AL-Mustaqbal university college
Pharmacy department

Physical pharmacy II

lec5

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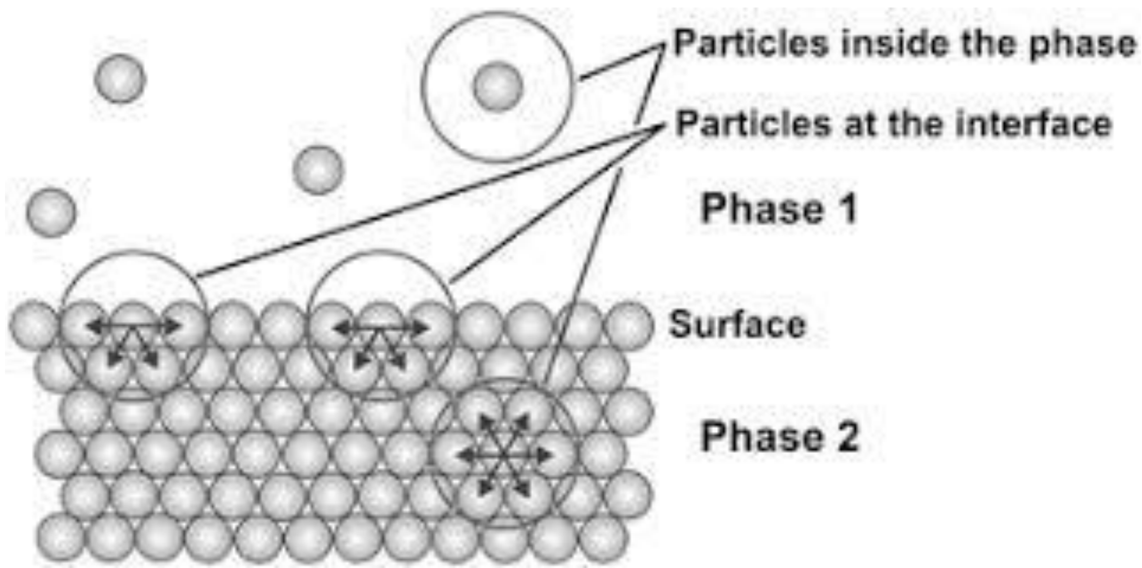
Interfacial phenomena

Objectives

1- Differentiate among different types of interfaces and describe relevant examples in the pharmaceutical sciences.
2- Understand the terms surface tension and interfacial tension and their application in pharmaceutical sciences.
3- Appreciate the different methods of surface and interface tension measurements.
4- Calculate surface and interface tensions, surface free energy, its changes, work of cohesion and adhesion, and spreading coefficient for different types of interfaces.
5- Understand the mechanisms of adsorption on liquid and solid interfaces.
6- Classify surface-active agents and appreciate their applications in pharmacy.

When phases exist together, the boundary between two of them is termed an **interface.**

- The properties of the molecules forming the interface are often sufficiently different from those in the bulk of each phase that they are referred to as forming an interfacial phase.
- Several types of interface can exist, depending on whether the two adjacent phases are in the solid, liquid, or gaseous state .For convenience, these various combinations are divided into two groups, namely, liquid interfaces and solid interfaces



CLASSIFICATION OF INTERFACES

Phase	Interfacial Tension	Types and Examples of Interfaces
Gas–Gas	—	No interface possible
Gas–liquid	γ_{LV}	Liquid surface, body of water exposed to atmosphere
Gas–solid	γ_{SV}	Solid surface, table top
Liquid–liquid	γ_{LL}	Liquid–liquid interface, emulsion
Liquid–solid	γ_{LS}	Liquid–solid interface, suspension
Solid–solid	γ_{SS}	Solid–solid interface, powder particles in contact

Surface and Interfacial Tension

- **Surface:** The term surface is commonly used when referring to either a gas-solid or a gas-liquid interface.

"**Every surface is an interface.**"

