Physical Pharmaceutics

• SURFACE AND INTERFACIAL PHENOMENON

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Surface tension



Surface tension relates a boundary that form between two different phases (they may solid-liquid, liquid–liquid, Liquid-gases etc). The term surface is also used to describe interphase where one phase must be gas. Surface tension is denoted by $\sigma/\gamma/T$.

• **Definition** - It is defined as force in dynes acting on surface of liquid at right angle to any length of surface 1 cm.

<u>C.G.S UNIT</u> - dyne/cm or & <u>S.I UNIT</u> - Newton/m.



Some practical example related to Surface tension is as follows -

- **1.**Formation of spherical globules in emulsion.
- 2.Falling of water droplets.
- 3.shape of mercury in thermometer
- 4. Rise of liquid in capillary tube .
- Two kinds of intermolecular forces responsible for extent of surface tension



- \rightarrow Cohesive force -- the attraction force exert between same molecules \rightarrow Adhesive force-- the attraction force exert between different molecules
- Surface tension denotes cohesive force rather than adhesive force.

Factors affecting Surface Tension & Interfacial

INTRINSIC FACTORS-

→ it is due to <u>intermolecular forces.</u> Examples H-bonding (strong), London forces (non-polar, weak)

 \rightarrow Polar Compounds such as water have high surface Tension (72.8 dyne/cm)

→ Semi-polar such as <u>benzene</u> (28.9 dyne/cm) have London & inductive forces and they are less strong than H- bonding.

→Non-polar such as <u>Carbon Tetrachloride</u> also have London type of forces and exert less surface tension (26.7d/cm.)

EXTRINSIC FACTORS-

→ Outsiders such as <u>electrolytes</u> and <u>Surface- active agents</u> affect surface tension.

 \rightarrow on addition of electrolyte, it is seen that surface tension becomes high.

→ Surface active agents decrease surface tension.

→T<u>emperature</u> also play important role as it also decreases surface tension of system, it is just because of enhancement of Kinetic energy that loses cohesive force b/w molecules MEASUREMENT OR DETERMINATION OF SURFACE TENSION

There are following methods that are used for determination of Surface tension

Capillary rise Method
Tensiometer (The Du Nauy ring Method)/ring detachment
Bubble Pressure Method
Drop weight / Drop Count Method.

CAPILLARY RISE METHOD

When a capillary tube is placed in a liquid sample containing beaker, it is seen that there is a rise of some of liquid in the capillary tube. This is just because of <u>adhesive force (b/w water</u> <u>molecule & glass) is stronger than cohesive force</u>. The rise of liquid in the capillary tube will continue until the upward movement of liquid is balanced by downward movement (gravitational force of the liquid).



- Surface Tension is determined by capillary method as follows cos θ= Contact angle b/w surface of liquid & capillary wall
- \rightarrow Upward component 'a' = Surface Tension (γ) × cos θ
- $a = \gamma \times \cos\theta \times 2\pi r$
- a = 2πrγcosθ
- In case of Water, value of θ is considered 0, it Completely wets glass tube. So, cos0=1
- Liquid Sample (water) $a=2\pi r \times \gamma$
- → Downward Component 'b' The counteracting force is gravity and it is
- determined as follows:
- "b" = weight of water x acceleration

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b=m×a
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b=Density x Volume x acceleration (m=d/v)
B=d×v×a (v=\pi r^2 \times h)
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b=d×πr<sup>2</sup>h×a
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At equilibrium ,

Upward Component=Downward Component

 $2\pi r \times \gamma = d \times \pi r^2 ha$



The phenomenon of capillary rise is seen in

- \rightarrow Underground water rising on the surface.
- \rightarrow Oil rising through wick in a lamp.
- \rightarrow Water rising from soil to branches of plant.

What should be precautions taken by Capillary rise Method ?

- \rightarrow Capillary tube and water should be free from grease.
- → Capillary tube should be set vertical.
- \rightarrow Internal diameter of capillary tube should be measured in two mutually perpendicular directions.
- → Temperature of water should be noted.
- \rightarrow Presence of impurities in the liquid or immerse tubes can alter the surface tension so cleanliness is desired.

Drop weight/Drop Count Method

With the help of stalagmometer one can determine surface tension in a laboratory. It is a glass pipette kind of glassware containing a bulb in between with two distinct marks. Sample of liquid which surface tension is to be determined is placed in a beaker and now stalagmometer is allowed to dip in beaker, the bottom of this glass apparatus contain an orifice and a minute inbuilt capillary tube. Due to presence of capillary tube, there is rise of liquid sample up to a height. One has to suck or pull, the sample up to a height A & and noted down no. of drops made from the mark B.

