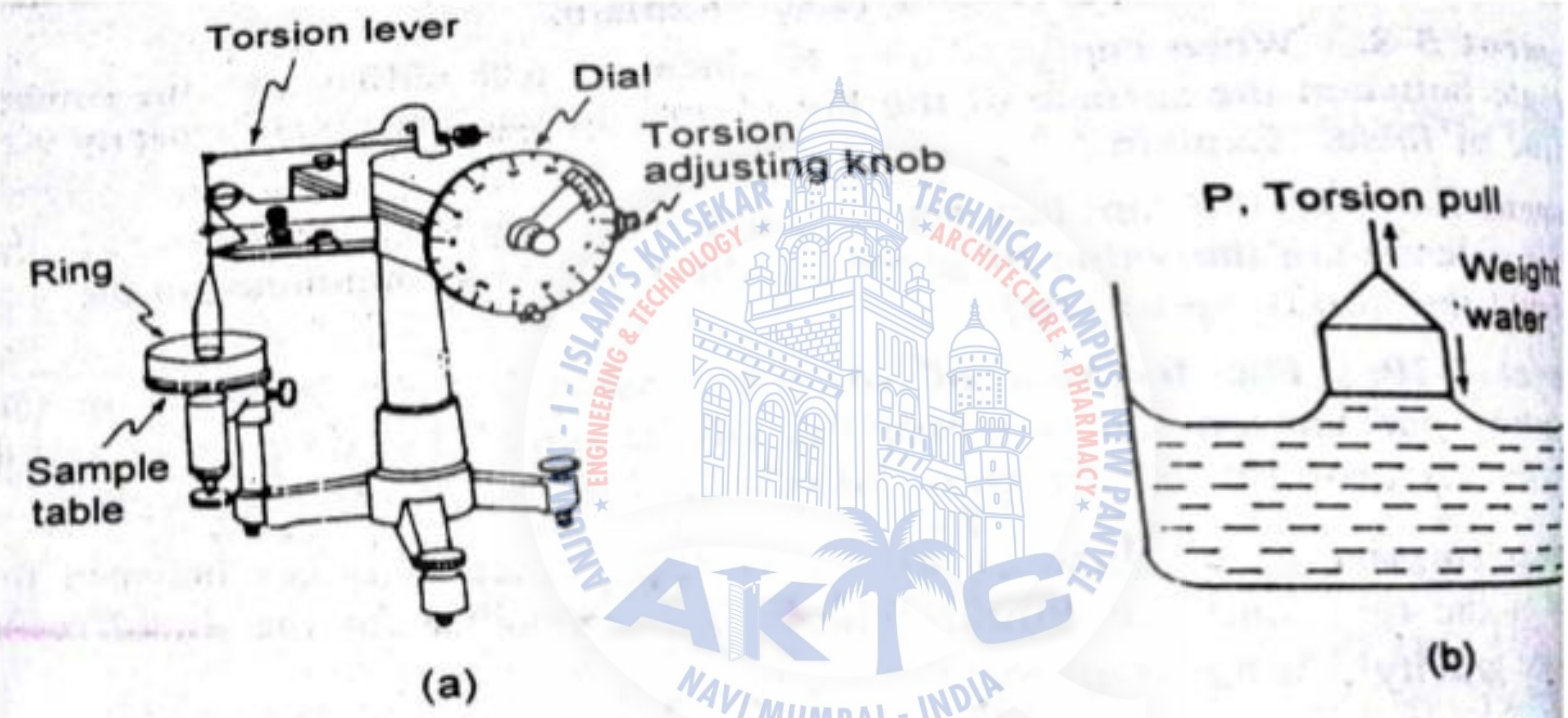


Figure 5-4. DuNouy tensiometer (a). Representation of the tensiometer ring pulling the liquid column above its surface (b).

- Upward pull= dial reading in dynes
- Downward pull= $\gamma.2\pi r.2$
- Upward pull = downward pull
- dial reading in dynes = $\gamma.2\pi r.2$

$$\gamma = \frac{dial\ reading\ in\ dynes}{2\pi r.2}$$

$$\gamma = \frac{dial\ reading\ in\ dynes}{2\pi r.2} * \text{Correction factor}$$

Error upto 25% is possible if the correction factor is not applied.

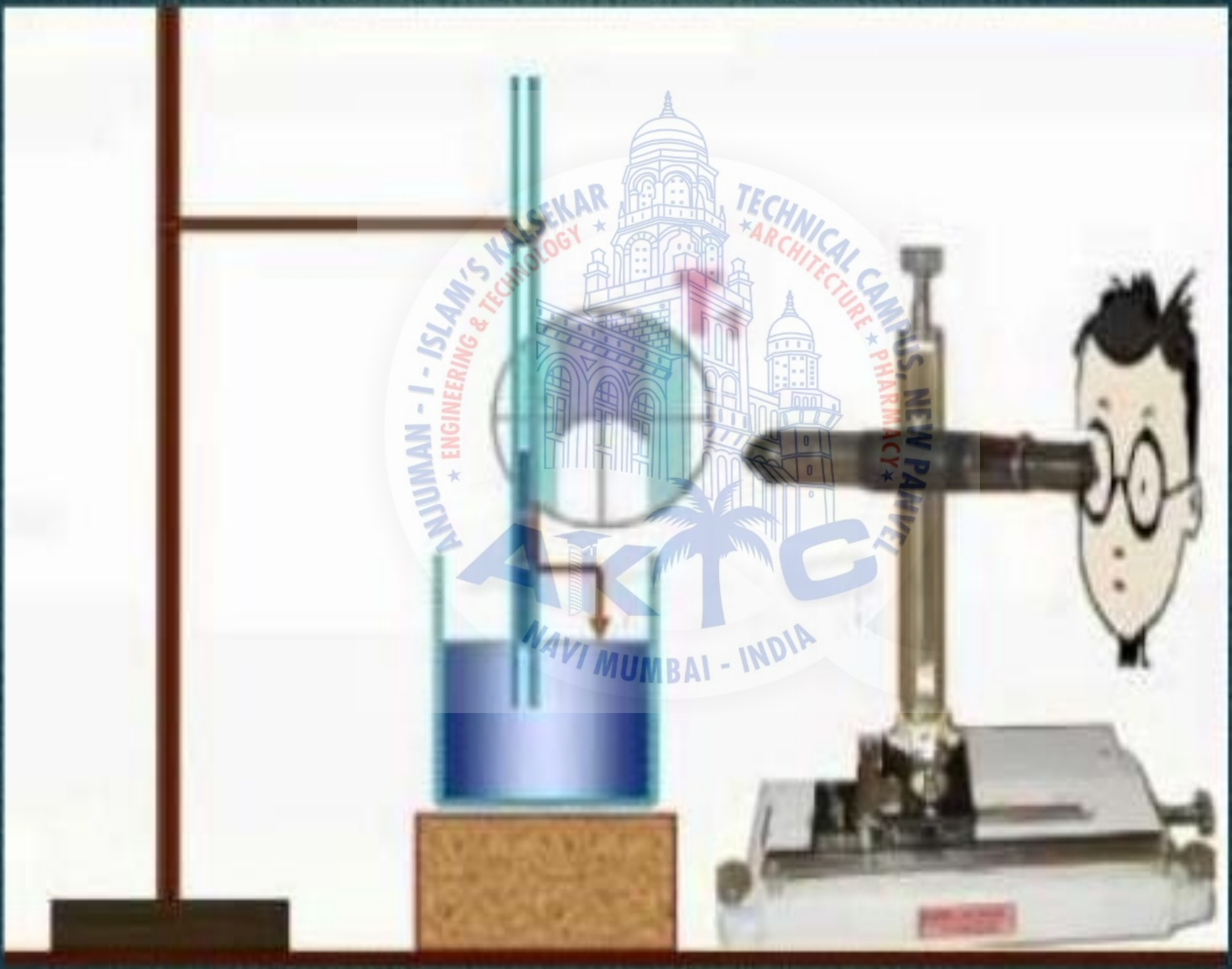
Chapter 5
Interfacial phenomena

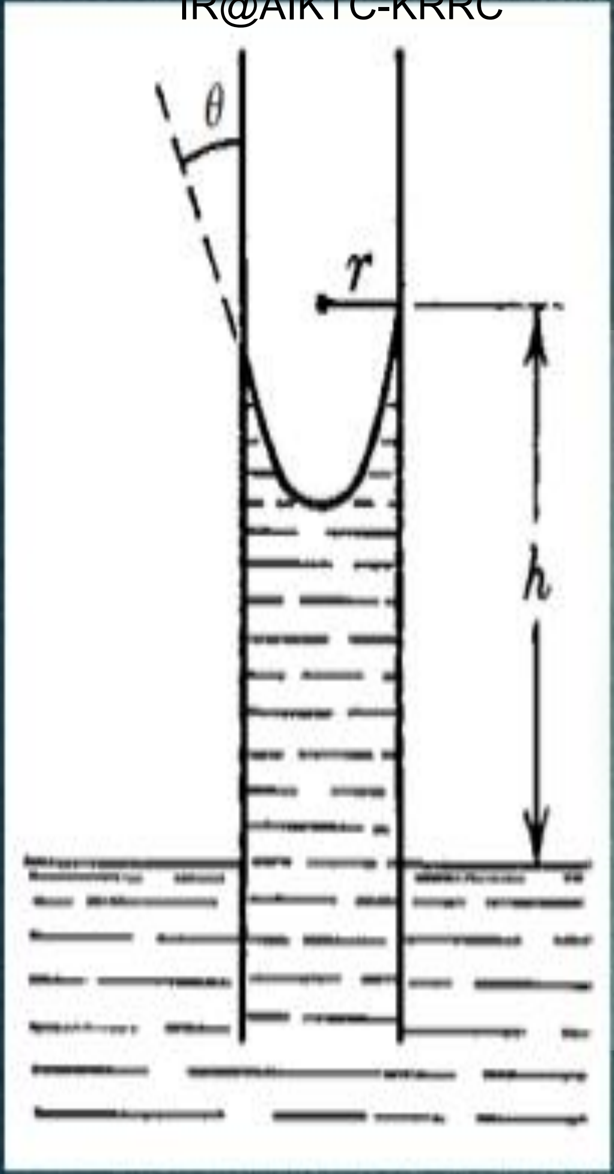
Lecture 2

MEASUREMENT OF SURFACE AND INTERFACIAL TENSION

- Capillary Rise Method
- Maximum Bubble Pressure Method
- Drop Method
- Wilhelmy Plate Method
- Ring Detachment Method (Du - Nuoy Tensiometer)

Capillary Rise Method





Capillary rise occurs because of upward force due to surface tension

Upward movement stops when this force is counterbalanced by the downward force due to weight of the capillary column

Surface tension at any point of circumference of capillary tube = $\gamma \cos\theta$

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

Counter balancing force due to weight of the column = m g

$= \pi r^2 h\,(\rho - \rho_0)\,g + w$

ρ – Density of Liquid
ρ_0 – Density of vapour
w – Weight of liquid above meniscus

$\rho >> \rho_0$

W is very negligible when compared to weight of column

Therefore Downward force due to weight of the column = $\pi r^2 h \rho g$

At equilibrium

Upward force = Downward force

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

$$\gamma = \frac{rh\rho g}{2\cos\theta}$$

In case of water θ is taken as 0. ie, cosθ = 1

Thus

$$\gamma = {}^1/_2\, rh\rho g$$

Precautions to be taken

✓Outer vessel should have larger diameter

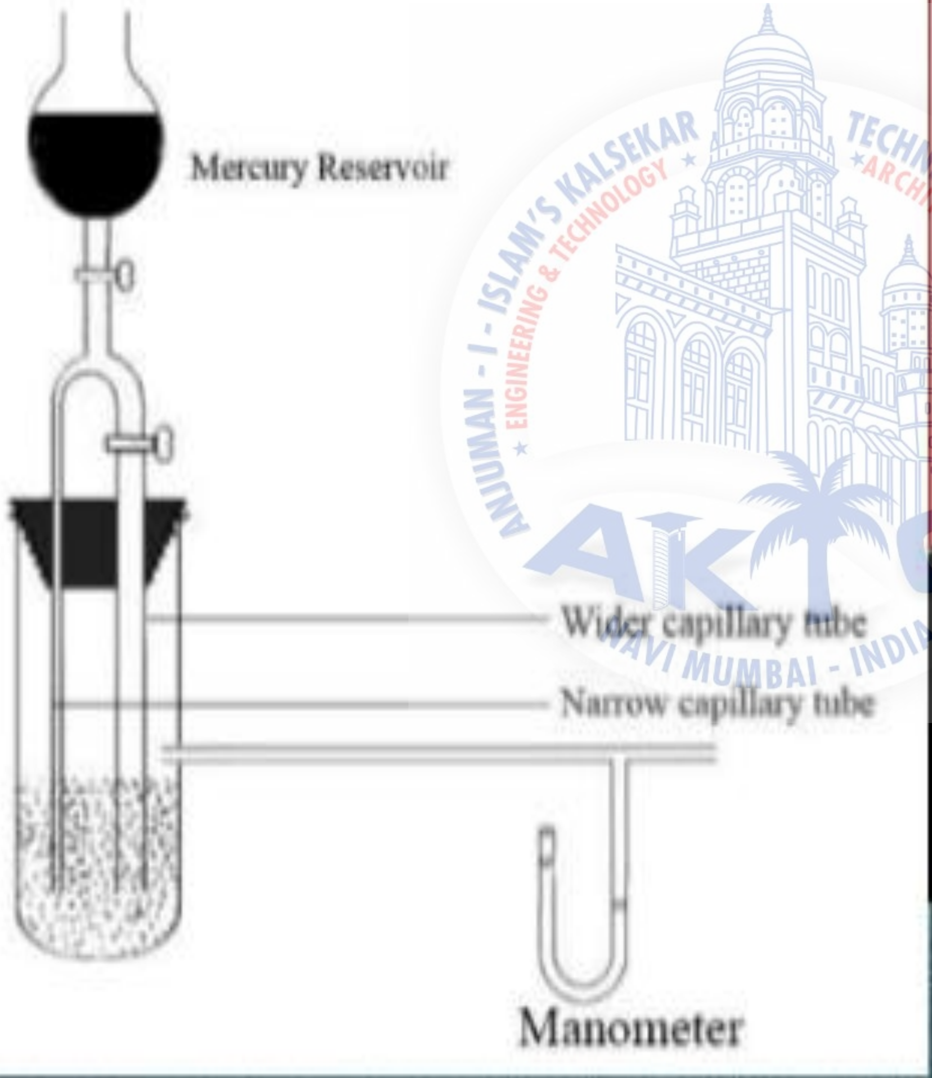
✓Capillary tube should have uniform diameter through out its length

✓Height of the column should measure accurately

✓Temperature must be maintained uniform

✓Better to allow meniscus to fall down than allow to rise

Maximum Bubble Pressure Method



Mercury is allowed flow through each capillaries

Difference in pressure when bubbles form in sider and narrow capillaries noted.