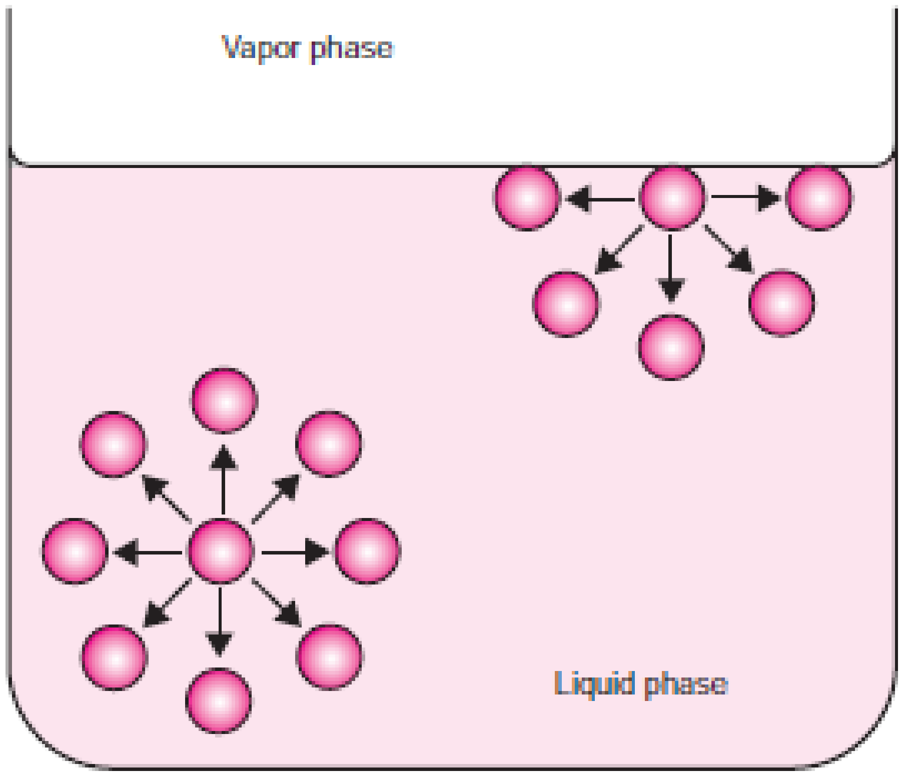
- **Cause of surface tension:**

Surface tension is caused by the attraction between the liquid's molecules by various intermolecular forces.

- **In the bulk of the liquid:** each molecule is pulled equally in all directions by neighboring liquid molecules net force of zero .
- **At the surface of the liquid**, molecules are pulled inwards by other molecules deeper inside the liquid and are not attracted as intensely by the molecules in the neighboring medium. i.e.:

-- They develop attractive **cohesive forces** with other liquid molecules situated below & adjacent to them.

-- They create **adhesive forces** of attraction With the other phase involved at the interface.



Representation of the unequal attractive forces acting on molecules at the surface of a liquid as compared with molecular forces in the bulk of the liquid

Surface tension- a force pulling the molecules of the interface together resulting in a contracted surface.

- Force per unit length applied parallel to the surface . Unit in dynes/cm or N/m

- At l/g interface, the *adhesive forces are weak*;

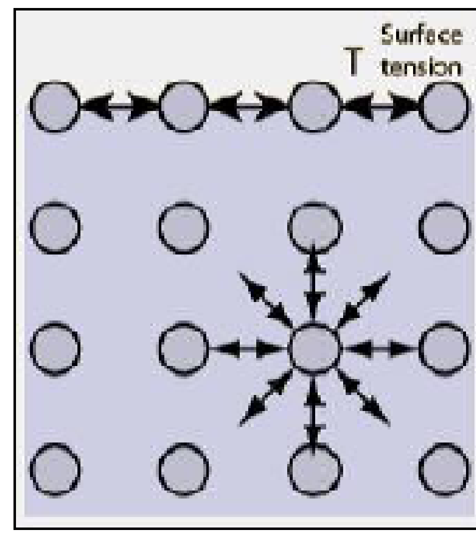
The Net Effect

Inward force toward the bulk

Such a force **pulls the molecules** of the interface together &
contracts the surface.

Development

Surface tension



Interfacial tension

- Is the force per unit length existing at the interface between two immiscible liquid phases and like surface tension, has the units of dyne/cm

Surface Free Energy

To move a molecule from the inner layers to the surface , work must be done against the force of surface tension .In other words , each molecule near the surface of liquid possesses a certain excess of potential energy as compared to the molecules in the bulk of the liquid . The higher the surface of the liquid, the more molecules have this excessive potential energy.

Therefore , if the surface of the liquid increases , e.g. when water is broken into a fine spray), the energy of the liquid also increases. Because this energy is proportional to the size of the free surface, it is called a **surface free energy.**

- Each molecule of the liquid has a tendency to move inside the liquid from the surface ; therefore the liquid takes form with minimal free surface and with minimal surface energy . for example , liquid droplets tend to assume a spherical shape because a sphere has the smallest surface area per unit volume.

Surface Free energy

W = γ Δ A

where **W** is work done or surface free energy increase express in ergs(dyne cm); **gamma(γ)** is surface tension in dynes/cm and **Δ A** is increase in area in cm^2.

Example

What in the work required to increase area of a liquid droplet by 10 cm^2 if the surface tension is 49 dynes/cm?

$$W = \gamma \, \Delta A$$

Because the area is increased by 10 cm^2, the work done is given by the equation

W = 49 dynes/cm×10 cm^2 = 490 ergs

Repeat the calculations using SI units. We have

$$1 \text{ dyne} = 10^{-5} \text{ N}, \text{ or } 49 \text{ dynes} = 49 \times 10^{-5} \text{ N}$$

$$49 \text{ dynes/cm} = 49 \times 10^{-3} \text{ N/m} = 49 \times 10^{-3} \text{ Nm/m}^2$$

