FACULTY OF PHARMACEUTICAL SCIENCES
RAMAUNIVERSITY, KANPUR

B.PHARM 3rd SEM
PHYSICAL PHARMACEUTICS-I
BP302T

Surface and interfacial tension phenomena

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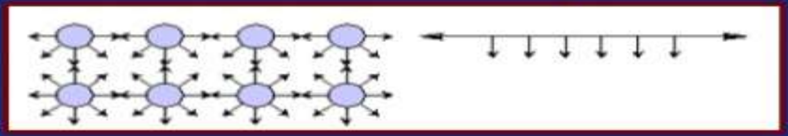
Interface

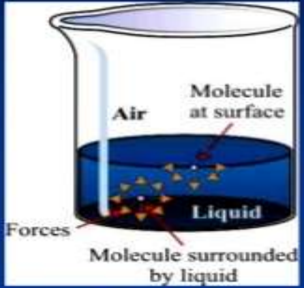
- ***Interface*** is the boundary between two or more phases exist together
- The properties of the molecules forming the interface are different from those in the bulk that these molecules are forming an ***interfacial phase.***
- Several types of interface can exist depending on whether the two adjacent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

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

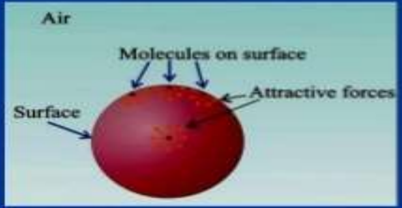
erg = dyne . cm

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.



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

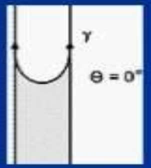
The Principle

- 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:***

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



Cont. angle water and glass

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

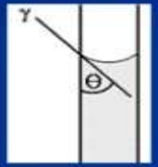
$$\boxed{a = 2 \pi r \gamma \cos \theta}$$

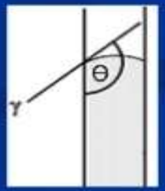
Where

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



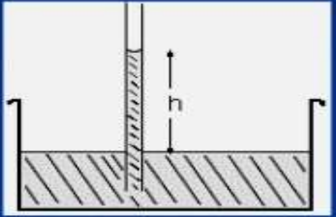


Cont. angle Mercury and glass

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

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

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

$$2 \pi r \gamma \cos \theta = \pi r^2 h (p - p\,o) g + w$$

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

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

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

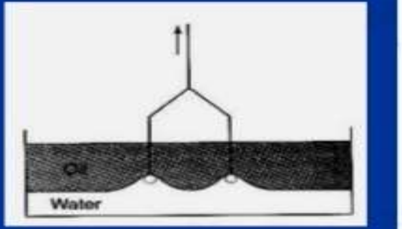
Ring (Du Nouy) Tensiometer

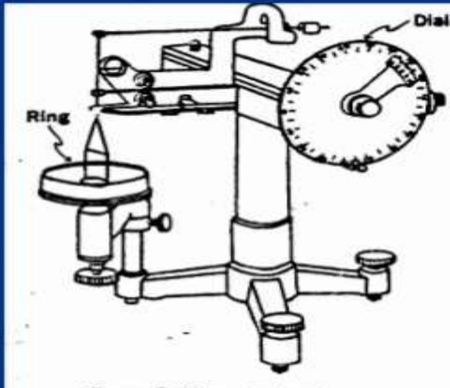
- For measuring surface and interfacial tensions.