When radius of narrow capillary is less than 0.01cm (r_1) and wider is greater than 0.2cm (r_2) surface tension is given by

$$\gamma = AP\left[1 + 0.67 r_2 g \frac{D}{P}\right]$$

A – Instrument constant
D – Density of the liquid
P – Difference in pressure

4. Maximum bubble pressure method

This method is also called the bubble pressure method. In this method air gas bubble is blown at constant rate through a capillary which is submerged in the tested liquid.

The scheme of the apparatus proposed by Rebinder is shown in Fig. 12.11.

The pressure inside the gas bubble is increasing. Its shape from the very beginning is spherical but its radius is decreasing. This causes the pressure increase inside it and the pressure is maximal when the bubble has a hemispherical size. At this moment the bubble radius equals to the radius of the capillary, inner if the liquid wets the tip of the capillary and outer if it does not wet it.

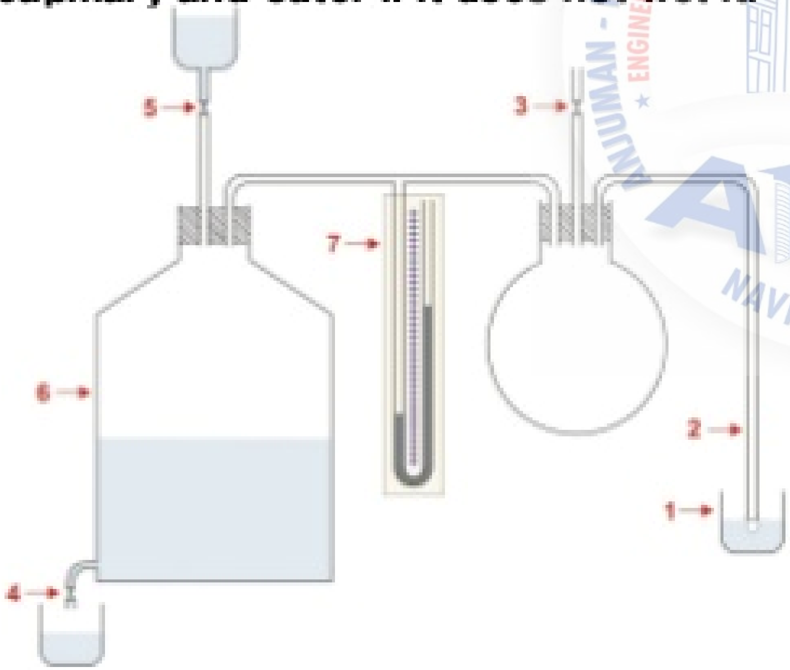
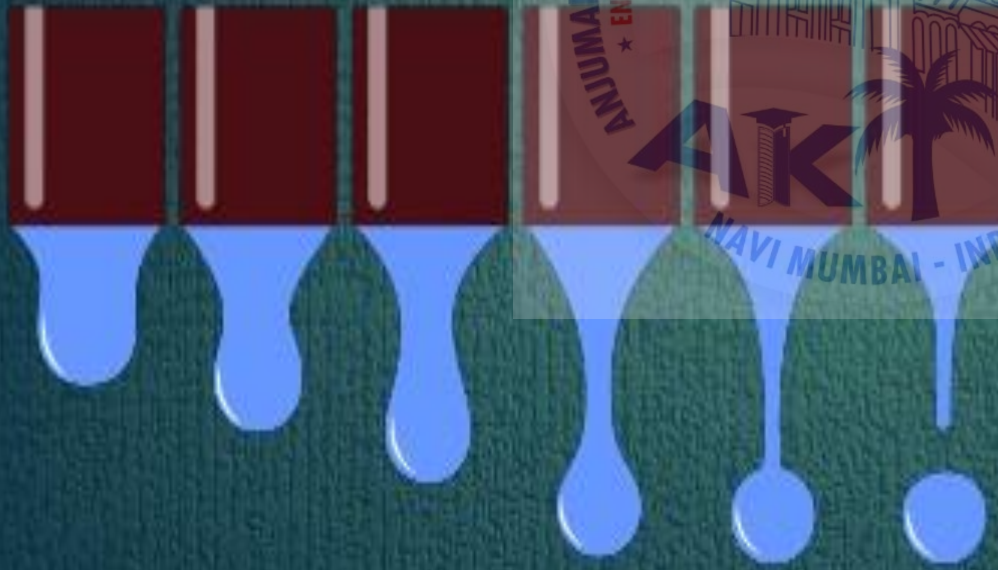


Fig. 12.11. Scheme of the apparatus for surface tension measurements by the bubble pressure method.

Drop Method

When a liquid is allowed to flow through a capillary tube it forms a drop at the tip of the tube

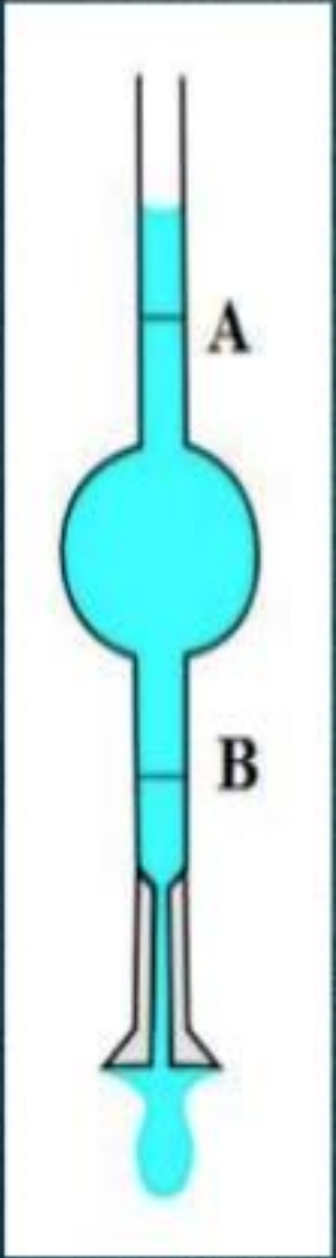
It increases in size and detaches from the tip when weight of the drop just equals the surface tension at the circumference of the tube



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

$$\gamma = \frac{w}{2\pi r}$$

STALAGMOMETER



- Drop Method
  - Drop Weight
  - Drop Count

Drop Weight Method

1. Suck the liquid up to the mark A
2. Allow the liquid to drop from tip of the stalagmometer
3. Collect 20 – 30 drops and find out the weight
4. Find average weight of drops

$$\gamma = \frac{W}{2\pi r}$$

Generally relative surface tension with respect to water is found out

$$\frac{\gamma_l}{\gamma_w} = \frac{W_l}{W_w}$$

Drop Count Method

1. Suck the liquid up to the mark A
2. Allow the liquid to drop from tip of the stalagmometer
3. Count the number of drops formed till the liquid reach mark B

$$\gamma = \frac{W}{2 \pi r n}$$

W(weight of total number of drops)= mg = vdg

d- density of the liquid

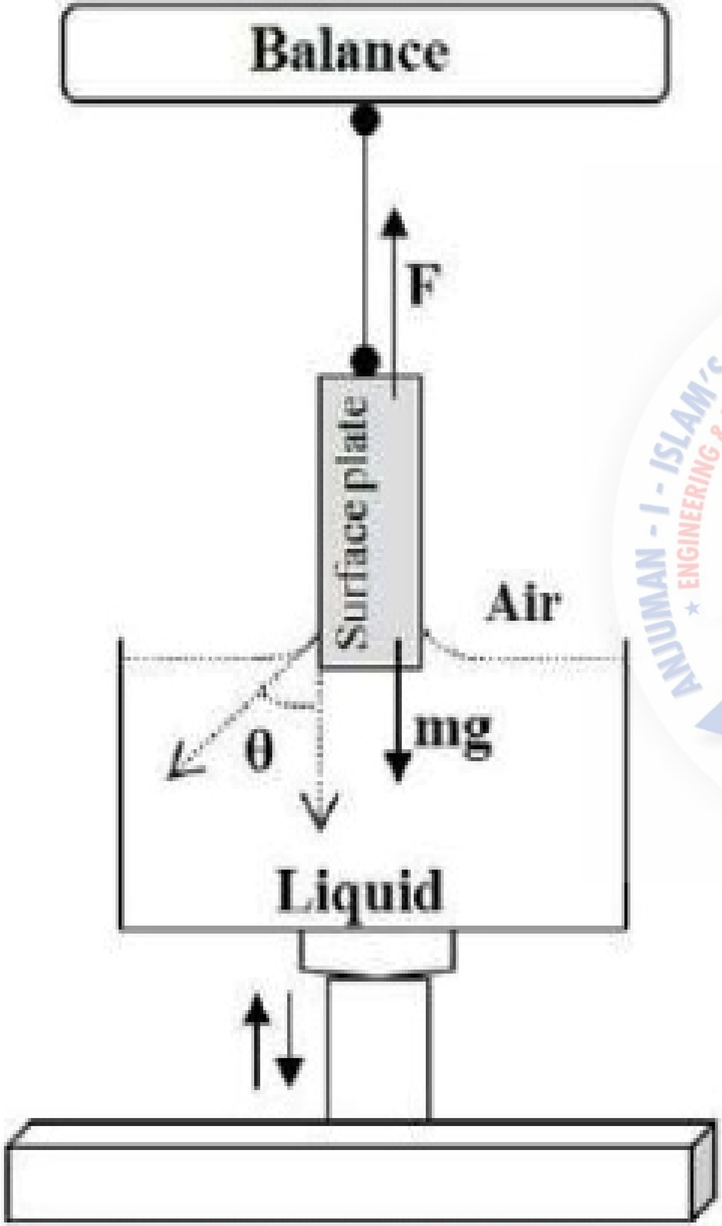
Generally relative surface tension with respect to water is found out

$$\frac{\gamma_l}{\gamma_w} = \frac{d_l n_w}{d_w n_l}$$

Precautions to be taken

- ✓ Tip of pipette should have no imperfections in the outer circumference
- ✓ Drops should be formed slowly
- ✓ About 20 – 30 drops should be collected to find the average weight
- ✓ Temperature should be maintained constant

Wilhelmy Plate method

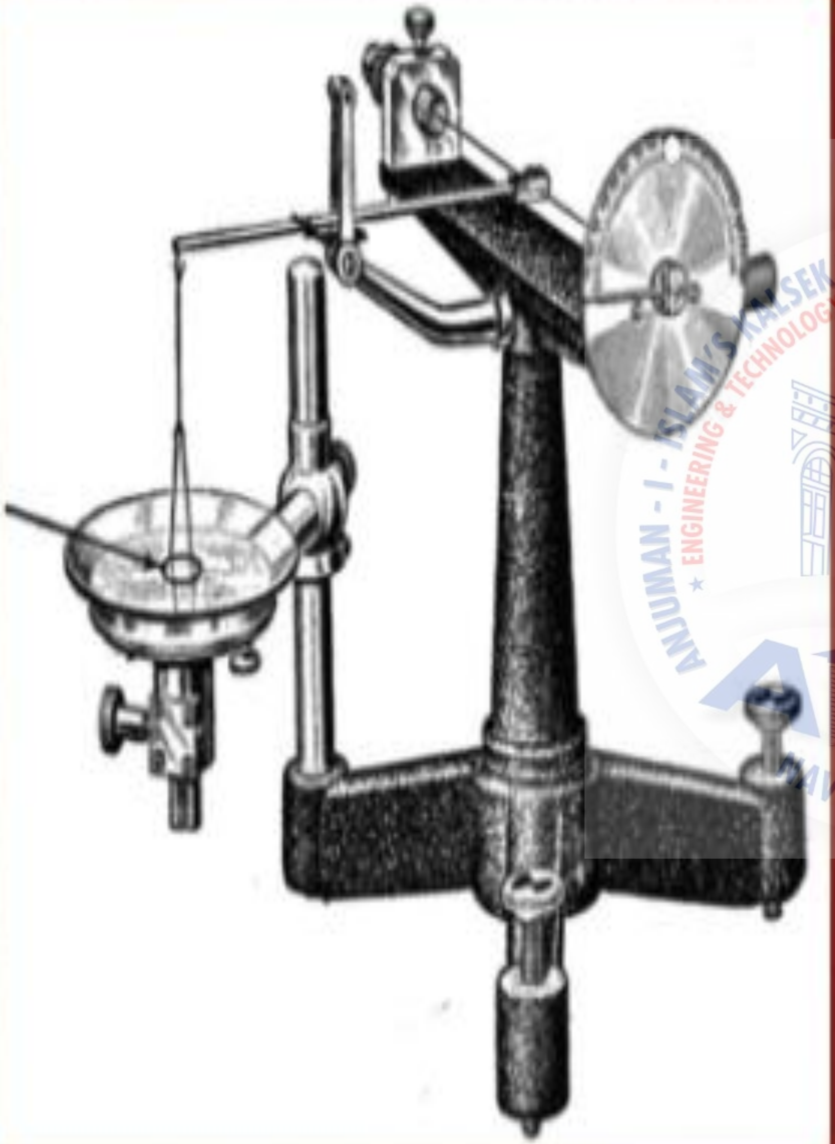


- Consist of a plate made up of platinum suspended vertically from a beam attached to a torsion balance
- Liquid is taken in a dish and raised until it just touches bottom of the plate
- When plate touches the surface, the surface force will drag the plate downward
- Rotate the torsion wire and measure the force required to bring back the plate to former position
- The force measured in torsion balance will be equal to the surface tension around the perimeter of the plate