$$= 49 \times 10^{-3} \text{joule/m}^2$$

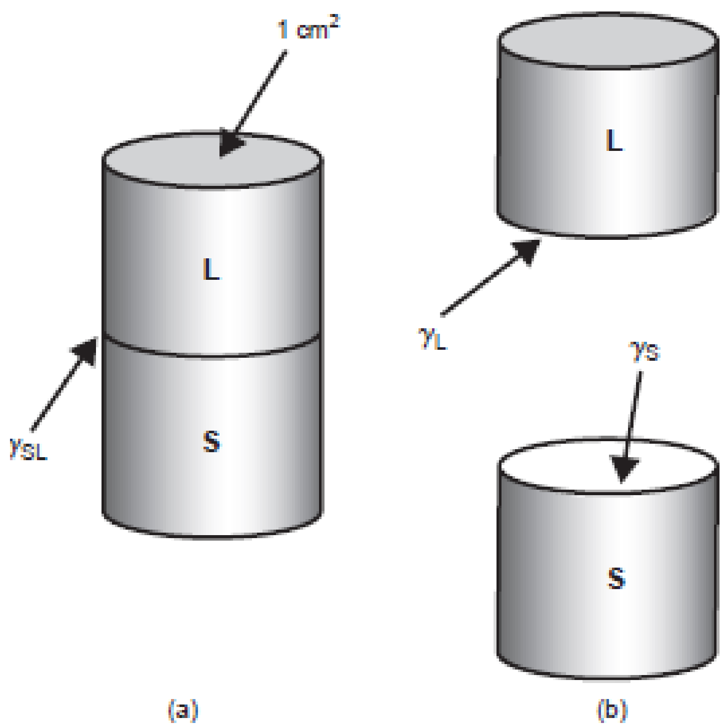
Spreading Coefficient

When oleic acid is placed on the surface of a water , a film will be formed if the force of **adhesion** between oleic acid molecules and water molecules is greater than the **cohesive** forces between the oleic acid molecules themselves.

Work of adhesion (Wa), which is the energy required to break the attraction between the unlike molecules(water to oil)

figure 1

Representation of the work of adhesion involved in separating a substrate and an overlaying liquid.



Work = Surface tension x Unit area change

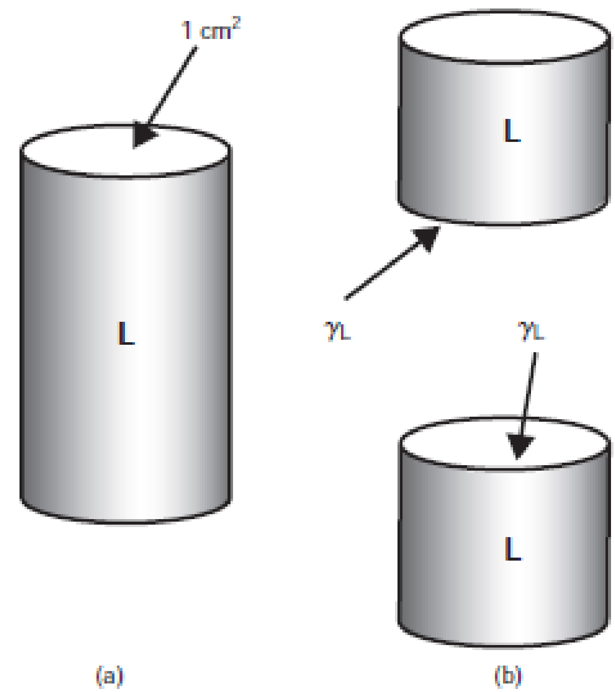
Accordingly, it is seen in **figure 1** that the work done is equal to the newly created surface tensions ,yL and YS ,minus the interfacial tension ,YLS that has been destroyed in the process.

Wa= YL+YS-YLS

Work of cohesion (Wc), required to separate the molecules of the spreading liquid so that it can flow over the sublayer.

figure 2

Representation of the work of cohesion involved in separating like molecules in a liquid

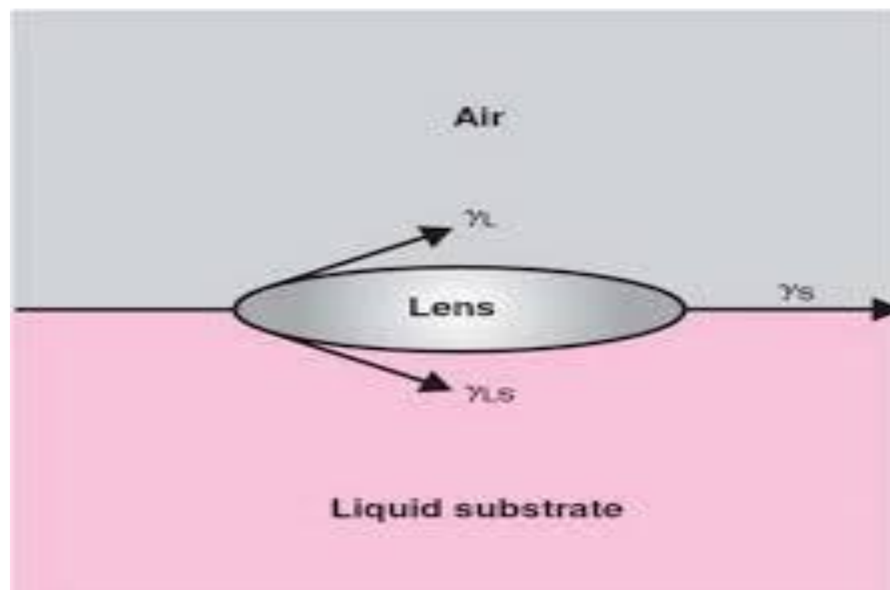


Obviously , no interfacial tension between the like molecules of the liquid , and when the hypothetical 1 cm^2cylinder in **figure 2** is divided , two new surfaces are created each with surface tension of YL, therefore the work of cohesion is

Wc =2YL

Spreading of oil to water occurs if the work of adhesion (a measure of the force of attraction between the oil and the water) is greater than the work of cohesion.