Inspite of counting the no. of drops one can weigh formed drops b/w A to B mark. After applying appropriate formula, surface tension of test sample can be determined.



METHOD OF DETERMINATION OF SURFACE TENSION BY DROP COUNT METHOD IS BASED ON FOLLOWING FORMULA

WE KNOW THAT DENSITY IS DENOTED AS <u>d</u> OR <u>p</u>.

where γ_1 = surface tension of unknown

- γ_2 = surface tension of water
- $n_1 = drops of unknown$
- $n_2 = drops of water$
- ρ_1 = density of unknown
- ρ_2 = density of water

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

Drop weight method is also imply with Stalagmometer and basically collected drops from point A to B is weighed and surface tension is determined by applying following formula

$$\frac{m_2}{m^2} = \frac{\gamma_2}{\lambda^1}$$

Ring Detachment Method /tensiometer

This apparatus consist of a ring made up of **Platinum - Iridium**. This ring is attached

to a Tensiometer that contain pulley and Torque. This ring is allowed to immersed in test liquid sample with the help of assembled pulley and torque. There is a scale which determine force required to detach the ring (made up of water)and recorded in dynes. The surface tension is determined by the following formula

γ= dial reading ×apparatus calibration (ring) factor
2×(ring circumference)



Bubble Pressure Method-

In this method maximum Pressure required break bubble formed at the end of capillary tube is determine. When we passes air through the capillary tube that is inserted in a test sample beaker, an air - Bubble is formed at the end of tube. We have to note down the pressure that breaks the formed Bubble through manometer. After determine that pressure, one can determine Surface tension as follows



- h = height of formed bubble in beaker
- g- Acceleration
- d= density of sample
- γ= Surface tension
- r =Radius of capillary tube



SURFACE ACTIVE AGENTS

- These compounds get adsorbed at the interface or surface of two immiscible phases and trying to mix them by the action of lowering the surface tension.
- These are **amphiphilic** compounds having polar head & non-polar tail and used to solubilize two different category phases.
- 'Those agent which reduce the surface tension and interfacial tension between two liquids are called surface active agents '.





Anionic Surfactant – Mostly compounds containing carboxylate (coo⁻) sulphonate R-SO₃ sulphate (_{SO4}) for example - Sodium lauryl Sulphate. Cationic Surfactant – They contain amine salts quaternary ammonium salts for example- Cetrimide (Tetradecyltrimethyl ammonium bromide) Amphoteric Surfactant – They contains both anionic as well as cationic ions e.g. Botanies, amine oxides Non – Ionic – they are not cationic & anionic examples – Span → sorbitan trioleate /Tween → Polyoxyethylene sorbitan , PEGs monolaurate Sorbitane ester Polyoxyethylene derivative of spans.

Application of Surface Active Agents

Adjuvants - These S.A. improves product Characteristics e.g. Solubilizing agent, Wetting agent, detergent, suspending emulsifying and Foaming agent.

Influence drug action - They increases penetration Of drug known as hexylresorcinol into pineworm.

• Antibacterial action - Most of surfactants which are ionic in nature get adsorb on the cell Surface of bacteria and make electrostatic interaction . As a result, cell surface of bacteria looses its integrity and causes leak of nutrients & materials to outside. Both gram negative & Gram positive bacteria are killed by the action of cationic quaternary ammonia Containing SA (NH_4 +) examples-cetrimide

Enhances absorption of antibiotics - S.A-enhance

Absorption of antibiotic through GIT route Examples – Bile salt improves absorption of anti-biotic.

Hydrophilic Lipophilic Balance (HLB)

Griffin a scientist proposed HLB theory or Arbitrary HLB scale. According to him, surfactants are categorized in following categories depending upon their HLB value

 $1-3 \rightarrow$ Antifoaming agent. $3-8 \rightarrow$ W/o emulsifying agent $7-9 \rightarrow$ spreading & wetting agent $8-16 \rightarrow 0/w$ emulsifying agent $13-16 \rightarrow$ Detergent $14->18 \rightarrow$ Solubilizing agent



ESTIMATION OF HLB

<u>Method-1</u>- This method is applicable for that Surfactant molecule which got split into 2 different groups (Hydrophilic & Lipophilic)

HLB = \sum (Hydrophilic group no.) - \sum Lipophilic group no. +7

<u>Method -2-</u> This method is used for surfactant Molecule that contain polyoxyethylene chain HLB = E + P5