$$W = 2\,(L+T)\,\gamma$$

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

Ring Detachment Method



- Torsion Balance or Du Nuoy balance consist of a platinum ring of around 4 cm in circumference suspended on a torsion wire attached to a scale
- Liquid is taken in a pan and position of pan is adjusted so that the ring just touches the liquid
- Torsion wire is rotated till the ring just detached from the surface of the liquid
- Force require to detach the ring from the surface is obtained from the scale
- The force is proportional to surface tension

$$P = 2\pi(r_1+r_2)\,\gamma$$

$$\gamma = P / 2\pi(r_1+r_2)$$

r_1 and r_2 are inner and outer radius of the ring

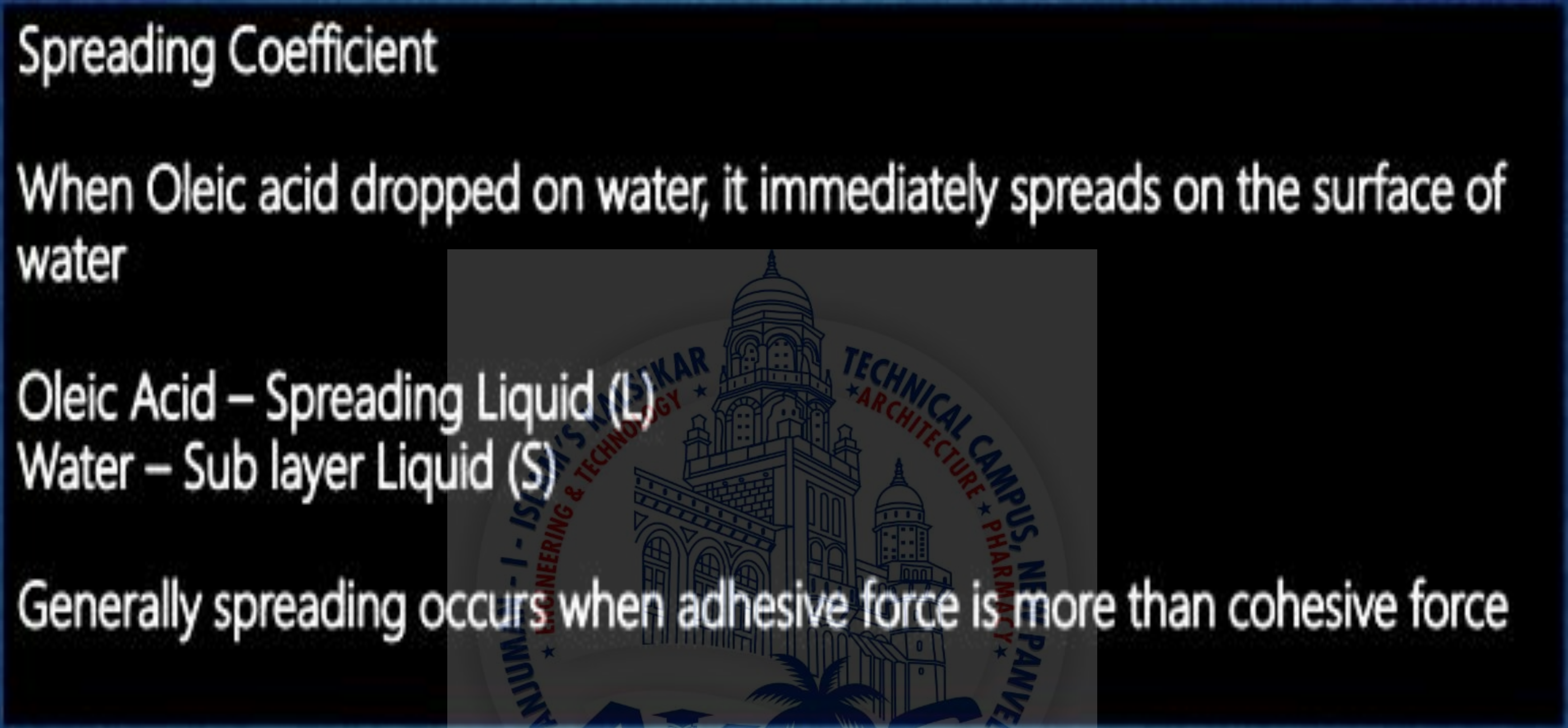
For thin rings $r_1 = r_2 = r$

$$\gamma = P / 4\pi r$$

Precautions to be taken

- ✓ The ring should lie in flat plane
- ✓ The plane of the ring must be horizontal
- ✓ Vessel containing liquid should have wider diameter
- ✓ Temperature must be kept constant

Spreading Coefficient

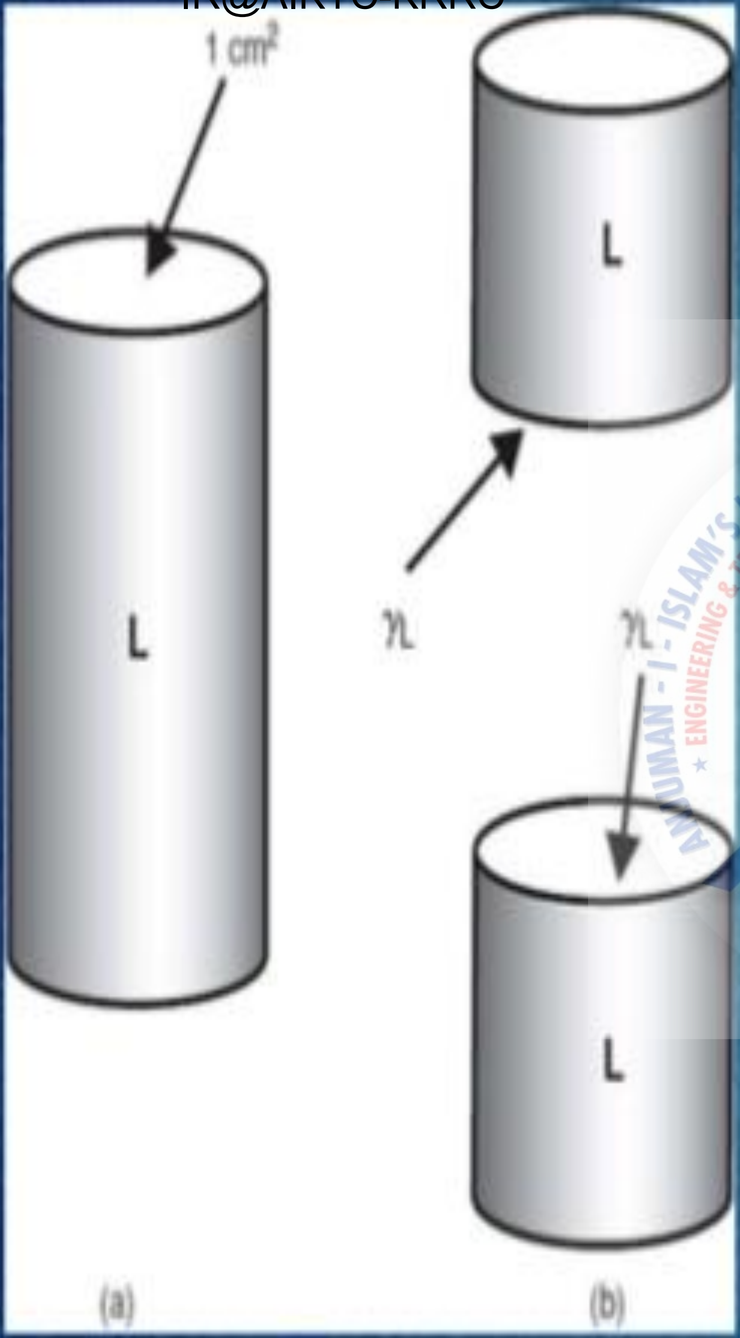


Spreading Coefficient

When Oleic acid dropped on water, it immediately spreads on the surface of water

Oleic Acid – Spreading Liquid (L)
Water – Sub layer Liquid (S)

Generally spreading occurs when adhesive force is more than cohesive force



Work of Cohesion (W_c) may be defined as the surface free energy increased by separating a column of pure liquid into two halves

Surface free energy increase = $\gamma\, dA$

$W_c = \gamma_L (dA + dA) = 2\, \gamma_L\, dA$

Here the column is of cross sectional area 1cm^2

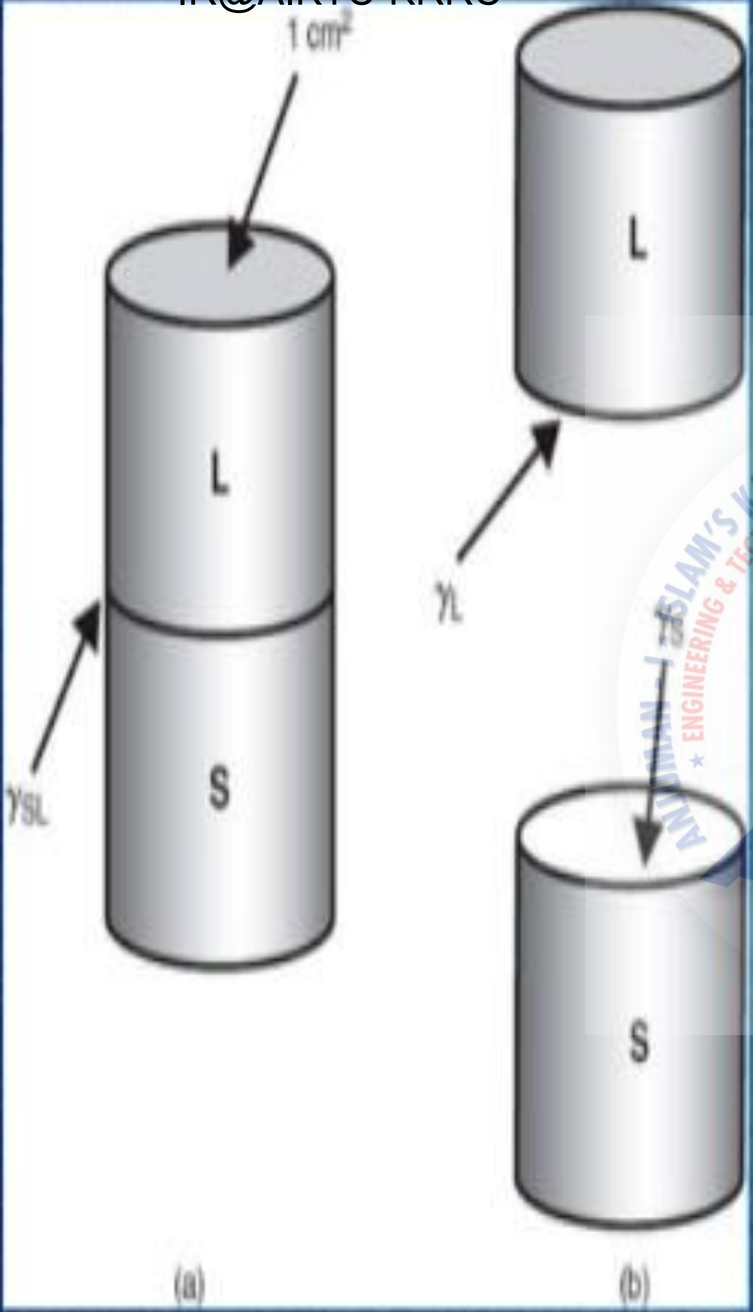
$$W_c = 2\, \gamma_L$$

Work of Cohesion

- It is the energy required to separate the like molecules of the spreading liquid, say oleic acid.

Work of cohesion=Wc = $2\gamma_L$

Where γ_L surface tension of liquid (L)



Work of Adhesion (W_a) may be defined as the surface free energy increased by separating a column of two immiscible liquids at its boundary into two sections

As two sections of immiscible liquids are already separated by a boundary, the energy requirement will be less by an amount γ_{LS} dA

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

Here the columns are of cross sectional area $1 cm^2$

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

Work of Adhesion

- It is the energy required to separate the unlike molecules.

Work of Adhesion= Wa= $\gamma_L + \gamma_S - \gamma_{LS}$

Where, γ_S =interfacial tension of sublayer

γ_{LS}= interfacial tension of liquid/solid surface

Spreading coefficient (S) is the difference between work of adhesion and work of cohesion