•The term (**Wa-Wc**) is known as the **Spreading coefficient(S)**



If it is **Positive (+)** the oil will spread over a water surface.

Wa-Wc

S=(YL+YS-YLS) -2YL

rearrangement :

S= Ys-YL-YLS

Or S= Ys – (YL+YLS)

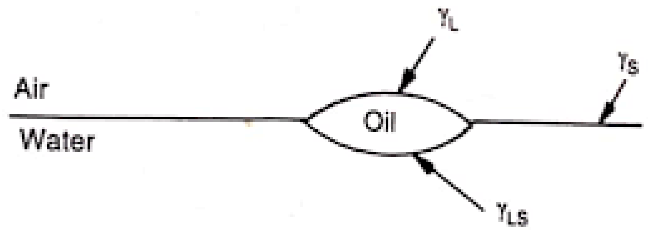


Fig. 3.10. Lens of oil at water surface.

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

- If (YL+YLS)is greater than YS i:e **negative(-)** , the substance forms globules or a floating lens fails to spread over the surface . An example is mineral oil on water.

Example

Spre**ading Benzene over Water**

If the surface tension of water γS is 72.8 dynes/cm at 20∘C, the surface tension of benzene, γL, is 28.9 dynes/cm, and the interfacial tension between benzene and water, γLS, is 35.0 dynes/cm, what is the initial spreading coefficient? We have

$$\mathbf{S = Ys - (YL + YLS)}$$

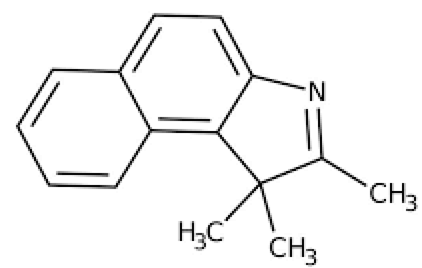
S = 72.8−(28.9+35.0) = 8.9 dynes/cm (or 8.9 ergs/cm2)

Therefore, although benzene spreads initially on water, at equilibrium there is formed a saturated monolayer with the excess benzene (saturated with water) forming a lens

Effects of Molecular Structure on Spreading Coefficient(S)

- Polar groups such as COOH or OH such as propionic acid and ethanol have high values of S.
- Increase in carbon chains of acids will lead to decrease of polar-nonpolar character ratio thus decrease in S on water. Ex are nonpolar liquid petrolatum fail to spread on water.
- Benzene spreads in water <u>because of its weak cohesive forces.</u>
- For lotions with mineral oil base to spread freely and evenly on the skin , its polarity and spreading coefficient <u>should be increase by the addition of surfactants</u>**.**

petrolatum



INITIAL SPREADING COEFFICIENT, *S*, AT 20° C*

Substance	*S* (dynes/cm)
Ethyl alcohol	50.4
Propionic acid	45.8
Ethyl ether	45.5
Acetic acid	45.2
Acetone	42.4
Undecylenic acid	32 (25°C)
Oleic acid	24.6
Chloroform	13
Benzene	8.9
Hexane	3.4
Octane	0.22
Ethylene dibromide	−3.19
Liquid petrolatum	−13.4

Adsorption at Liquid Interfaces

Certain molecules and ions ,when dispersed in the liquid ,move of their own to the interface.

•**the surface tension of the system automatically reduced (why?)**

•Such a phenomena when the added molecules are partitioned in favor of interface is called **adsorption.**

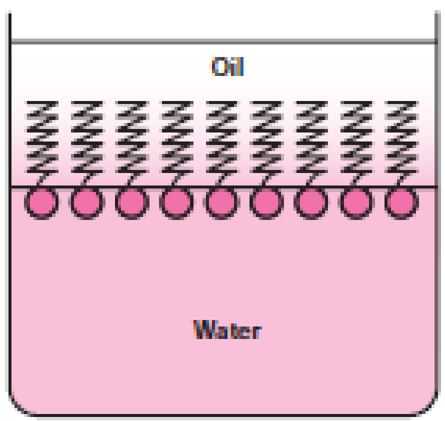
•The molecules and ions that are adsorbed at the interface are termed surface active agents or surfactant or (amphiphile)

Surface active agents

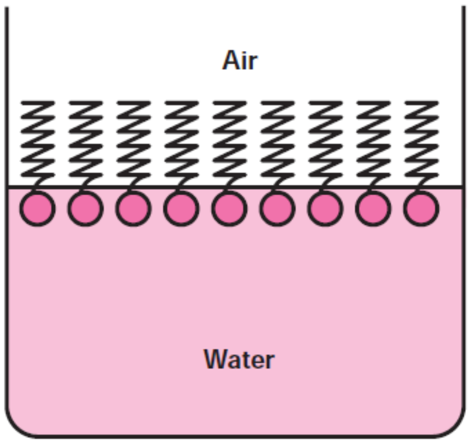
A surfactant molecule is described schematically as a cylinder representing the hydrocarbon (hydrophobic) portion with a sphere representing the polar(hydrophilic) group attached at one end.