Where

E= % by weight of ethylene oxide chain

P = % by weight of polyhydric alcohol group

Example beeswax, Lanolin (lipid from sheep)

<u>Method -3-</u> If a surfactant contains ester functional Group in form of stearate them, HLB is estimated As

Where S = saponification no of that ester A = acid no. of that fatty acid

Required HLB or RHLB

When blend of surfactants are used for preparation of dosage form then, RHLB is calculated. This is also known as critical HLB. **Examples**; for preparation of emulsion two or more kinds of emulgents are applied and their HLB is calculated as follows-

HLB mixer= f.HLB_A + (1-f) HLB_B

Where, f- fraction or Total amount of emergent

<u>Absorption at solid interface</u> \rightarrow Adsorption of gas and liquid on solid surface is very important in pharmacy and can be seen in surrounding depending on nature of interaction, Adsorption is classified as-

- 1-- physical adsorption (physisorption)
- 2-- chemical adsorption (chemisorption)

Adsorption at solid surface

Physisorption

- It is reversible .
- It has weak vanderwall forces.
- It is non specific.
- the process occurs at low temperature.
- Heat of adsorption is low (20-40 KJ/mole).
- Example- Adsorption of gases over charcoal.

chemisorption

- It is irreversible.
- It has strong chemical bonds.It is specific.
- > It occurs at high temperature.
- Heat of adsorption is high (40-400KJ/ mole).
- Example- Adsorption of oxygen gas on silver and gold.

- Adsorbent The material used to adsorb gases and liquids is known as adsorbent.
- <u>Adsorbate</u> The Substance that is adsorbed over the surface of solid is known as adsorbate.
- **Sorption** It is combination of adsorption .
- **Opposite of sorption is known as desorption**.
- Note- The degree of adsorption of gas on solid surface depends on-
- 1. Nature of adsorbent and its surface area.
- 2. Nature of adsorbate and it's partial pressure .
- 3. Temperature of reaction .

Adsorption at solid gas interface

- Adsorption of gas on solid surface is important in pharmacy -
- 1. Removal of unwanted odour from room.
- 2. Prevention of obnoxious gases entering into the body .
- 3. Estimation of surface area and particles size of powder

The amount of gas adsorbed per unit area of solid is measured at different pressure of gas. The study is usually conducted at constant temperature and graph are plotted between and partial pressure (P) and amount of gas adsorbed per unit mass of solid (x/m). These are Adsorption isotherm.

- Few theorems are discussed that make relationship between adsorbed gas and solid surface-
- **<u>FREUNDLICH ISOTHERM-</u>** It dictates the relationship between **<u>pressure of</u> <u>gas and amount</u>** adsorbed over solid surface at constant temperature.



LANGMUIR ADSORPTION THEOREM

 \rightarrow The surface of solid shows fixed no. of active sites for process of adsorption. \rightarrow At maximum adsorption ,the gas layer for monomolecular thick layer . \rightarrow The rate of adsorption condensation is proportional to no. of sites unoccupied and vice –versa.

Equation of langmuir Isotherm



where, P= pressure of gas in mmhg y = mass of vapour /g y _m = amount of vapour adsorbed over b= constant



 \rightarrow The above theorem is applicable where gas follow monomolecular adsorption process if there is multimolecular adsorption process, the BET equation is followed.

B – Brauraur, E- Emmette, T- Teller

Multimolecular adsorption shows by N, Kr.

→ <u>5 DIFFERENT TYPES OF ADSORPTION ISOTHERMS</u>

--**Type I:** This Isotherm represents a significant increase in adsorption with increasing pressure and followed by leveling off .This is due to saturation of available specific chemical groups on entire surface is covered by monomolecular layer same as freundlich or Langmuir adsorption isotherm **e.g.** Adsorption of N_2 at 78°k or O2 at 83°K on charcoal.

-- **Type II** - This isotherm is sigmoidal in shape and occurs when gases undergo physical adsorption onto non-porous solids. The first inflection point represents formation of a monolayer. When pressure is increase further, multilayer formation is observed. This isotherm is described by BET equation, constant 'b 'is greater than 2. When monolayer is formed this plot reduces to langmuir adsorption isotherm e.g. **Adsorption of nitrogen on iron or platinum catalyst at 78°C**

Type -III - This is seen rarely. The heat of adsorption of gas in the first layer is less than the latent heat of condensation of subsequent layers. In BET equation, the constant b' is smaller than 2 e. g.- Adsorption of bromine on silica or alumina. **Type - IV** - This plot represents adsorption of gases on porous solids. First point of inflection extrapolated to zero represents monomolecular layer adsorption Condensation within pores of solid & multimolecular layer is represented by further adsorption. e.g. -Example is adsorption of benzene on silica gel. **Type V**- This is seen rarely and indicates capillary condensation. Here the adsorption