$$S = W_a - W_c = (\gamma_L + \gamma_S - \gamma_{LS}) - 2\gamma_L$$

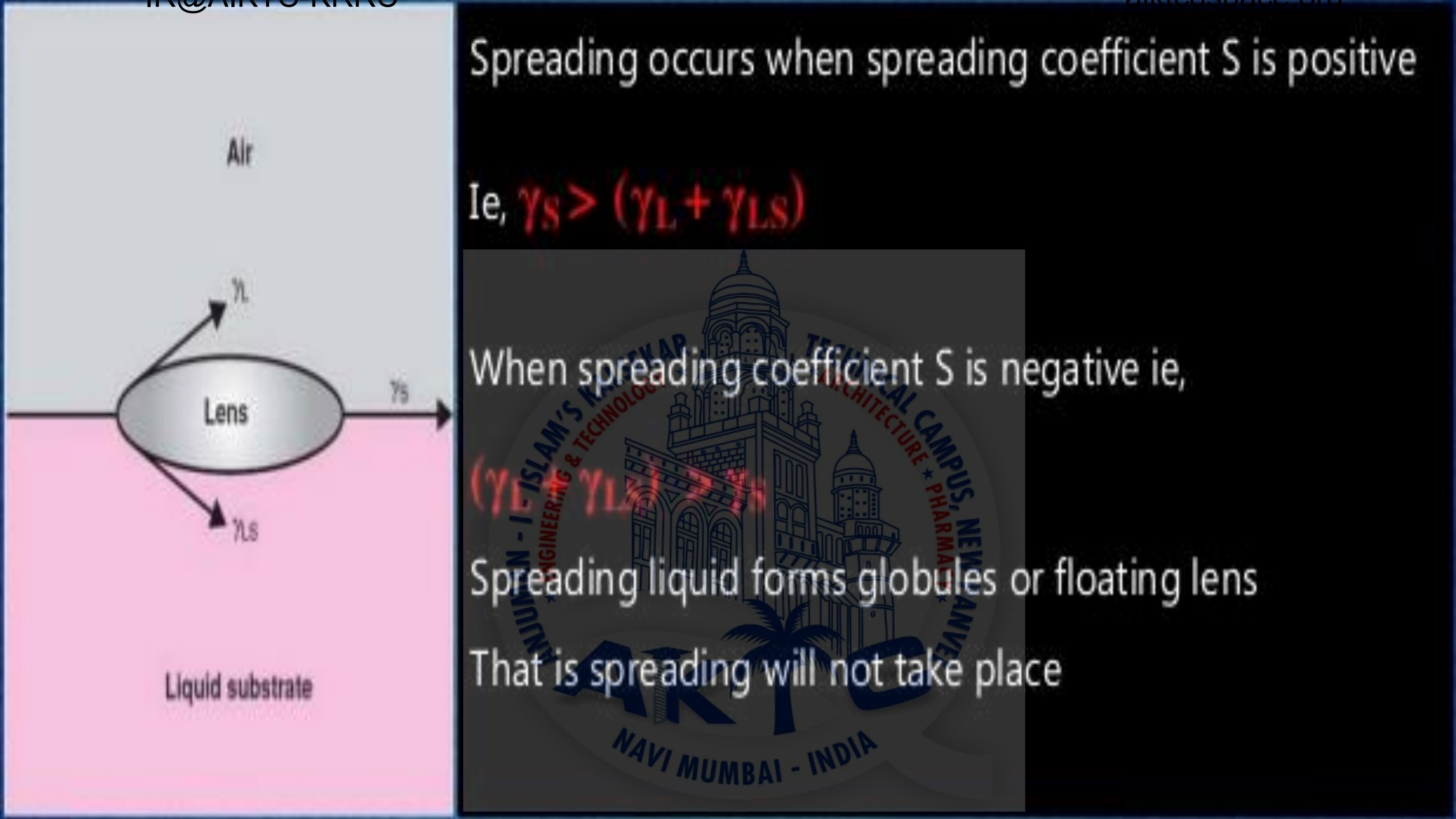
$$= \gamma_S - \gamma_L - \gamma_{LS}$$

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

γ_L - Surface tension of spreading liquid

γ_S - Surface tension of sublayer liquid

γ_{LS} - Interfacial tension



Spreading occurs when spreading coefficient S is positive

Ie, $\gamma_S > (\gamma_L + \gamma_{LS})$

When spreading coefficient S is negative ie,

$(\gamma_L + \gamma_{LS}) > \gamma_S$

Spreading liquid forms globules or floating lens

That is spreading will not take place

- When free energy of the spreading liquid and the interfacial tension with the sub layer is less than that of sublayer the spreading becomes spontaneous in an attempt to reduce free energy of sublayer.

- There may be saturation of the liquid with the other and there may be change in the surface tension of the sublayer liquid

- In that case the spreading coefficient may become negative after saturation, the spreading liquid coalesces and form a lens on the surface of the sublayer

- In the case of a DUPLEX FILM if S become negative after saturation, it forms a monolayer and excess liquid remains as lens on the surface

- Fatty acids and alcohols have high spreading coefficient
- As non polar chain length increases in an acid or alcohol spreading coefficient decreases
- Propionic acid and ethyl alcohol having high spreading coefficient
- Liquid petroleum do not spread on water

APPLICATIONS OF SPREADING COEFFICIENTS

- Absorption of medicament from creams, lotions, etc.
- Stabilization of emulsions
- Coating of tablets

Chapter 5

Lecture 3

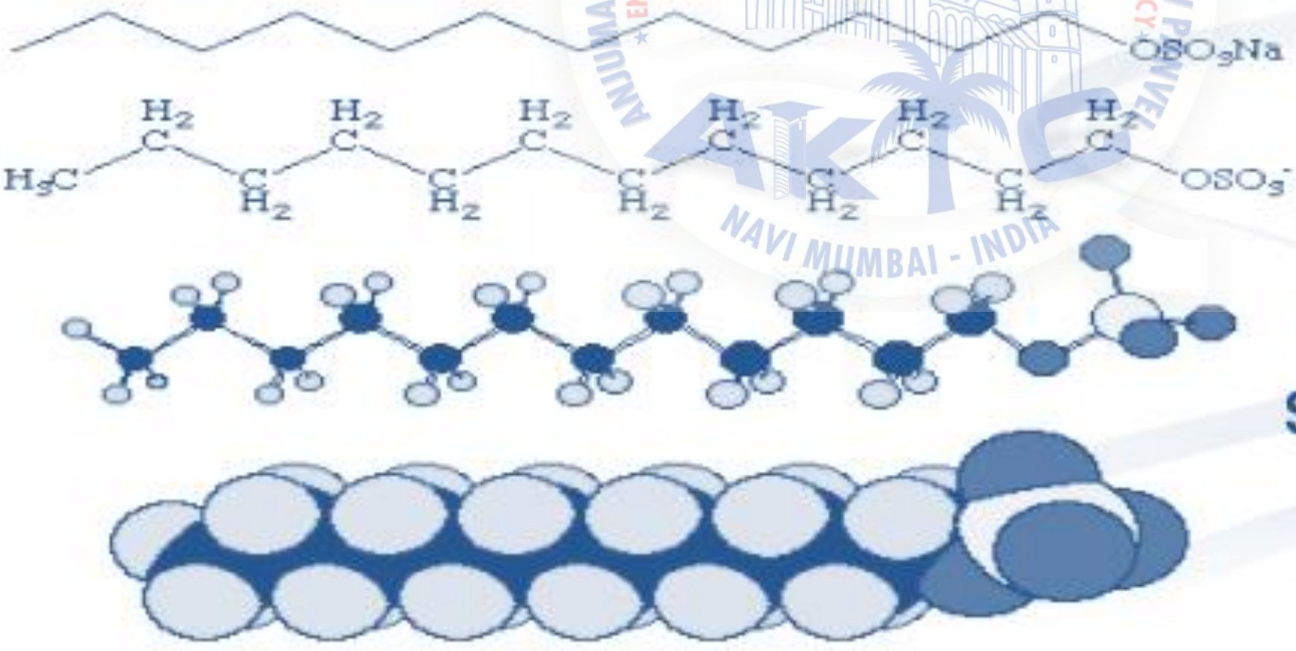
Surface Active Agents

Surface Active Agents

A surfactant molecule is depicted schematically as a cylinder representing the hydrocarbon (hydrophobic) portion with a sphere representing the polar (hydrophilic) group attached at one end.

The hydrocarbon chains are straight because rotation around carbon-carbon bonds bends, coils and twists them.

$CH_3(CH_2)_{11}OSO_3^-Na^+$



Sodium Lauryl Sulfate molecule

Surface Active Agents

Surface Active Agents

- Molecules and ions that are adsorbed at interfaces are termed *surface active agents*, *surfactants or amphiphile*
- The molecule or ion has a certain affinity for both polar and nonpolar solvents.
- Depending on the number and nature of the polar and nonpolar groups present, the amphiphile may be *hydrophilic*, *lipophilic* or be reasonably well-balanced between these two extremes.
- It is the amphiphilic nature of surface active agents which causes them to be adsorbed at interfaces, whether these be liquid/gas or liquid/liquid.

As surface or interfacial work is equal to surface tension multiplied by the area increment.

- The *work of cohesion*, which is the energy required to separate the molecules of the spreading liquid so as it can flow over the sub-layer= $W_c = 2\gamma_L$

  Where 2 surfaces each with a surface tension = γ_L

- The *work of adhesion*, which is the energy required to break the attraction between the unlike molecules=

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

Where: γ_L =the surface tension of the spreading liquid

γ_S =the surface tension of the sub-layer liquid

γ_{LS} =the interfacial tension between the two liquids.

- Spreading occurs if the work of adhesion is greater than the work of cohesion, i.e. $W_a > W_c$ or $W_a - W_c > 0$

Spreading Coefficient is The difference between the work of adhesion and the work of cohesion

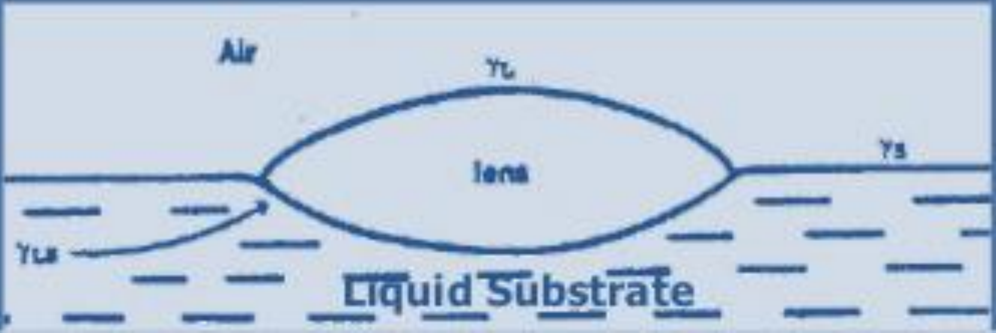
$$S = W_a - W_c = (\gamma_L + \gamma_S - \gamma_{LS}) - 2\gamma_L$$

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

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

Spreading occurs (S is positive) when the surface tension of the sub-layer liquid is greater than the sum of the surface tension of the spreading liquid and the interfacial tension between the sub-layer and the spreading liquid.

If $(\gamma_L + \gamma_{LS})$ is larger than γ_S, (S is negative) the substance forms globules or a *floating lens* and fails to spread over the surface.



Factor affecting Spreading Coefficient

- **Molecular Structural:**
  - The greater the polarity of the molecule → the more positive [S] as ethyl alcohol and propionic acid
  - Non polar substances as Liquid petrolatum have negative [S] fail to spread on water
  - For organic acids, as Oleic acid,

the longer the carbon chain → decrease in polar character → decrease [S]

  - Some oils can spread over water because they contain polar groups as COOH and OH

- **Cohesive forces:**

Benzene spreads on water not because it is polar but because the cohesive forces between its molecules are much weaker than the adhesion for water.

Application of Spreading coefficient in pharmacy

- ✓ The requirement of film coats to be spreaded over the tablet surfaces
- ✓ The requirement of lotions with mineral oils to spread on the skin by the addition of surfactants

Classification of Surface Active Agents

Functional Classification

According to their pharmaceutical use, surfactants can be divided into the following groups:

- ☐ Wetting agents
- ☐ Solubilizing agents
- ☐ Emulsifying agents
- ☐ Dispersing, Suspending and Defloculating agents
- ☐ Foaming and antifoaming agents
- ☐ Detergents

Wetting agents

- Wetting agent is a surfactant that when dissolved in water, lower the contact angle and aids in displacing the air phase at the surface and replacing it with a liquid phase.
- Solids will not be wetted if their critical surface tension is exceeded than the surface tension of the liquid. Thus water with a value of 72 dynes/cm will not wet polyethylene with a critical surface tension of 31 dynes/cm.
- Based on this concept we should expect a good wetting agent to be one which reduces the surface tension of a liquid to a value below the solid critical surface tension.

When the forces of adhesion are greater than the forces of cohesion, the liquid tends to wet the surface and vice versa.

Place a drop of a liquid on a smooth surface of a solid. According to the wettability, the drop will make a certain angle of contact with the solid.

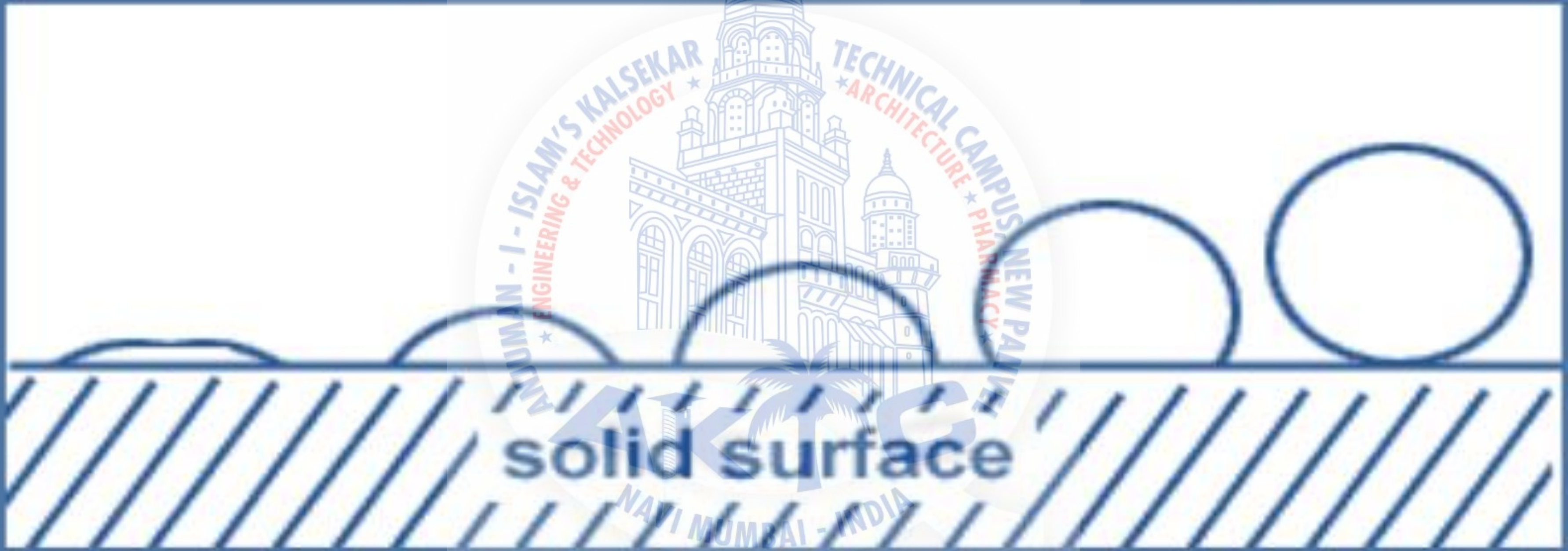
A contact angle is lower than 90°, the solid is called wettable

A contact angle is wider than 90°, the solid is named non-wettable.

A contact angle equal to zero indicates complete wettability.