Surface Active Agents

- It is the amphiphilic nature of surface active agents that causes them to be absorbed at interfaces,
- Thus, in an aqueous dispersion of amphiphile the polar group is able to associate with the water molecules .The nonpolar portion is rejected,
- As a result, the amphiphile is adsorbed at the interface



Adsorption of fatty acid molecules At water–oil interface



Adsorption of fatty acid molecules at a water–air interface

For the amphiphile to be concentrated at the interface, it must be balanced with the proper amount of water and oil soluble groups

- If the molecule is **too hydrophilic**, it remains within the body of the aqueous phase and exerts no effect at the interface
- if it is **too lipophilic** it dissolves completely in the oil phase and little appears at the interface

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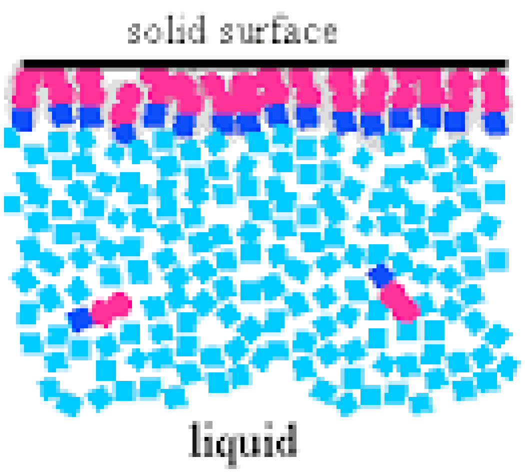
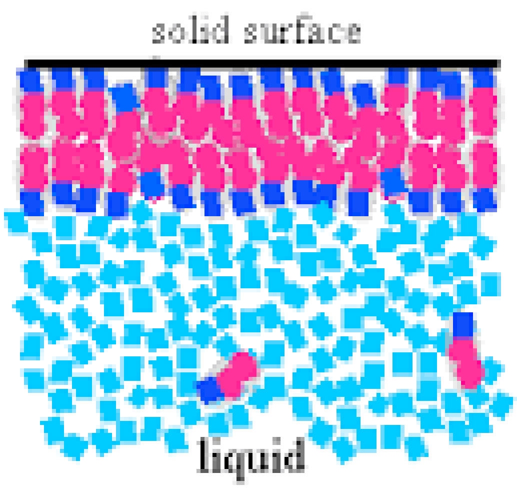
Formation of a monolayer at a hydrophobic solid surface by a surface active agent



Formation of a bilayer at a hydrophilic solid surface by a surface active agent



Surfactants are classified as:

- **Anionics:**

Sodium Dodecylsulphate (SDS):

$CH_3(CH_2)_{11}\ SO4^{-}Na^{+}$

- **Cationic:**

Dodecylamine hydrochloride:

$CH_3(CH_2)_{11}\ NH3^{+}Cl^{-}$

- **Non ionics**

Polyethylene Oxides (PEO):

e.g. $CH_3\ (CH_2\ )_{11}(OCH_2CH_2\ )_n\ OH$

(Spans) sorbitan esters)

(Tweens)polyoxyethylene sorbitan esters)

- **Ampholytics**

Dodecyl betaine

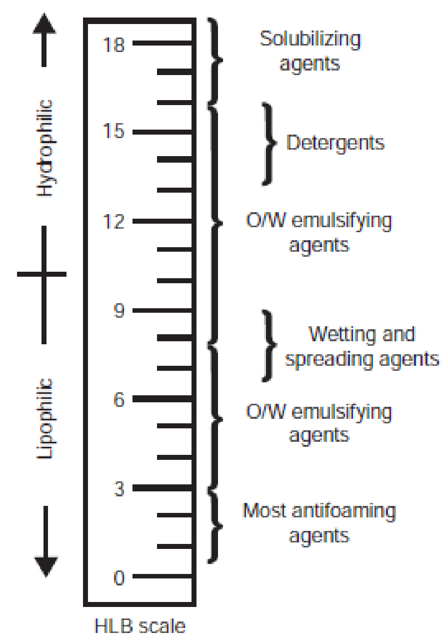
$C_{12}H_{25}\ N^{++}(CH_3)_2(CH_2COO^{-})$

Hydrophilic Lipophilic Balance (HLB)

It is an arbitrary scale from 0 to 20 serve as a measure of the Hydrophilic/Lipophilic balance of a surfactant

- Products with **low HLB** are more oil soluble
- **High HLB** represents good water solubility
- The oil phase of the oil water(o/w) emulsion requires a specific HLB called the required hydrophilic lipophilic balance (RHLB)
- A different RHLB is required to form a water in oil emulsion(w/o) from the same oil phase

scale showing surfactant function on the basis of hydrophilic–lipophilic balance (HLB) values. Key: O/W=oil in water.