ISOTHERM	TYPE OF ADSORPTION	NATURE OF ADSORBENT
Type I	Langmuir type	is found for porous materials with small pores e.g. charcoal
Туре 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 po	staged adsorption (first monolayer then build up of additional layers
Туре V	Elongated S-type	porous materials with cohesive force between adsorbate molecules and adsorbent being greater than that between adsorbate molecules

Wetting Phenomenon

This phenomenon comes under principle of adsorption of liquid over solid surface .In pharmaceutical field, there are various solid components (powders, charcoal, talc) that show poor wetting and requires wetting agent for preparation of dosage form .

- Wetting is an adsorption process in which a contact between solid & liquid takes place. This process is important in following ways.-
- #For preparation of suspension & emulsion
- #for preparation of tablet granules.
- #For film coating over tablet.
- #Dissolution of tablet in given physiological solution.
- To motivate wetting phenomenon, surface active-agents are used-
- # They lower interfacial tension b/w solid & liquid .
- #Decrease contact angle b/w solid & liquid i.e. increasing wetting . #Displace air and permit contact b/w solid & liquid.

Contact Angle - It is defined as an angle b/w liquid droplets & surface. This angle varies b/s (0-180°).

It can be estimated by placing a drop of liquid on solid surface.

 $Ys = Y_{LS} + Y_{L} \cos\theta$

where

Ys - Interfacial tension solid & gas Y_{Ls} - inter facial tension of liquid that derives through tangential alignment due to $\cos \theta$ θ - contact angle Y_{Ls} 9.7. b/w solid and liquid if θ =0° then $\cos \theta$ = 1

In case of complete wetting \rightarrow

Contact angle of selected drugs

Drugs	Degree
Indomethacin	* 90
 Tolbutamide 	* 72
Nitrofurantoin	* 69
Phenylbutazone	* 109
Chloramphenicol Palmitate alpha form	* 122
Ampicillin [trihydrate]	* 21
✤ Lactose	* 30

<u>Detergency</u> –

Surface active agents required for the purpose of cleaning of equipment, container packaging material to maintain hygiene in industries. It is a complex process and involve no. of steps – -- initially wetting the dirt of the surface --Solubilize the dirt.

--Removing the insoluble dirt. (De flocculating process).

- --Suspending the dirt particles in detergent solution
- --Removing the oil soluble material.
- -- Converting the dirt in form of foam .

Electrical properties of Interface-

Electrical property of Interface is very important in study of stabilization of Colloidal dispersion-

- --Preparation of flocculated suspension
- --Stabilization of Emulsion

When a solid is dispersed in liquid there is formation of solidliquid inter face which may be charged. The extent of charge depends on following parametersElectrolytes present in solution may get adsorb on solid surface e.g.
 (Hydronium ion), OH (Hydroxyl ion).

•Presence of functional groups in solid compound that get dissociate and provide change.

•Difference b/w dielectric constant b/w solid and liquid which is responsible for origin of charge.



Electrical Double Layer-- when a solid particle are dispersed in an aqueous solution that contain electrolytes following kinds of charges assembly are seem --**Interface**- aa' is a solid liquid interface . Solid particles which are containing positive charge get adsorbed on the aa' boundary and known as potential-determining ions .

--**Tightly bound layer** - This layer extents up to the area (ab-a'b'). When cationic solid particles get adsorb over aq. solution. They will attract negative charges from the solution. Thus excess of anions will move towards interface but the concentration of positive ions may be high than this layer . These counter ions are also known as **gegenions.** The boundary of bb' is known as **shear plane**.

--Diffused Second Layer - This area is extends up to bb' to cc'. Here excess negative ions are present whole the area is electrically neutral although there are higher concentration of negative charge .

--**Nernst potential**- It is the potential at the interface due to the presence of potential determining ions 'E'.

--Zeta Potential- Z- This is electro-kinetic potential and calculated b/w estimating diff. in potential b/w interface & tightly bound layer (shear plane).

- --Zeta potential governs degree of repulsion b/w adjacent ions of like charges.
- --It is used to predict particle interaction.

-- It provides information regarding stability of formulation [suspension, emulsion, coll. Dispersion

-- Zeta potential decreases when conc. of electrolyte increases.

--for optimum stability zeta potential ranges-30- +30 mv

Phenomenon of detergency