The contact angle of a liquid with a solid is used as wettability index. For α < 90° the liquid wet the wall (eg: water on glass), for α > 90° the liquid does not wet the wall (eg: mercury on glass). If α = 0° the liquid perfectly wet the wall.

complete wetting	incomplete wetting			no wetting



$\theta = 0°$	$\theta < 90°$	$\theta = 90°$	$\theta > 90°$	$\theta = 180°$
$\gamma_s - \gamma_{sL} > 0$	$\gamma_s - \gamma_{sL} \approx 0$			$\gamma_s - \gamma_{sL} < 0$

- The surface of liquid water (meniscus) has a concave shape because water wets the surface and creeps up the side
- The surface of Mercury has a convex shape it does not wet glass because the cohesive forces within the drops are stronger than the adhesive forces between the drops and glass.

Micellar Solubilization

- Surfactant molecules accumulate in the interfaces between water and water insoluble compound. Their hydrocarbon chains penetrate the outermost layer of insoluble compound which combine with the water-insoluble molecules. Micelles form around the molecules of the water-insoluble compound inside the micelles' cores and bring them into solution in an aqueous medium. This phenomenon is called micellar solubilization.

- The inverted micelles formed by oil-soluble surfactant which dissolves in a hydrocarbon solvent can solubilize water-soluble compound which is located in the center of the micelle, out of contact with the solvent.

- Micelles of nonionic surfactants consist of an outer shell containing their polyethylene glycol moieties mixed with water and an inner core formed by their hydrocarbon moieties. Some compounds like phenols and benzoic acid form complexes with polyethylene glycols by hydrogen bonding and/or are more soluble in liquids of intermediate polarity like ethanol or ethyl ether than in liquids of low polarity like aliphatic hydrocarbons. These compounds locate in the aqueous polyethylene glycol outer shell of nonionic micelles on solubilization.

Drugs which are soluble in oils and lipids can be solubilized by micellar solubilization.

- As Micellar solubilization depends on the existence of micelles; it does not take place below the CMC. So dissolution begins at the CMC. Above the CMC, the amount solubilized is directly proportional to the surfactant concentration because all surfactant added to the solution in excess of the CMC exists in micellar form, and as the number of micelles increases the extent of solubilization increases .

- Compounds that are extensively solubilized increase the size of micelles in two ways:
  - The micelles swell because their core volume is augmented by the volume of the solubilizate.
  - The number of surfactant molecules per micelle increases.

Foaming and Anti Foaming agents

- *Foams are dispersion of a gas in a liquid (liquid foams as that formed by soaps and detergents) or in a solid (solid foams as sponges).*
- **Foaming agents**

Many Surfactants solutions promote the formation of foams and stabilize them, in pharmacy they are useful in toothpastes compositions.

- **Anti Foaming agents**

They break foams and reduce frothing that may cause problems as in foaming of solubilized liquid preparations. in pharmacy they are useful in aerobic fermentations, steam boilers.

Detergents

- 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.

The polar and hydrophilic heads, carry the dirt in the water. The agitation of the fluid make easier the process.

The molecules insert their hydrophobic tail inside the fat.

How surfactants remove the dirt

Structural Classification

- A single surfactant molecule contains one or more hydrophobic portions and one or more hydrophilic groups.
- According to the presence of ions in the surfactant molecule they may be classified into:

☐ Ionic surfactants

- Anionic surfactants: the surface active part is anion (negative ion) e.g. soaps, sodium lauryl sulfate
- Cationic surfactants: the surface active part is cation (positive ion) e.g. quaternary ammonium salts
- Ampholytic surfactants: contain both positive and negative ions e.g. dodecyl-B-alanine.

Ionic surfactants

Anionic surfactants

- They are the metal salts of long - chain fatty acids as lauric acid.
- *Sodium dodecyl sulfate or Sodium Lauryl Sulfate* is used in toothpaste and ointments
- *Triethanolamine dodecyl sulfate* is used in shampoos and other cosmetic preparations.
- *Sodium dodecyl benzene sulfonate* is a detergent and has germicidal properties.
- *Sodium dialkvlsulfosuccinates* are good wetting agents.

Cationic surfactants

- These are chiefly quaternary ammonium compounds.
- They have bacteriostatic activity probably because they combine with the carboxyl groups in the cell walls and of microorganisms by cation exchange, causing lysis.
- Among the most popular antiseptics in this category are benzalkonium chloride, cetylpyridinium chloride and cetyltrimethylammonium bromide,

Ampholytic Surfactants

- These are the least common, e.g. dodecyl-β-alanine

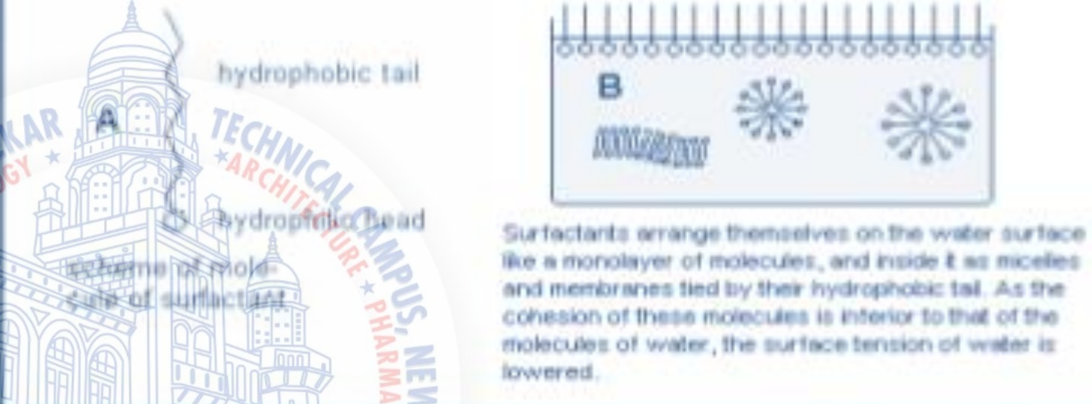
Non-ionic surfactants

- Widely used in pharmaceutical formulations e.g. Tweens, Spans, Brij and Myrj.
- They are polyethylene oxide products.
- Surfactants based on sorbitan are of pharmaceutical importance.
- Esterification of the primary hydroxyl group with lauric, palmitic, stearic or oleic acid forms sorbitan monolaurate, monopalmitate, monostearate or monooleate

  These are water-insoluble surfactants called Span 20, 40, 60 or 80, respectively.
- Addition of about 20 ethylene oxide molecules produces the water-soluble surfactants called polysorbate or Tween 20, 40. 60 or 80.

Absorption of surfactant at interfaces.

As a Surface active substance contains a hydrophilic and a hydrophobic portions, it is adsorbed as a monolayer at the interfaces.



Surfactants arrange themselves on the water surface like a monolayer of molecules, and inside it as micelles and membranes tied by their hydrophobic tail. As the cohesion of these molecules is inferior to that of the molecules of water, the surface tension of water is lowered.

At water-air interface

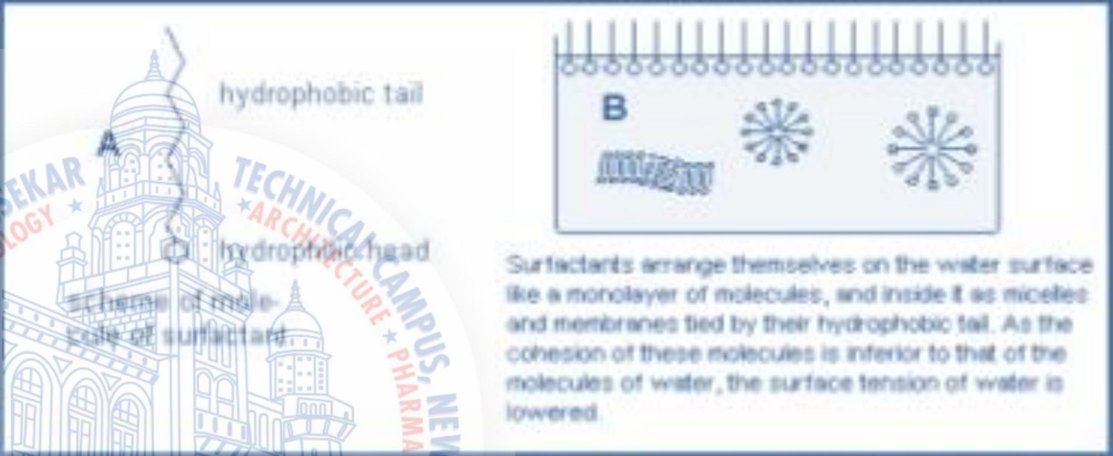
Surface-active molecules will be adsorbed at water-air interfaces and oriented so that the hydrocarbon chains of are pushed out of the water and rest on the surface, while the polar groups are inside the water. Perhaps the polar groups pull the hydrocarbon chains partly into the water.

At oil-water interface

Surface-active molecules will be oriented so that the hydrophobic portion is inside the oil phase and the hydrophilic portion inside the water phase.

At low surfactant concentrations:

The hydrocarbon chains of surfactant molecules adsorbed in the interface lie nearly flat oh the water surface.



Surfactants arrange themselves on the water surface like a monolayer of molecules, and inside it as micelles and membranes tied by their hydrophobic tail. As the cohesion of these molecules is inferior to that of the molecules of water, the surface tension of water is lowered.

At higher concentrations:

They stand upright because this permits more surfactant molecules to pack into the interfacial monolayer.

As the number of surfactant molecules adsorbed at the water-air interface increased, they tend to cover the water with a layer of hydrocarbon chains. Thus, the water-air interface is gradually transformed into an non polar-air interface. This results in a decrease in the surface tension of water.

- At a given concentration, temperature, and salt content, all micelles of a given surfactant usually contain the same number of molecules, i.e. they are usually monodisperse. For different surfactants in dilute aqueous solutions, this number ranges approximately from 25 to 100 molecules.

- The diameters of micelles are approximately between 30 and 80 A°. Because of their ability to form aggregates of colloidal size, surfactants are also called association colloids.

- Micelles are not permanent aggregates. They form and disperse continually.

Surfactant shapes in colloidal solution

a- Cone-shaped surfactant resulting in b-normal micelles

c- Hampagne cork shaped surfactant resulting in d-reverse micelles with control of their size by the water content

e- Interconnected cylinders .

f- Planar lamellar phase .

g- Onion-like lamellar phase.

- **Normal spherical micelles**

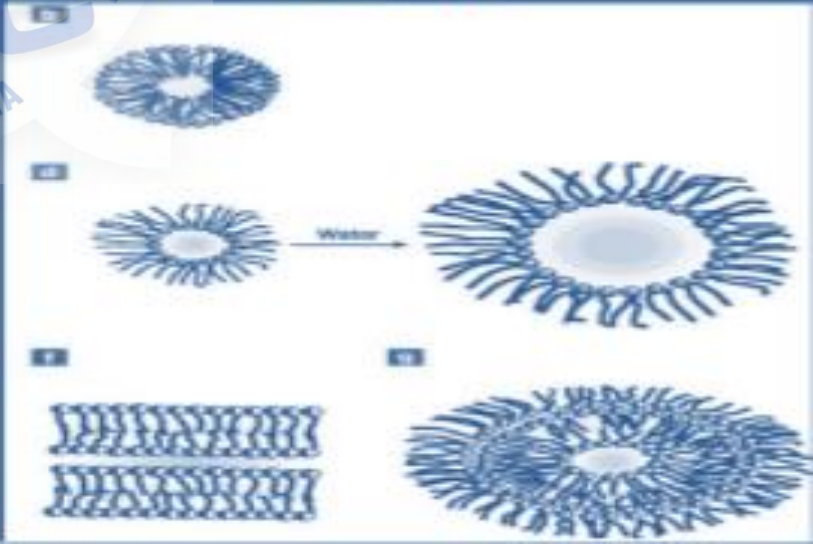
  In dilute aqueous solutions micelles are approximately spherical. The polar groups of the surfactants are in the periphery and the hydrocarbon chains are oriented toward the center, forming the core of the micelles

- **Inverted spherical micelles**

  In solvents of low polarity or oils micelles are inverted. The polar groups face inward to form the core of the micelle while the hydrocarbon chains are oriented outward

- **Cylindrical and lamellar micelles**

  In more concentrated solutions of surfactants, micelles change from spherical either to cylindrical or lamellar phase.