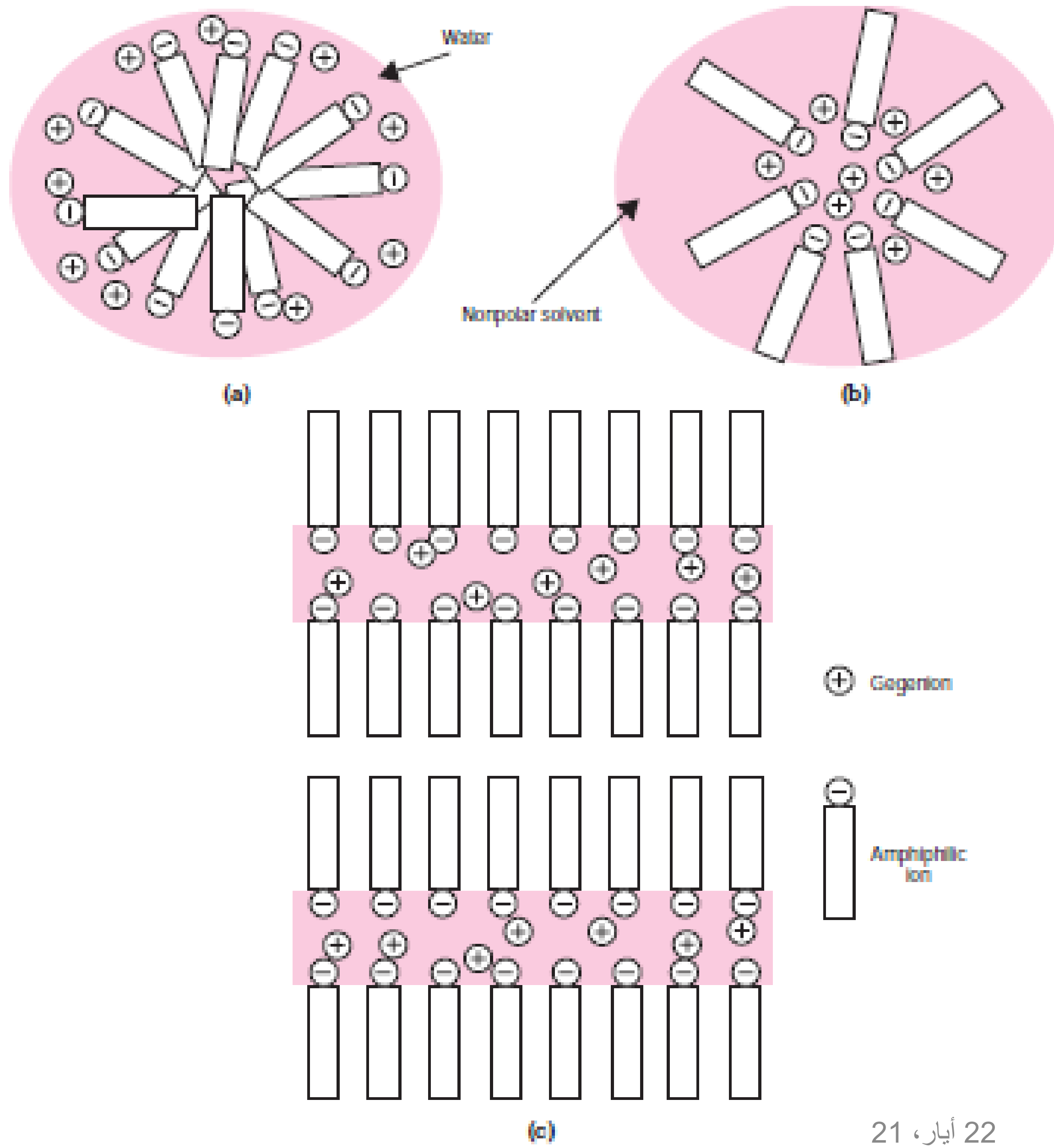


Micelle formation

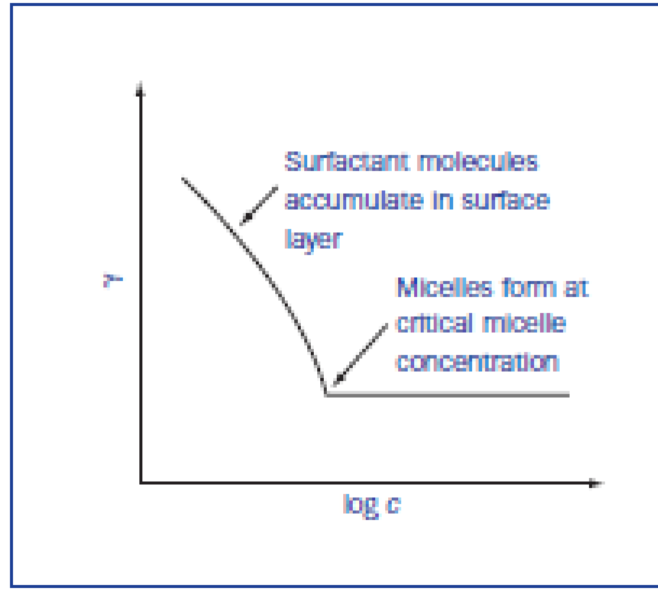
The surface tension of a surfactant solution decreases progressively with increase of concentration as more surfactant molecules enter the surface or interfacial layer However, at a certain concentration this layer becomes saturated and an alternative means of shielding the hydrophobic group of the surfactant from the aqueous environment occurs through the formation of aggregates (usually spherical) of colloidal dimensions, called micelles

The concentration at which micelles first form in solution is termed the ***critical micelle concentration*** or CMC.

Some probable shapes of micelles: (a) spherical micelle in aqueous media, (b) reversed micelle in nonaqueous media, and (c) laminar micelle, formed at higher amphiphile concentration, in aqueous media.