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

$$\gamma = \frac{\Phi \, mg}{2 \pi r} = \frac{\Phi \, V pg}{2 \pi r}$$

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.***

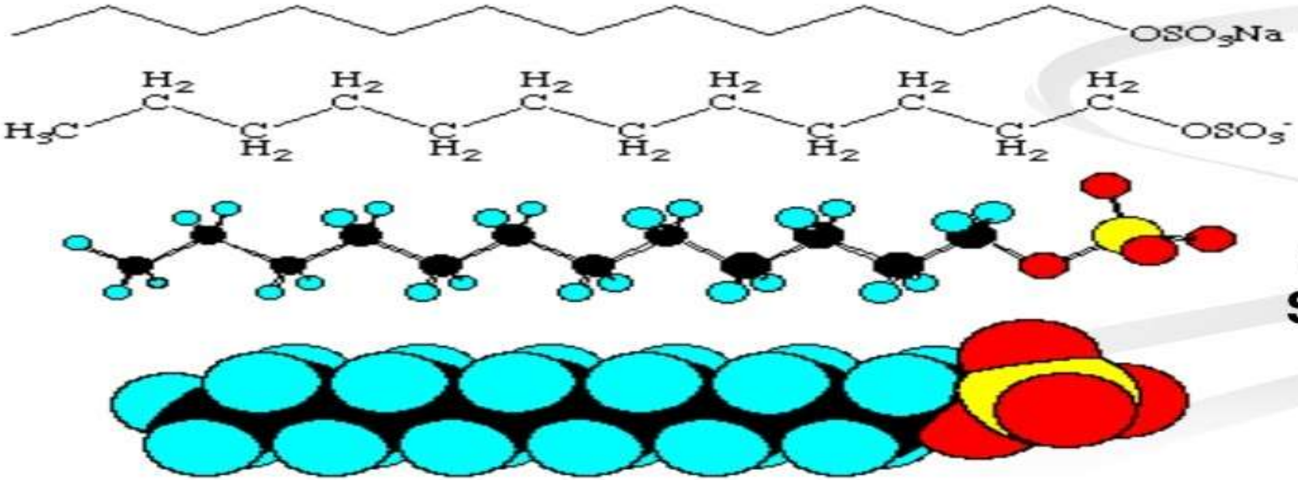
Surface Active Agents

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

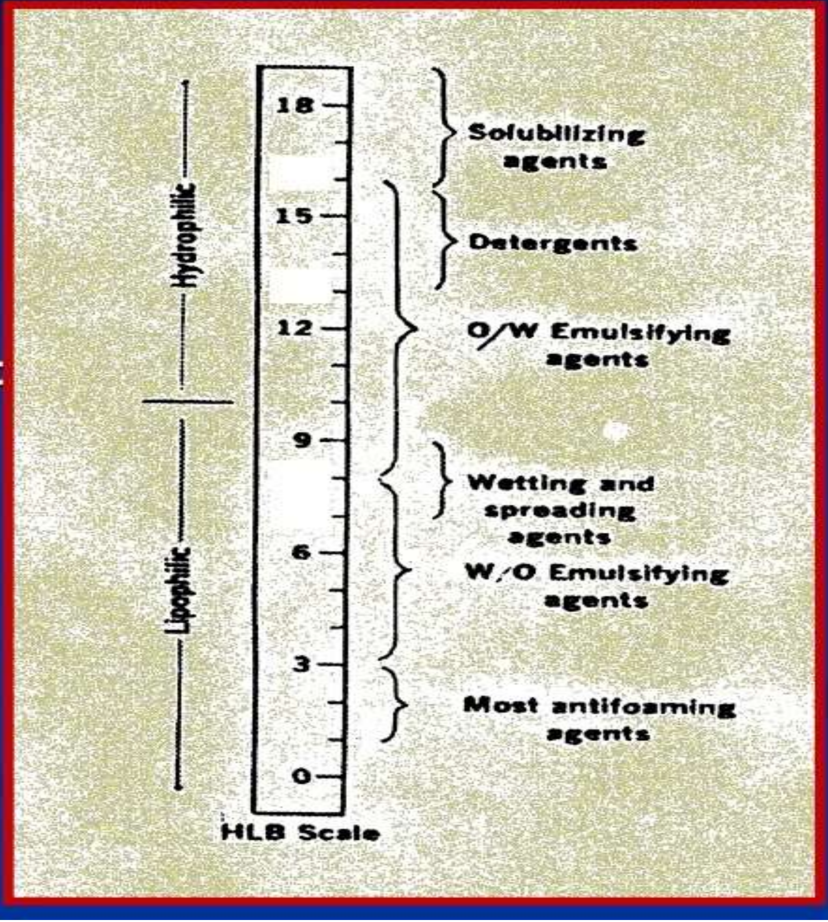
Surface Active Agents

Surface Active Agents

- Molecules and ions that are adsorbed at interfaces are termed *surface active agents,* surf*actants 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.

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)**

$$\text{HLB} = 20\,(1 - S / A)$$

S = Saponification number of the ester

A = Acid number of the fatty acid

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

$$\text{HLB} = E + P / 5$$

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**

$$\text{HLB} = E / 5$$

When a liquid is placed on the surface of other liquid, it will spread as a film if the adhesion force is greater than the cohesive forces.

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

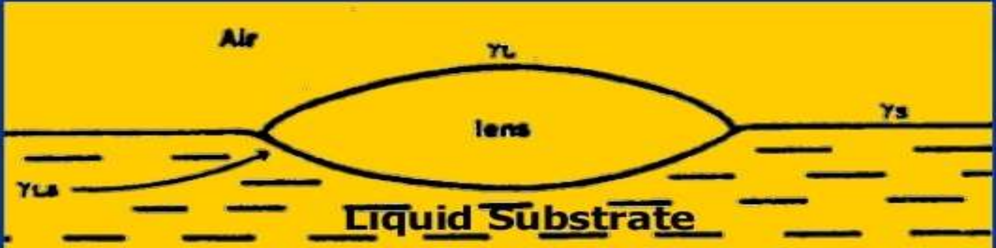
$$S = W_a - W_c = (\gamma_L + \gamma_S - \gamma_{LS}) - 2\gamma_L$$

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

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

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

Define the following terms:

[solid, liquid, gas, pure substance, compound, mixture, element, heterogeneous mixture, homogeneous mixture, extensive properties, intensive properties, chemical properties, physical properties, density, color, texture, conductivity, malleability, ductility, boiling point, melting point, flammability, corrosiveness, volatility, pounding, tearing, cutting, dissolving, evaporating, fermenting, decomposing, Exothermic, endothermic, mass, density, gravity, adhesive force, cohesive force, interface, adsorption, catalyst, dipole, physisorption, Chemisorption, hydrophilic, hydrophobic, detergent, surfactant, surface tension, adsorbate, adsorbent, etc]

Respond to the following questions:

- Give a descriptive account of the phases of matter with logical relevance to state of medicines as they are taken for their respective therapeutical values
- What is viscosity and its relation with fluids
- What are surface and Inter-facial tension forces and respective association with activities of a substance material with surface area
- Describe some key phase changes of materials substance when exposed to some environmental conditions .
- How is a chemical change different from a physical change at the surface of a material
- What is contact angle of a substance and its significant role when two materials surface are in contact
- Describe the role of contact angle during the wetting process of a material substance
- What is a detergent and justified reasons for its variable composition
- Differentiate the role of adsorption process of a material substance in surface and interfacial tension
- State and explain the factors that have direct adsorptive effect on surface and interfacial tension process
- Describe some practical applications of surface and interfacial tension process with some examples
- What is the micelle made up of in terms of its physical form and shape
- What are some of the practical uses of micellular material
- State and explain some of the medical and pharmaceutical applications of named surface active agents.