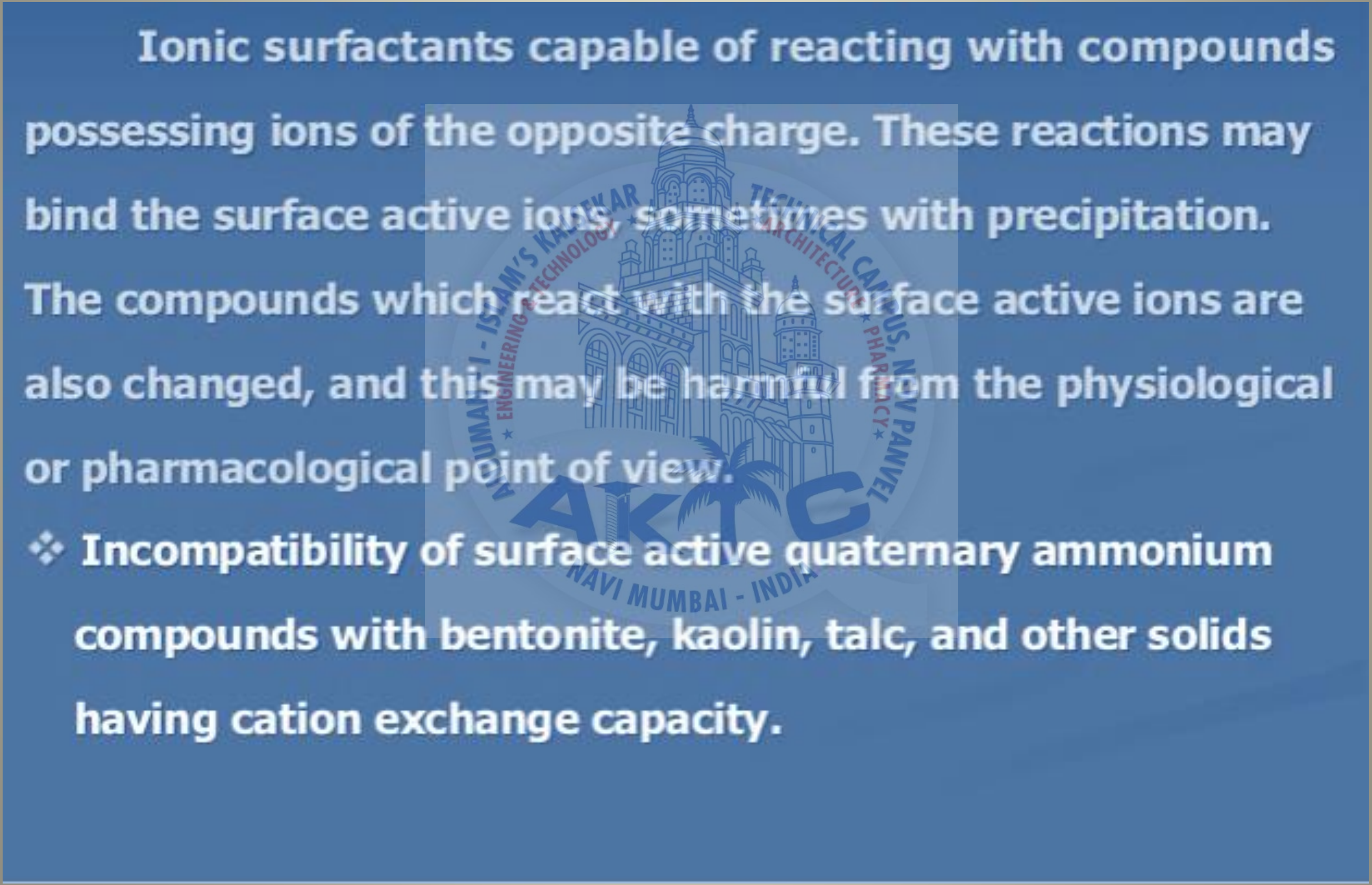
Incompatibilities Involving Surfactants

Nonionic surfactants

Nonionic surfactants have few incompatibilities with drugs and are preferred over ionic surfactants. even in formulations for external use, except when the germicidal properties of cationic and anionic surfactants are important.

Nonionic surfactants form weak complexes with some preservatives as phenols, including esters of p-hydroxybenzoic acid (Parabenzes) and with acids like benzoic and salicylic via hydrogen bonds. This reduces the antibacterial activity of these compounds.

Ionic surfactant



Ionic surfactants capable of reacting with compounds possessing ions of the opposite charge. These reactions may bind the surface active ions, sometimes with precipitation. The compounds which react with the surface active ions are also changed, and this may be harmful from the physiological or pharmacological point of view.

- Incompatibility of surface active quaternary ammonium compounds with bentonite, kaolin, talc, and other solids having cation exchange capacity.

Chapter 5

Lecture 4,5

Adsorption

- **Adsorption** is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (**adsorbent**), forming a molecular or atomic film (**adsorbate**).
- It is different from **absorption**, in which a substance diffuses into a liquid or solid to form a solution.
- **Adsorbent** (also called *substrate*) - The solid that provides surface for adsorption.
- **Adsorbate** - The gas or liquid substances which are to be adsorbed on Substrate.

ADSORPTION	ABSORPTION
1. It is mainly surface phenomenon. Surface concentration of adsorbed material is very high as compared to bulk. In fact, the bulk has practically no adsorbed material	1. The solid or liquid absorbs the gaseous or liquid matter. Concentration of the material is uniform throughout the absorbing material.
2. A distinct chemical reaction occurs specially in chemisorption.	2. No chemical reaction is involved between the absorbed material and solid .
3. Some reactions is usually the result.	3. The absorbed material is recovered unchanged, as in case for the absorbent
4. Only limited quantities of material are absorbed. It reaches saturation very easily.	4. Considerable amounts of absorbed material is ingested.
5. For example, Ammonia is absorbed by charcoal.	5. For example, ammonia is absorbed in water.

ABSORBATE

ADSORBATE

	Physisorption	Chemisorption
Equilibrium	Rapidly	Slowly
Nature	Reversible	Irreversible
Depends on	Adsorbent	Adsorbent and Adsorbate
Pressure	Increases	Decreases
Example	Hydrogen adsorbed on charcoal	Hydrogen adsorbed on nickel

Adsorption On Solid Surface

Characterisation of adsorption system

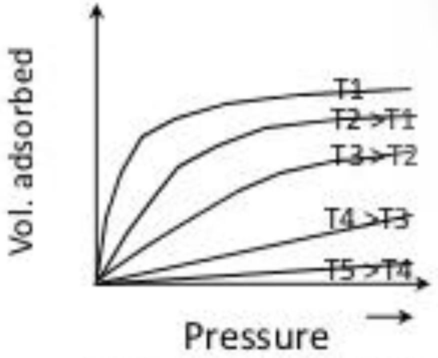
Adsorption isotherm - most commonly used, especially to catalytic reaction system, T=const. The amount of adsorption as a function of pressure at set temperature

Adsorption isobar - (usage related to industrial applications)

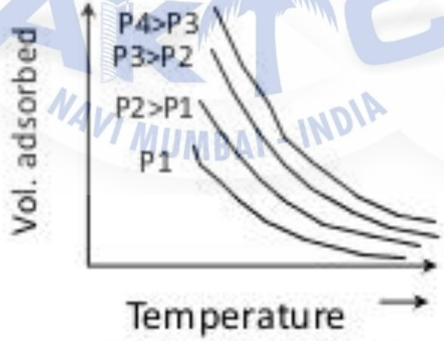
The amount of adsorption as a function of temperature at set pressure

Adsorption Isostere - (usage related to industrial applications)

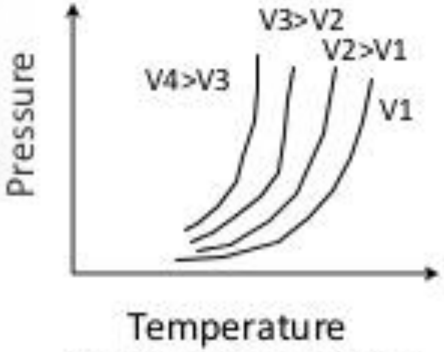
Adsorption pressure as a function of temperature at set volume



Adsorption Isotherm



Adsorption Isobar



Adsorption Isostere

ISOTHERM	TYPE OF ADSORPTION	NATURE OF ADSORBENT
Type I	Langmuir type	is found for porous materials with small pores e.g. charcoal
Type II	Sigmoid type	for non-porous materials
Type III	Hyperbolic type	porous materials with cohesive force between adsorbate molecules greater than the adhesive force between adsorbate molecules and adsorbent
Type IV	Sharp approach to the line p_0	staged adsorption (first monolayer then build up of additional layers
Type V	Elongated S-type	porous materials with cohesive force between adsorbate molecules and adsorbent being greater than that between adsorbate molecules

Freundlich Adsorption Isotherm

- The Freundlich isotherm is the most important multisite adsorption isotherm for rough surfaces.
- The freundlich equation or freundlich adsorption isotherm , is a curve relating the concentration of a solute on the surface of adsorbent to the concentration of the solute in a liquid with which it is in contact.
- In 1909.freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as <u>FREUNDLICH ADSORPTION ISOTHERM</u>

$$x/m = k\,P^{1/n}$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and gas at particular temperature.

Explanation of Freundlich Adsorption equation

At low pressure, extent of adsorption is directly proportional to pressure (raised to power one).

$$x/m \infty P'$$

At high pressure, extent of adsorption is independent of pressure (raised to power zero).

$$x/m \infty P^{\circ}$$

Therefore at intermediate value of pressure, adsorption is directly proportional to pressure raised to power 1/n .Here n is a variable whose value is greater than one.

therefore,

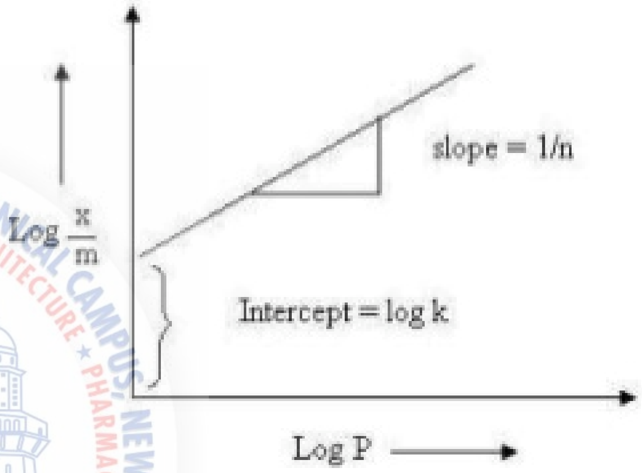
$$x/m \infty k P^{1/n}$$

Using constant of proportionality, k, also known as adsorption constant we get

$$x/m = k P^{1/n}$$

The above equation is known as Freundlich adsorption equation.

Plotting of Freundlich Adsorption Isotherm



As per Freundlich adsorption equation

$$x/m = k P^{1/n}$$

Taking log both sides of equation, we get,

$$\log\{x/m\} = \log k + 1/n \log p$$

The equation above equation is comparable with comparable with equation of straight line, $y = m x + c$ where, m represents slope of the line and c represents intercept on y axis.

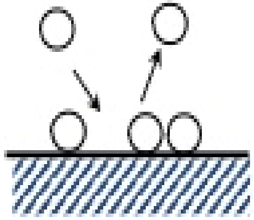
Plotting a graph between log(x/m) and log p, we will get a straight line with value of slope equal to 1/n and log k as y-axis intercept.

It has limited applicability. It can be applied to study adsorption from solutions.

LIMITATION OF FREUNDLCH ADSORPTION EQUATION

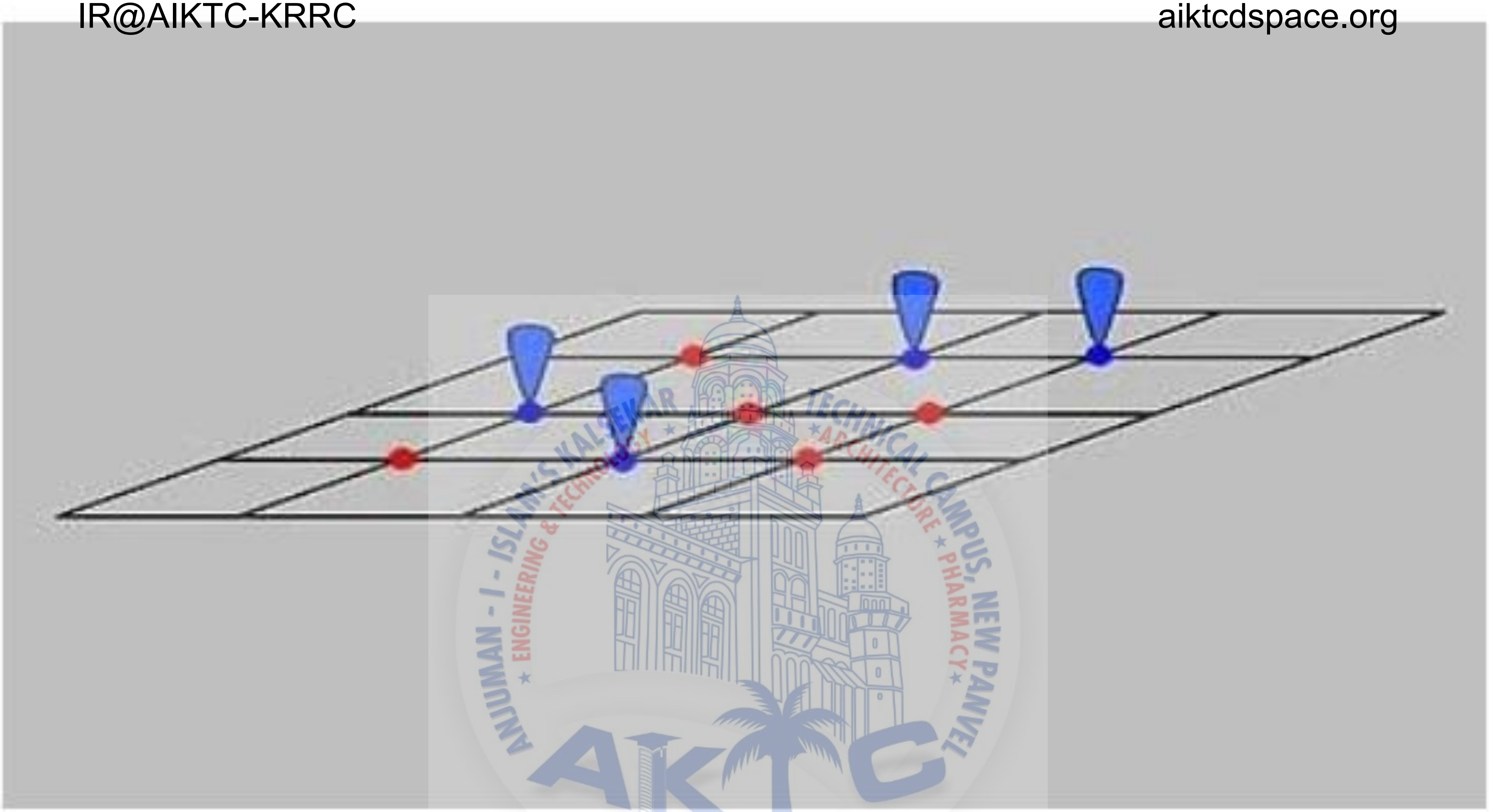
- Experimently it was determined that extent of adsorption varies directly with presssure till saturation pressure is reached. Beyond that point rate of adsorption saturates even after applying higher pressure .
- Thus, Freundlich adsorption equation failed at higher pressure.