Surface tension decrease with increasing conc. Of surfactant Until CMC is reached then become constant



- The CMC decreases with an increase in the length of the hydrophobic chain
- The addition of electrolytes to ionic surfactants decreases the CMC and increases the micellar size
- The effect is simply explained in terms of a reduction in the magnitude of the forces of repulsion between the charged head groups in the micelle, allowing the micelles to grow and also reducing the work required for their Formation

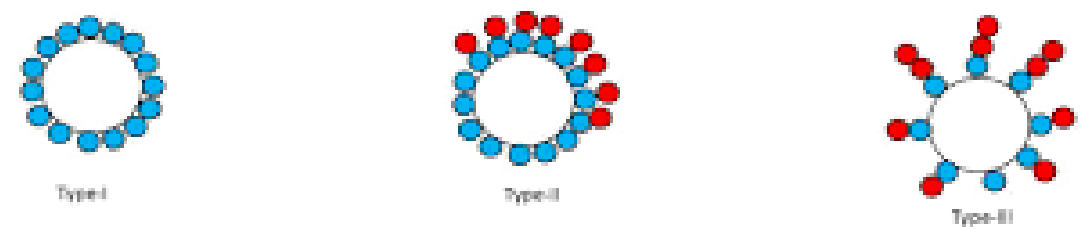
Micellar Solubilization

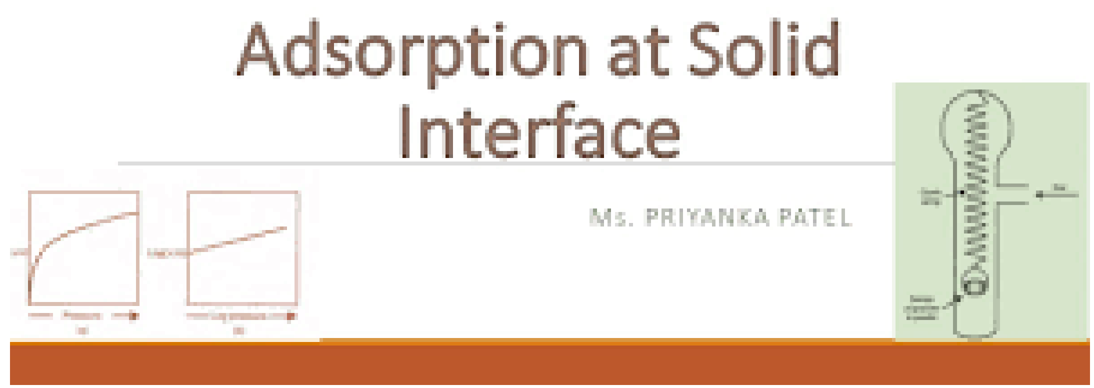
Surfactant molecules accumulate in the interfaces between water and water insoluble compound Their hydrocarbon chains penetrate the outermost layer of insoluble compound which combine with the water insoluble molecules .Micelles form around the molecules of the water insoluble compound inside the micelles' 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

Adsorption at solid interfaces

Adsorption of materials at solid interfaces can take place from either an adjacent liquid or gas phase.

- The study of adsorption at gases arises in applications as removal of objection able odors from rooms or food.
- The principle of solid liquid adsorption are used in decolorizing solutions ,adsorption chromatography ,detergency and wetting



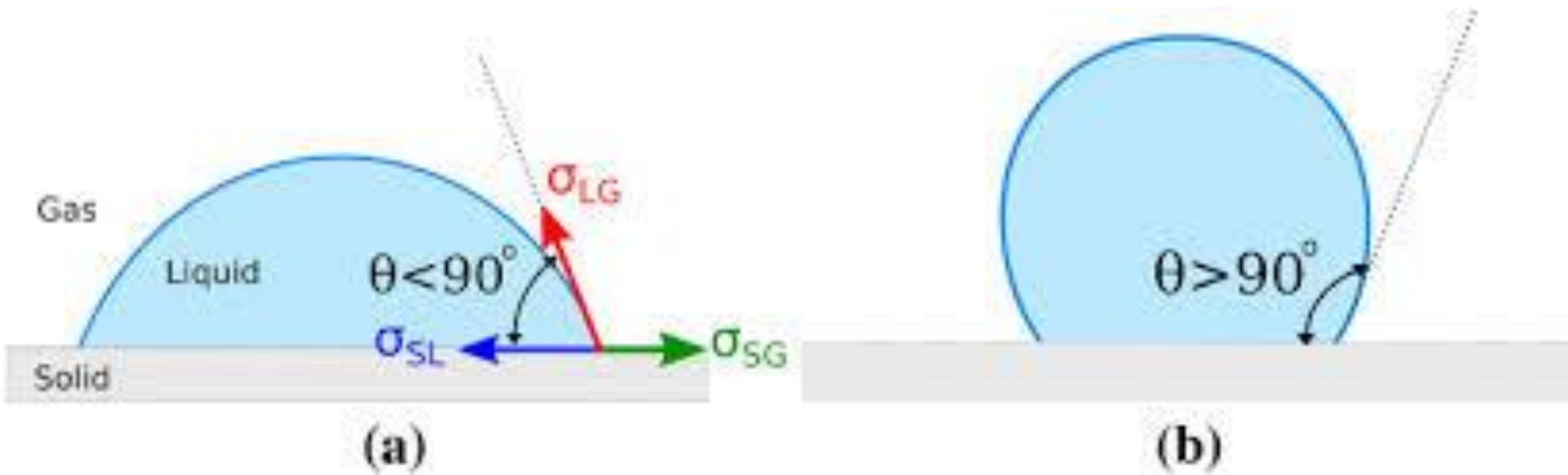


Wetting

- Adsorption at solid surfaces is involved in the phenomena of wetting and detergency
- When a liquid comes into contact with the solid the forces of attraction between the liquid and the solid phases begin to play a significant role
- In case of water and glass attractive forces between the solid and liquid molecules are <u>greater</u> than the forces between molecules of liquid themselves And so the liquid is able to wet the surface of the glass
- The most important action of **wetting agent** is <u>to lower the **contact angle** between the surface of and the wetting liquid</u>
- **The contact angle** is the angle between a liquid droplet and the surface over which it spreads.
- The contact angle may be 0°,signifying complete wetting ,or may be 180° at which wetting is in significant.
- Or any value between these limits.

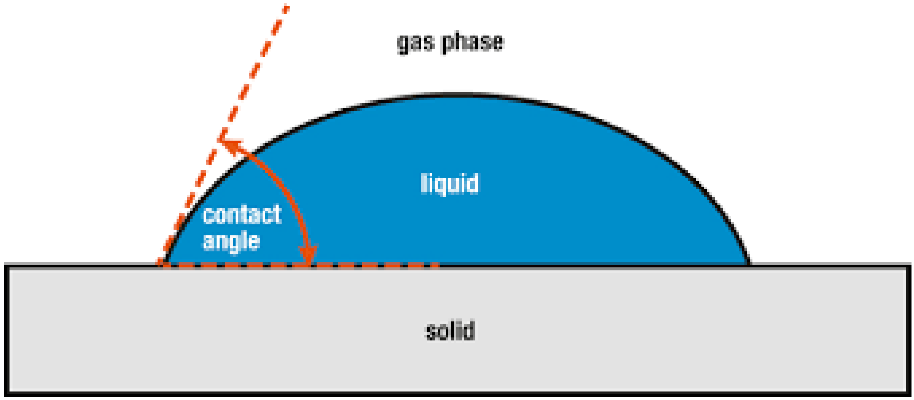
A contact angle is lower than 90 the solid is called wettable

- A contact angle is wider than 90 the solid is named non wettable
- A contact angle equal to zero indicates complete wettability



wettable **non wettable**

Wetting agent A *wetting agent* is a surfactant that ,when dissolved in water, lowers the advancing contact angle, aids in displacing an air phase at the surface, and replaces it with a liquid phase. Examples of the application of wetting to pharmacy and medicine include the displacement of air from the surface of sulfur, charcoal, and other powders for the purpose of dispersing these drugs in liquid vehicles; the displacement of air from the matrix of cotton pads and bandages so that medicinal solutions can be absorbed for application to various body areas; the displacement of dirt and debris by the use of detergents in the washing of wounds; and the application of medicinal lotions and sprays to the surface of the skin and mucous membranes.

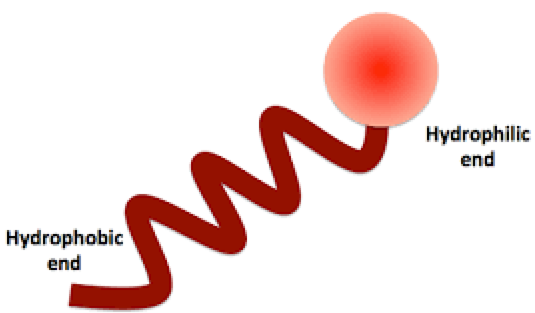


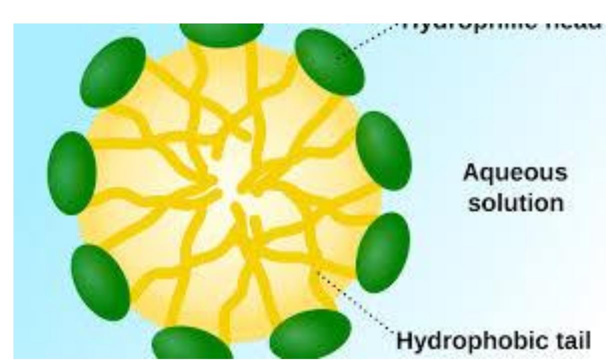
Detergents

Are surfactants that are used for the removal of dirt . Detergency is a complex process involving the removal of foreign matter form surfaces.

The process includes :

- Initial wetting of dirt and of the surface to be cleaned .
- Deflocculation and suspension Emulsification or solubilization of the dirt particles .
- And sometimes foaming for washing away the particles.






THANK
YOU

Calculate the amount of surfactants that need to be combined to prepare 20ml of surfactant with an HLB of 9.0,Arlacel 60,HLB4.7& Tween60,HLB,14.9

Tween 14.9		4.3
	9.0	
Arlacel 4.7		5.9
20ml		**10.2**

$$\frac{20ml}{10.2} \times 4.3 = 8.4 \text{ ml}$$

$$\frac{20ml}{10.2} \times 5.9 = 11.6\text{ml}$$