Langmuir isotherm



❑**Basic assumptions**

- ➢surface uniform
- ➢monolayer adsorption
- ➢no interaction between adsorbed molecules and adsorbed molecules immobile
- ➢Adsorbed molecule and desorbed molecule exist in equilibrium, as well as exhibit ideal gas behaviour



An schematic showing equivalent sites, occupied(blue) and unoccupied(red) clarifying the basic assumptions used in the model. The adsorption sites(heavy dots) are equivalent and can have unit occupancy. Also, the adsorbates are immobile on the surface

Case I - single molecule adsorption when adsorption is in a dynamic equilibrium

$A(g) + M(\text{surface site}) \leftrightarrows AM$

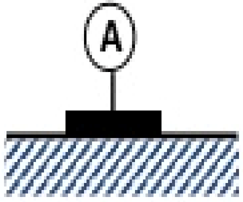
the rate of adsorption $r_{ads} = k_{ads}\,(1-\theta)\,P$

the rate of desorption $r_{des} = k_{des}\,\theta$

at equilibrium $r_{ads} = r_{des} \Rightarrow k_{ads}\,(1-\theta)\,P = k_{des}\,\theta$

rearrange it for θ $\theta = \dfrac{(k_{ads}/k_{des})P}{1+(k_{ads}/k_{des})P}$

let $B_0 = \dfrac{k_{ads}}{k_{des}} \Rightarrow \theta = \dfrac{C_s}{C_\infty} = \dfrac{B_0 P}{1+B_0 P}$ B_0 is *adsorption coefficient*



case I

Langmuir adsorption isotherm

case I $\theta = \dfrac{C_s}{C_\infty} = \dfrac{B_0 P}{1 + B_0 P}$

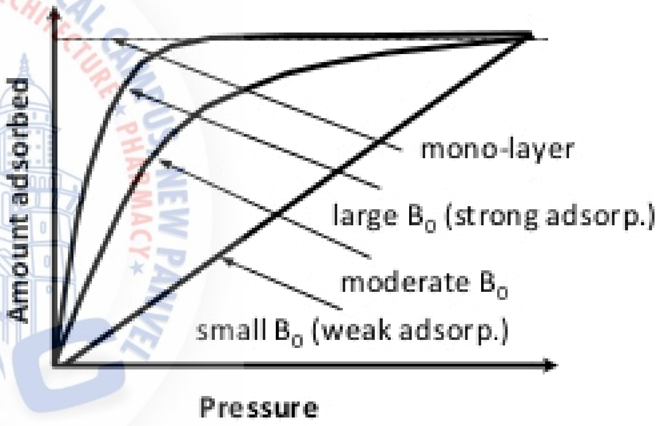
case II $\theta = \dfrac{C_s}{C_\infty} = \dfrac{(B_0 P_{AB})^{1/2}}{1 + (B_0 P_{AB})^{1/2}}$

Case III $\theta_A = \dfrac{C_{s,A}}{C_\infty} = \dfrac{B_{0,A} P_A}{1 + B_{0,A} P_A + B_{0,B} P_B}$

$\theta_B = \dfrac{C_{s,B}}{C_\infty} = \dfrac{B_{0,B} P_B}{1 + B_{0,A} P_A + B_{0,B} P_B}$

Strong adsorption $k_{ads} >> k_{des}$ $\theta = \dfrac{C_s}{C_\infty} \rightarrow 1$

Weak adsorption $k_{ads} << k_{des}$ $\theta = \dfrac{C_s}{C_\infty} = B_0 P$



- Langmuir adsorption isotherm established a logic picture of adsorption process
- It fits many adsorption systems but not at all
- The assumptions made by Langmuir do not hold in all situation, that causing error
  - Solid surface is heterogeneous thus the heat of adsorption is not a constant at different θ
  - Physisorption of gas molecules on a solid surface can be more than one layer

Disadvantages of the langmuir's model

The Langmuir adsorption model deviates significantly in many cases, primarily because it fails to account for the surface roughness of the adsorbate. Rough inhomogeneous surfaces have multiple site-types available for adsorption, and some parameters vary from site to site, such as the heat of adsorption.

The model also ignores adsorbate/adsorbate interactions. Experimentally, there is clear evidence for adsorbate/adsorbate interactions in heat of adsorption data.

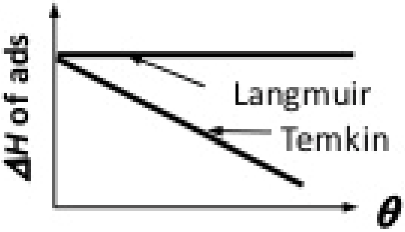
➢There are two kinds of adsorbate/adsorbate interactions:

Direct interaction and Indirect interaction

1. Direct interactions are between adjacent adsorbed molecules, which could make adsorbing near another adsorbate molecule more or less favorable and greatly affects high-coverage behavior.
2. In indirect interactions, the adsorbate changes the surface around the adsorbed site, which in turn affects the adsorption of other adsorbate molecules nearby.

The Temkin (or Slygin-Frumkin) isotherm

This isotherm takes into accounts of indirect adsorbate-adsorbate interactions on adsorption isotherms. Temkin noted experimentally that heats of adsorption would more often decrease than increase with increasing coverage.



From ads-des equilibrium, *ads. rate* ° *des. rate*

$$r_{ads} = k_{ads}(1-q)P \circ r_{des} = k_{des}q$$

where Q_s is the heat of adsorption. When Q_s is a linear function of q_i. $\mathbf{Q_s=Q_0\text{-}iS}$ (Q_0 is a constant, i is the number and S represents the surface site),

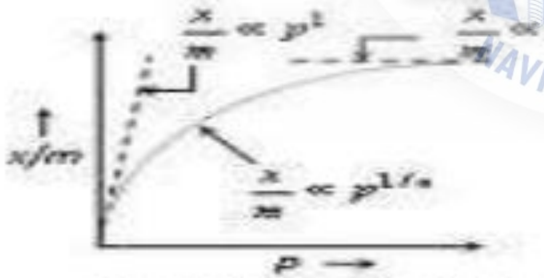
the overall coverage

When $b_1P >>1$ and $b_1P\exp(-i/RT) <<1$, we have $\boldsymbol{q = c_1\ln(c_2P)}$, where c_1 & c_2 are constants

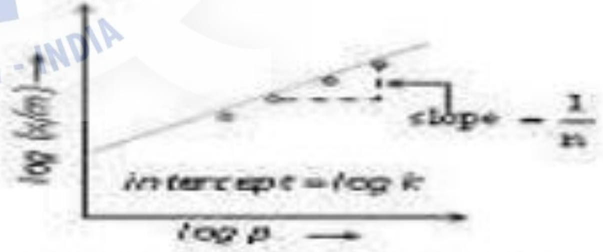
- Valid for some adsorption systems.

Fundamental Difference between Langmuir and Freundlich

- Langmuir's model was a theoretical construct, while the Freundlich isotherm is empirical.
- In the Langmuir model, it is assumed that at a maximum coverage there is only a monomolecular layer on the surface. This means that there is no stacking of adsorbed molecules. The Freundlich isotherm does not have the restriction.



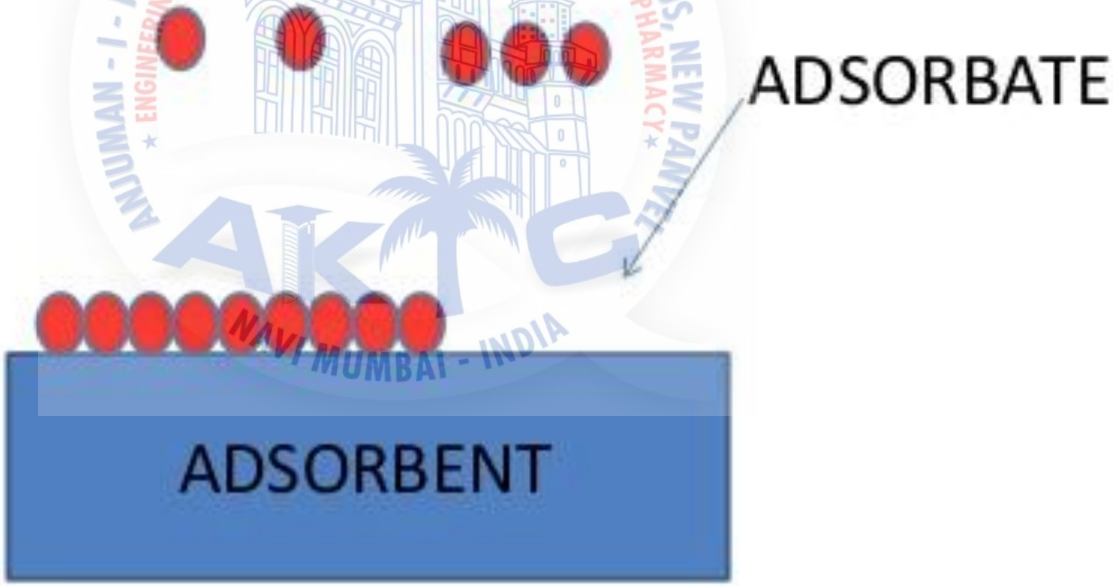
Freundlich adsorption isotherm: plot of x/m against



Plot of log x/m against log p for the adsorption of a gas on a solid

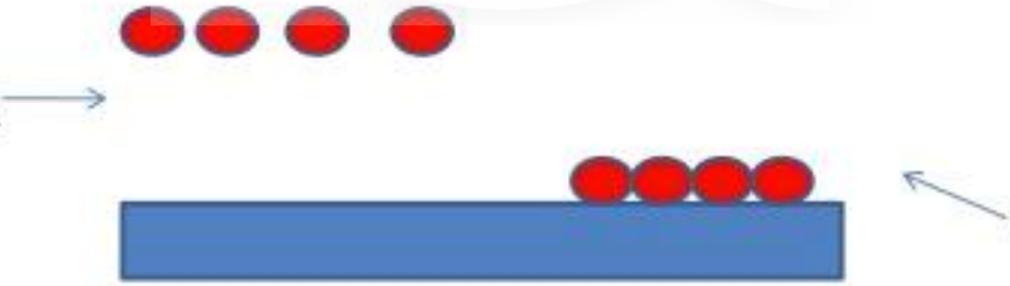
BET (Brunauer-Emmett-Teller) isotherm

- Many *physical* adsorption isotherms were found, such as the types II and III, that the adsorption does not complete the first layer (monolayer) before it continues to stack on the subsequent layer (thus the S-shape of types II and III isotherms



Postulates of B.E.T Equation

- This equation is an extension of the interpretation, of the monomolecular layer adsorption.
- The derivation is based on the same kinetic picture and the assumption that the condensation force are the principle force or the main force in adsorption.
- As in Langmuir's adsorption theory, the rate of evaporation from the first layer is equal to rate of condensation on each bare or uncovered surface.
- Additionally, the rate of the evaporation from each succeeding layer is equal to rate of condensation on the preceding layer.
- The heat of adsorption is exponentially involved in each of the equilibrium evaporation rate expression.
- The heat of adsorption in each layer other than the first is equal to the heat of liquefaction of the bulk adsorbate material.



Rate of condensation
On bare surface

Rate of evapoarion
from first layer

Derivation of B.E.T. equation

- The derivation can be carried out by various steps on basis of the postulates.

Let S_0, S_1, S_2, ……….S_i represent the surface area of the adsorbent which is covered by 0,1,2,..........i layers of the adsorbed molecules.
Since at equilibrium S_0 remains constant, the rate of evaporation from the first layer is equal to rate of condensation on each bare or uncovered surface.

Rate of condensation is directly proportional to pressure of gas, **i.e., pS_0, S_0,**

Rate of condensation on bare surface = a_1pS_0 ,where a_1 is a constant

Rate of evaporation is propotional to the surface which is covered, **i.e., k_1S_1.**

Rate of evaporation from first layer= $b_1S_1\ e^{-E1/RT}$

Therefore, $a_1pS_0 = b_1S_1\ e^{-E1/RT}$ ....(1)

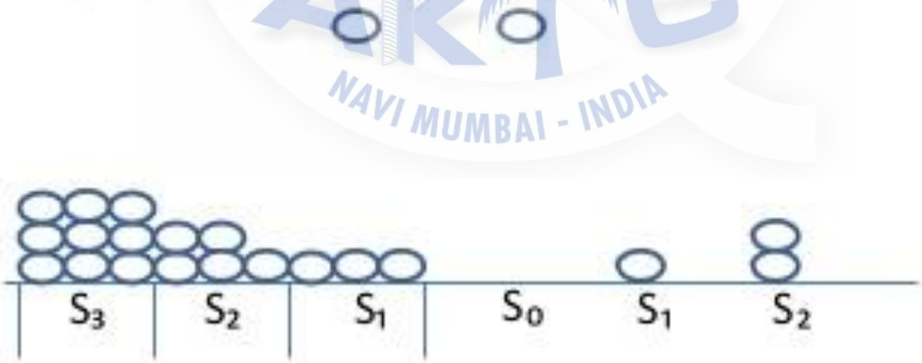
At equilibrium, S_1 must also remains constant. S_1 can change in four different ways:

i. By condensation on the bare surface

ii. By evaporation from first layer

iii. By condensation on the first layer

iv. By evaporation from the second layer



Comment on the BET isotherm

- BET equation fits reasonably well all known adsorption isotherms observed so far (types I to V) for various types of solid, although there is fundamental defect in the theory because of the assumptions made (no interaction between adsorbed molecules, surface homogeneity and liquefaction heat for all subsequent layers being equal).

- BET isotherm, as well as all other isotherms, gives accurate account of adsorption isotherm only within restricted pressure range. At very low ($P/P_0<0.05$) and high relative pressure ($P/P_0>0.35$) it becomes less applicable.

- The most significant contribution of BET isotherm to the surface science is that the theory provided the first applicable means of accurate determination of the surface area of a solid (since in 1945).

- Many new development in relation to the theory of adsorption isotherm, most of them are accurate for a specific system under specific conditions.

Summary of adsorption isotherms

Name	Isotherm equation	Application	Note
Langmuir	$\theta = \frac{C_s}{C_\infty} = \frac{B_0 P}{1 + B_0 P}$	Chemisorption and physisorption	Useful in analysis of reaction mechanism
Temkin	$q = c_1 \ln(c_2 P)$	Chemisorption	Chemisorption
Freundlich	$\theta = c_1 p^{1/C_2}$	Chemisorption and physisorption	Easy to fit adsorption data
BET	$\frac{P/P_0}{V(1-P/P_0)} = \frac{1}{cV_m} + \frac{c-1}{cV_m}(P/P_0)$	Multilayer physisorption	Useful in surface area determination

Chapter 5

Lecture 6

Factor affecting adorption

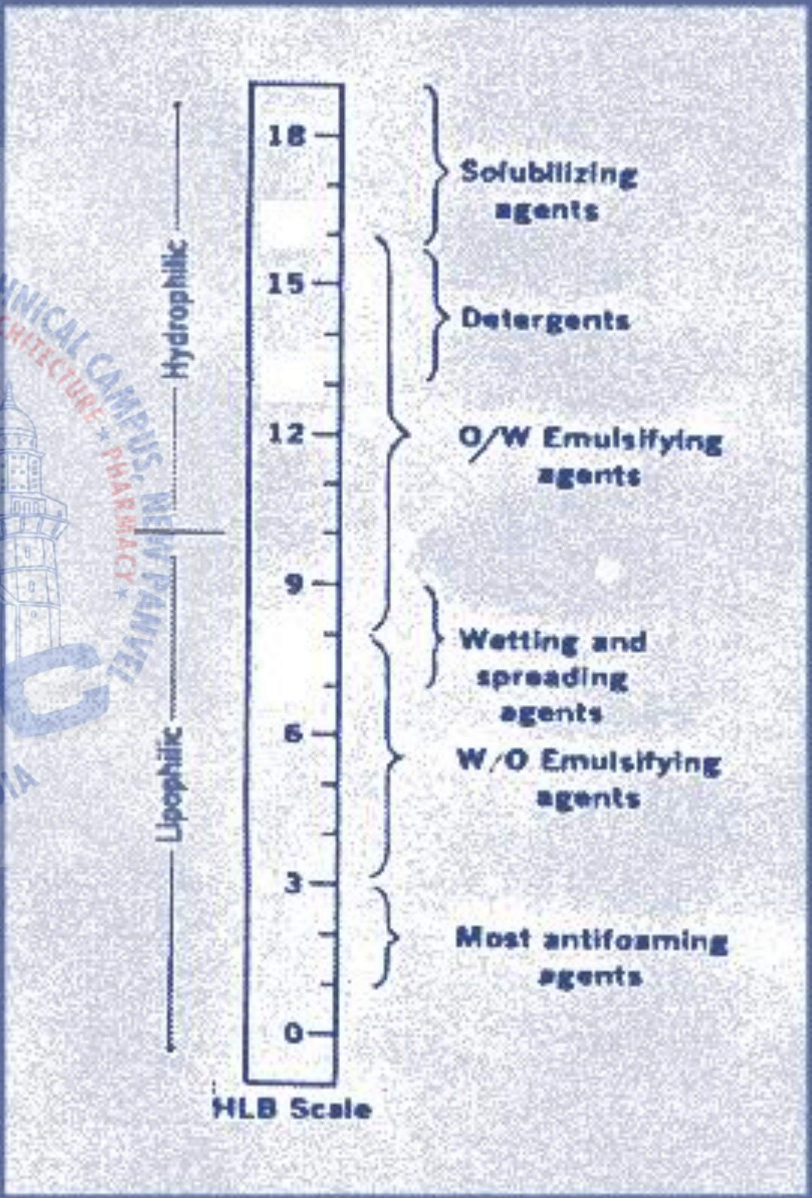
- Solute concentration
- Surface area of adsorbent
- Temperature
- Removal of adsorbed impurities
- Adsorbent solute interaction
- Solvent competition
- pH of medium

Application of adsorption

- Decolourising agent: talc
- Desiccant and drying agents: alumina or silica gel
- Surface area determination of powders: charcoal.
- Adsorption chromatography: silica gel
- Medicinal uses: kaolin and charcoal

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.



Hydrophilic Lipophilic Balance

Determination of HLB

- Polyhydric Alcohol Fatty Acid Esters (Ex. Glyceryl monostearate)

$$HLB = 20 (1 - S / A)$$

S = Saponification number of the ester

A = Acid number of the fatty acid

- Surfactants with no Saponification no (Ex. Bees wax and lanolin)

$$HLB = E + P / 5$$

E = The percent by weight of ethylene oxide

P = The percent by weight of polyhydric alcohol group in the molecules

- Surfactants with hydrophilic portion have only oxyethylene groups

$$HLB = E / 5$$

Common surface active agents

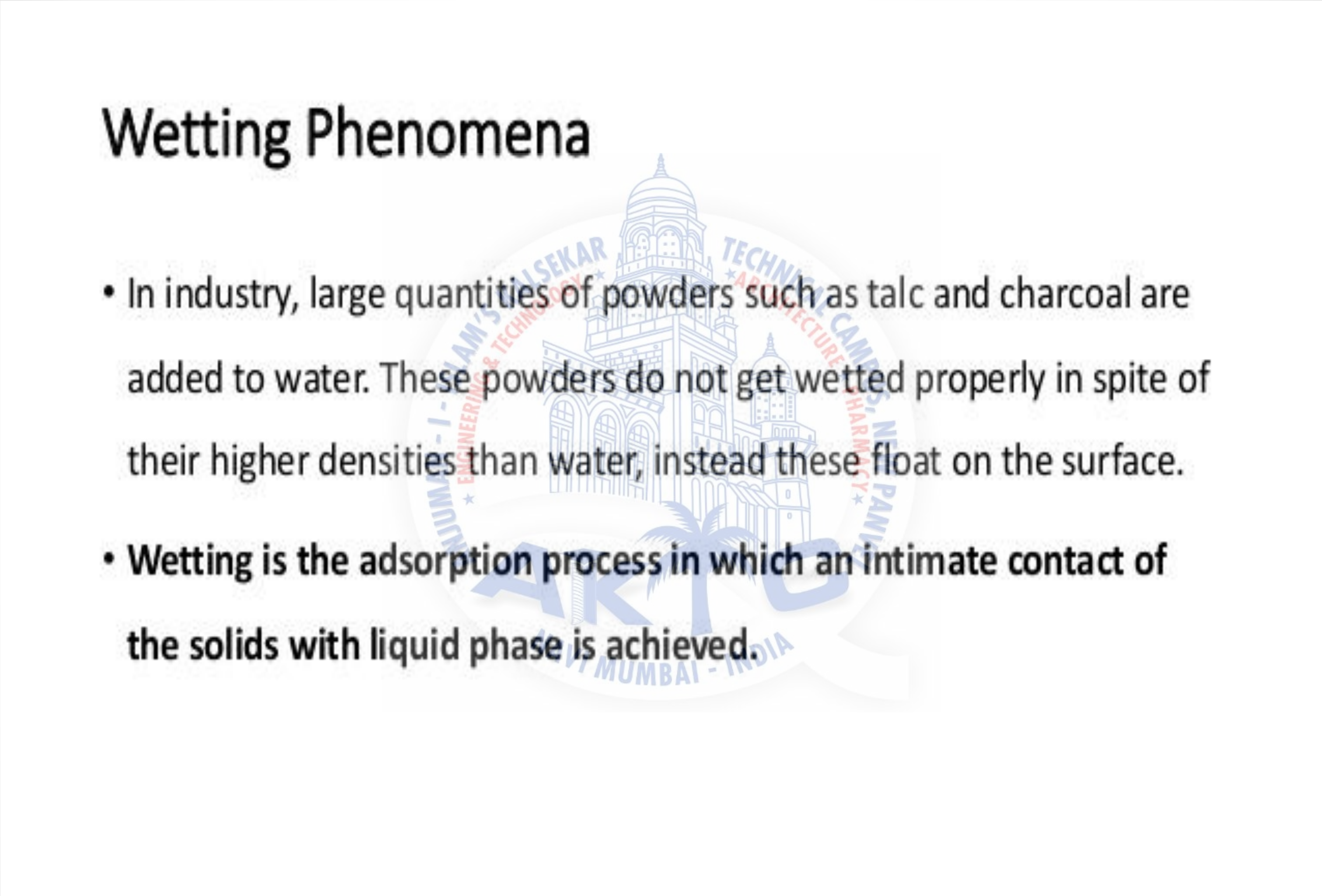
- Oleic acid- 1.0
- Glyceryl monostearate- 3.8
- Sorbitan monooleate(span 80)-4.3
- Span 60- 4.7
- Span 20- 8.6
- Polyoxyethylene sorbitan monooleate(Tween 80)- 15.0
- Tween 20- 16.7
- Sodium lauryl sulphate- 40.0

Calculation of required HLB (RHLB)

Calculate quantity of span 80 and tween 80 required to make the following o/w emulsion

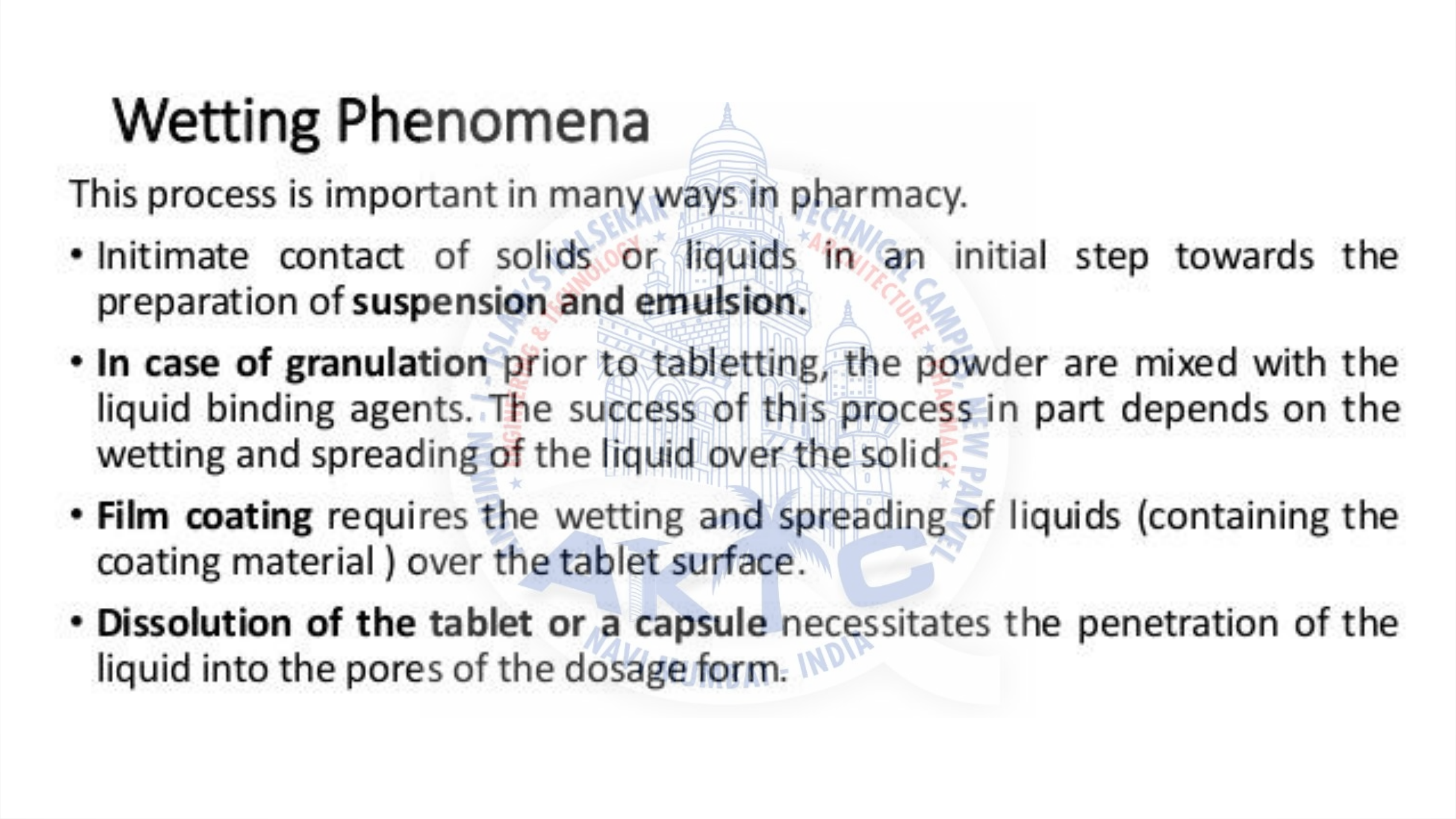
Liquid paraffin (HLB 10.5)	40 gm
Emulsifying agent	5gm
Span 80 (HLB 4.3)	
Tween 80 (HLB 15)	

Water quantity sufficient to 100 gm.



Wetting Phenomena

- In industry, large quantities of powders such as talc and charcoal are added to water. These powders do not get wetted properly in spite of their higher densities than water, instead these float on the surface.
- **Wetting is the adsorption process in which an intimate contact of the solids with liquid phase is achieved.**



Wetting Phenomena

This process is important in many ways in pharmacy.

- Initimate contact of solids or liquids in an initial step towards the preparation of **suspension and emulsion.**
- **In case of granulation** prior to tabletting, the powder are mixed with the liquid binding agents. The success of this process in part depends on the wetting and spreading of the liquid over the solid.
- **Film coating** requires the wetting and spreading of liquids (containing the coating material) over the tablet surface.
- **Dissolution of the tablet or a capsule** necessitates the penetration of the liquid into the pores of the dosage form.

Wetting Phenomena

- Surfactants are used to aid wetting of powders, because they are capable of:

1. Lowering the interfacial tension.
2. Lowering of the contact angle between the solids and liquids.
3. Displacing the air and permit the intimate contact.

- Contact angle is used as an indicator to evaluate the efficiency of wetting agent.

Wetting Phenomena

- **Contact angle** can be defined as an angle between the liquid droplet and surface over which it spreads.
- The contact angle can be taken up any value between 0° and 180° ·

REFRENCES

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- Internet access (wikipedia)

QUESTION BANK

Q1.Define
Surface tension, Interfacial tension, Surface free energy,Spreading coefficient, Surface active agents, Wetting, wetting agents and contact angle
Q2. Explain various method of Measurement of surface and interfacial tension-capillary rise method, drop number method, Drop weight method, Du Nuoy tensiometer method Q3. Explain concept of Spreading of liquids
Q4. Explain in brief Hydrophilic-Lipophilic balance
Q5. Define Adsorption isotherms Explain anyone in detail
Q6. Explain Freundlich adsorption isotherm, Langmuir adsorption isotherm.